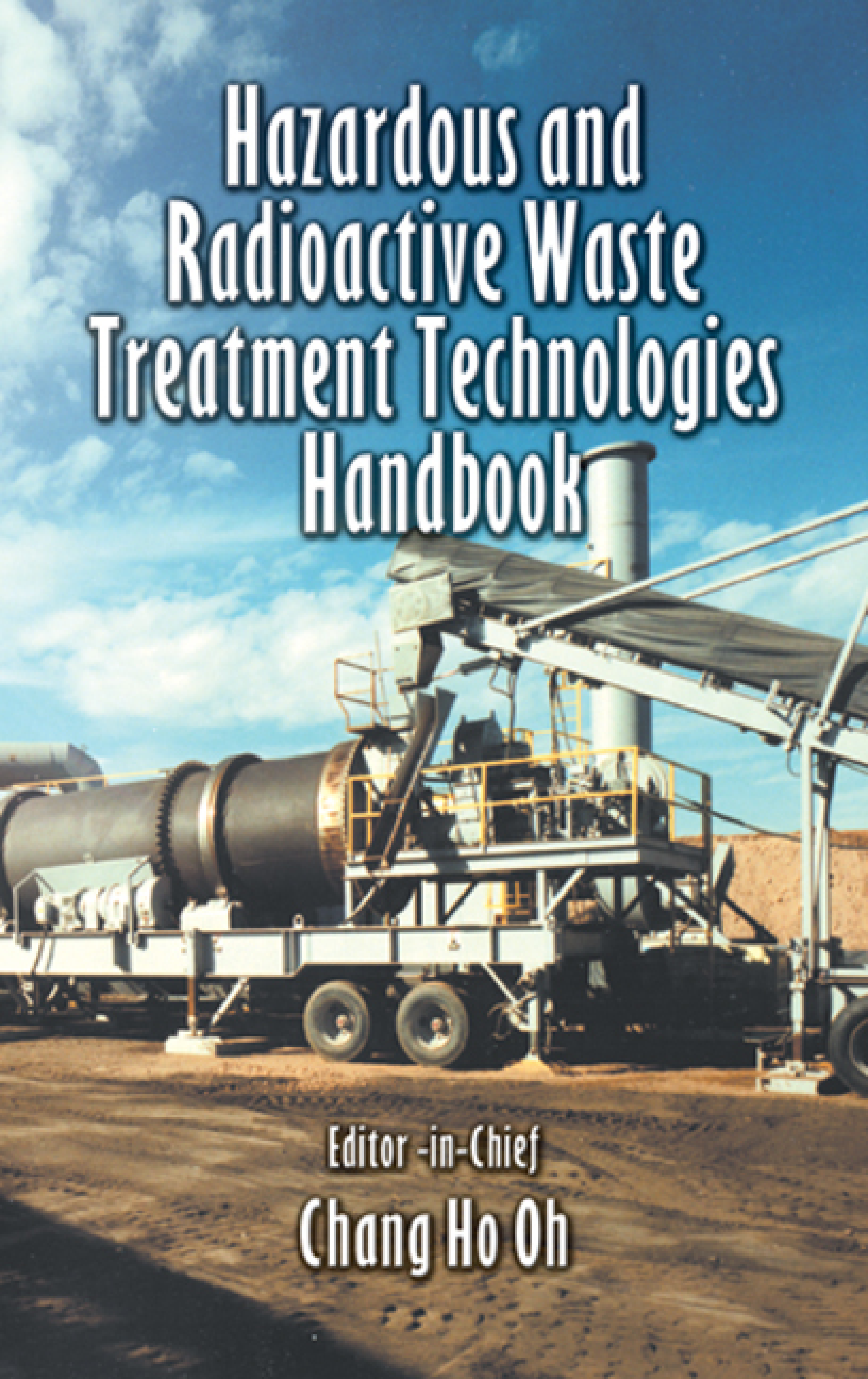

Hazardous and Radioactive Waste Treatment Technologies Handbook

Editor -in-Chief

Chang Ho Oh

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Editor-in-Chief

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Dedication

This book is dedicated to the memory of my late father, Peter Byung Rin Oh (1916–2000), who died during its preparation.

Preface

We have a responsibility to future generations to treat and dispose of hazardous and radioactive waste in a safe and compliant manner such that release into the environment is prevented. Mixed wastes, which are radioactive as well as hazardous, as defined under the Resource Conservation and Recovery Act, may be one of the more difficult waste categories to treat because of the variety of constituents that must be addressed and the myriad of laws and regulations that govern their treatment. The need for mixed waste treatment, the specifications that the treated waste must meet, the process operation and emission controls required at treatment facilities, and the requirements for worker safety are driven by such statutory and regulatory requirements.

In addition to understanding the laws and regulations that govern treatment of mixed waste, an understanding of the various methods and technologies for characterizing, treating, stabilizing and disposing of the various waste constituents is essential for developing a safe, reliable and economical system for dealing with such waste. Any selected process, or suite of technologies, must not only address the hazardous (both organic and inorganic) and the radioactive constituents, but also perform its function in the presence of the non-hazardous component of the waste.

Although several textbooks have been written on the subject of waste treatment, these books are usually devoted to hazardous or nuclear wastes separately. Therefore, it was difficult for engineers or scientists to find general descriptions for both subjects in a single volume. In addition, existing technologies in the waste treatment area are changing rapidly, new technologies are being proposed, and regulations are frequently changed or modified. The purpose of this handbook is to provide, under a single cover, up-to-date information on relevant mixed waste regulations and waste characterization, treatment, stabilization and disposal technologies.

The handbook consists of ten chapters containing sections that provide a comprehensive discussion of the various aspects of mixed waste treatment. Chapter 1 offers a survey of the various laws and regulations applicable to mixed waste and Chapter 2 discusses methods for waste characterization, including sample collection and analysis. An engineering overview of specific technologies that can be used to treat mixed waste or the effluent from a treatment facility are described in Chapters 3 through 7, often including a detailed schematic diagram of each technology so that the process can be readily understood. Often, difficult-to-treat constituents must be removed from the waste stream to allow for safe and economical treatment downstream. Several such separation technologies are described in Chapter 3. Thermal and non-thermal treatment technologies, discussed in Chapters 4 and 5, can be used to destroy the organic components of the mixed waste stream, through either high- or -low temperature chemical reactions, respectively. Chapter 6 discusses stabilization and solidification technologies that can be applied to the solid treatment residue prior to disposal, and Chapter 7 describes methods for treating the off-gas from the various treatment processes. System considerations are discussed in Chapter 8, decontamination; Chapter 9, system integration and deployment; and Chapter 10, planned life-cycle costs.

This handbook should be helpful to chemical, environmental, civil, and mechanical engineers; consultants; government officials; graduate students in this field; and others who are involved in the various aspects of mixed waste treatment.

Acknowledgments

The Editor-in-Chief wishes to thank the many contributors who made their time available and were willing to share their expertise with other members of the engineering profession through the sections of the handbook to which they contributed. Thanks are also extended to the many reviewers who offered excellent comments to each contributor. Last, but not least, I wish to thank my wife, Theresa, my sons, Paul and John, and my parents for their encouragement and support in the course of preparing this book.

Editor-in-Chief

Chang Ho Oh is a consulting engineer and project manager in the Nuclear Engineering Design and Research Department at the Idaho National Engineering and Environmental Laboratory (INEEL) in Idaho Falls Idaho. He serves from time to time as an affiliate professor at the University of Idaho, conducting graduate courses in chemical engineering. He is a member of the ASME, AIChE, and ANS, and is very active in the ASME heat transfer committee of multi-phase flow systems (K-13). Dr. Oh earned a Ph.D. in chemical engineering at Washington State University, an M.S. in chemical engineering at the University of Florida, and a B.S. in chemical engineering at Yonsei University in Seoul, Korea.

Dr. Oh has organized many technical sessions for the ASME, in particular, thermal hydraulics in waste technologies and thermal hydraulics of nuclear reactor systems. He has published many technical articles in peer-reviewed journals such as *AIChE Journal, International Journal of Heat and Mass Transfer,* and *Energy and Fuels* since he joined the INEEL in 1985. He has been active in research in waste technologies and management, thermal hydraulics of nuclear reactor systems, and heat transfer and fluid flow engineering.

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Chapter One

1

Overview of U.S. Federal Laws and Regulations Affecting Mixed Waste Treatment

Margaret A. Knecht
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Introduction

This chapter focuses on the federal legislative framework and regulatory requirements applicable to treatment of radioactive wastes that are also designated as hazardous wastes under the Resource Conservation and Recovery Act (RCRA) — "mixed waste." In addition, the chapter addresses radioactive wastes contaminated with polychlorinated biphenyls (PCBs) regulated under the Toxic Substances Control Act (TSCA) and radioactive and hazardous or toxic remediation-derived waste and environmental media subject to treatment/clean-up requirements under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA).

The need for mixed waste treatment, the technical specifications that the treated waste must meet, and the process operation, effluent, and emission controls required at treatment facilities are driven by statutory and regulatory requirements designed to protect public health and the environment and to provide some aspects of worker safety. One purpose of this chapter is to provide an understanding of the regulatory requirements to treat mixed wastes before land disposal and the specifications that the treated waste must meet. It also summarizes regulatory requirements that mixed waste treatment facilities must meet. Developers and users of mixed waste treatment technologies must understand both sets of requirements: for the waste itself and for the treatment facilities. This chapter provides an overview of such requirements as implemented by the Environmental Protection Agency (EPA), the Nuclear Regulatory Commission (NRC), and the Department of Energy (DOE).

A myriad of laws are in effect implementing regulations, policies, guidance, and site- and waste-specific regulatory agency decisions that may govern waste treatment and treatment facility design and operation. These requirements, for example, provide assurance of protection of human health and the environment and address historic, cultural, and other important issues. Therefore, the reader should recognize that discussions provided by this chapter might not cover all the requirements potentially applicable to a specific situation. For example, the EPA and NRC can delegate portions of their regulatory responsibilities to a state. When the EPA delegates portions of its RCRA authority to a state (e.g., for issuing hazardous waste regulations, permitting facilities, and related enforcement), the state implements the delegated element(s) of the RCRA waste management program and is termed an "authorized state." To extend delegated RCRA authority to mixed waste, the EPA must have additionally granted a state specific mixed waste RCRA authorization. An authorized state's RCRA program must not be less stringent than the EPA's, but can be broader and more stringent. For example, some authorized states' regulations include more hazardous wastes and more hazardous constituents than in EPA's hazardous waste regulations. Similarly, when the NRC agrees to delegate portions of its regulatory authority for radioactive materials and their handling facilities to a state, the state is termed an NRC "agreement state." Agreement states' regulations must also be at least as stringent as the corresponding NRC regulations. Again, however, agreement states can have more stringent regulations and enforcement policies than those of the NRC. Requirements in addition to those explicitly addressed in the regulations may be applied to certain mixed wastes or mixed waste management facilities as required conditions in the RCRA permit and NRC license. Site- and waste-specific requirements relevant to waste derived from RCRA or CERCLA clean-ups would typically be found in a Record of Decision (ROD), Consent Agreement, or Consent Order.

In addition to being complex and differing among states, the laws, regulations, policies, and guidance that govern the treatment of mixed waste and the treatment facilities change frequently. In 1998, for example, the EPA formally embarked on an ambitious plan to comprehensively reevaluate the LDR regulations to improve, where needed, their protectiveness, flexibility, scientific basis (including relationship to risk posed), multimedia approach, and applicability. As part of this "reinvention" process, the EPA is expected to examine and potentially revise treatment standards for LDR wastes, beginning with mercury-bearing wastes. Regional and local regulatory authorities may also be involved in setting the complete catalog of requirements for management of specific wastes, in particular those derived from site clean-ups. It is of utmost importance, therefore, to research the latest and most complete versions of all applicable laws, regulations, policies, guidance, RODs, consent agreements, and consent orders, as well as the corresponding proposed regulations that might soon become applicable, when regulatory information to develop or implement a waste treatment technology is required. Consultation with the appropriate regulators is invaluable in determining specific requirements when questions remain.

Federal Authorities that Govern Mixed Waste

Table 1.1 presents a chronology of major U.S. federal laws and regulations that govern mixed waste identification and cradle-to-grave management. EPA requirements applicable to the treatment and disposal of the hazardous component of mixed wastes differ, depending on the statutory authorities under which the waste is regulated (e.g., under RCRA, CERCLA, or TSCA). The radionuclides in mixed waste are regulated under the authority of the Atomic Energy Act (AEA) as amended, including the Energy Research and Development Act and the Energy Reorganization Act. These acts collectively authorize NRC and DOE to regulate radioactive materials, including wastes, and the facilities that generate or manage these materials. The AEA also authorizes the EPA to provide radiological standards for radioactive material and waste management. In general, the AEA and its amendments and the Nuclear Waste Policy Act authorize what is now the NRC to regulate, among other things, commercial generation and handling of radioactive materials and wastes, and all high-level radioactive waste (HLW) disposal. The AEA and its amendments, the Energy Research and Development Act, and the Energy Reorganization Act collectively authorize what is now the DOE to regulate DOE facilities that generate and manage radioactive materials and wastes — including DOE low-level waste (LLW), transuranic (TRU) waste, mixed LLW and mixed TRU waste, HLW, and wastes that contain accelerator-produced, AEA 11(e) by-product, or naturally occurring radioactive materials (NORM). The DOE and NRC must also implement the EPA's 40 CFR Part 191 and other standards for the disposal of TRU waste and HLW.

TABLE 1.1 Chronology of Major U.S. Laws and Regulations Governing Mixed Waste Treatment

Year	Law or Regulation
1954	AEA authorizes Atomic Energy Commission (AEC) and AEC regulation of radioactive materials defined in AEA.
1965	Solid Waste Disposal Act sets the stage to improve management of “solid waste.”
1970	National Environmental Policy Act (NEPA) governs potential federal projects that may affect the environment, requires consideration of alternatives, environmental review, and, for certain major projects, public participation in decision-making.
	The EPA is created by Executive Order and authorized to implement federal environmental legislation.
	The Clean Air Act (CAA) and subsequent amendments require the EPA to regulate point sources of air pollution and develop ambient air standards.
1972	Federal Water Pollution Control Act and subsequent amendments [now known as the Clean Water Act (CWA)] initiate EPA regulation to control pollution of surface waters.
1974	Energy Reorganization Act abolishes AEC and divides regulation of all radioactive materials between the Energy Research and Development Administration (ERDA) and the NRC. ERDA regulates primarily defense-related materials and NRC regulates commercial, industrial, medical, and university owned materials and some classes of DOE facilities (e.g., HLW storage).
1976	RCRA Subtitle C (actually amendments to Solid Waste Disposal Act) requires the EPA to regulate hazardous waste identification and management by waste generators, transporters, and owners/operators of hazardous waste treatment, storage, and disposal facilities (TSDFs). RCRA Subtitle C specifically excludes “source, special nuclear, or by-product material,” as defined by AEA, from the definition of “solid waste” (and therefore from the definition of hazardous waste).
	TSCA authorizes the EPA to control certain hazardous chemicals (e.g., PCBs, cradle-to-grave).
1977	Clean Water Act (CWA) initiates National Pollutant Discharge Elimination System (NPDES), authorizing the EPA to regulate, via permits, point source industrial discharges of pollutants to surface waters.
	Department of Energy Organization Act creates the DOE, which incorporates ERDA and other agencies and programs, and clarifies DOE’s environmental functions.
1980	CERCLA authorizes the EPA to regulate management and clean-up of sites contaminated by hazardous substances, including radionuclides, where actual or imminent “loss of control” of these substances threatens human health or the environment.
	The EPA issues first hazardous waste management regulations under RCRA: 40 CFR Part 261 — Identification and Listing of Hazardous Waste (45 FR 33119).
1981	The NRC issues licensing regulations for non-DOE operated LLW land disposal sites (10 CFR 61.56).
1982	Nuclear Waste Policy Act provides for HLW repository development.
1984	Hazardous Solid Waste Amendments (HSWA) to RCRA set phased deadlines for the EPA to prohibit land disposal of untreated hazardous wastes and provide treatment standards that such prohibited waste must meet prior to land disposal.
	In *Leaf v. Hodell*, court mandates that the DOE’s hazardous waste is subject to RCRA hazardous waste laws and regulations, but is unclear on status of the DOE’s source, special nuclear, and by-product materials.
1985	Low-Level Radioactive Waste Policy Amendments Act provides for states to develop system of LLW land disposal sites.
1986	An EPA notice clarifies that RCRA hazardous waste regulations apply to mixed wastes and that states must obtain EPA authorization to regulate the hazardous component of mixed wastes (51 FR 24504).
	Emergency Planning and Community Right to Know Act requires that the EPA provide for reporting of hazardous waste generation and management activities and for community involvement in related emergency planning.
	Superfund Amendment and Reauthorization Act (SARA) amends CERCLA to stress the importance of permanent remedies, risk considerations, and application of requirements from other authorities to govern clean-ups (Applicable or Appropriate and Relevant Requirements, ARARs).
	The EPA issues the initial rule that implements the land disposal restrictions (LDR) program (51 FR 10146) and 40572). The rule provides the regulatory framework for LDRs, LDR treatment standards for solvent and dioxin wastes, and the Toxicity Characteristic Leaching Procedure (TCLP) upon which toxicity characteristic waste determinations and certain LDR treatment standards are based.
1987	The DOE publishes rule that interprets AEA definition of “by-product material” and clarifies that nonradioactive, chemically hazardous component of DOE’s mixed wastes are subject to regulation under RCRA (52 FR 15937).
	EPA issues LDR treatment standards for hazardous wastes previously identified by California (52 FR 25759).
1988	DOE Order 5820.2A, “Radioactive Waste Management of Defense LLW,” establishes requirements for management of DOE LLW and mixed waste.

TABLE 1.1 Chronology of Major U.S. Laws and Regulations Governing Mixed Waste Treatment (Continued)

Year	Law or Regulation
	The EPA issues LDRs for the “First Third” hazardous wastes (53 FR 31138).
	An EPA notice clarifies that mixed waste TSDFs are subject to RCRA permitting requirements for hazardous waste TSDFs (53 FR 37045).
1989	The EPA issues LDRs for “Second Third” hazardous wastes (54 FR 26594).
1990	The EPA approves conditional no-migration variance exempting from RCRA LDRs a limited amount of untreated LDR mixed waste for experiments at DOE’s Waste Isolation Pilot Plant (WIPP) for defense transuranic waste disposal (55 FR 47700).
	The EPA issues LDRs for “Third Third” hazardous wastes (55 FR 22520)
1991	Because of limited treatment and disposal capacity, the EPA temporarily reduces priority of civil enforcement of RCRA Section 3004(j), storage prohibition for certain non-DOE mixed wastes (56 FR 42730).
1992	Federal Facilities Compliance Act sets mixed waste definition, clearly subjects federal facilities to RCRA hazardous waste requirements, requires DOE mixed waste generating and management sites to develop plans to achieve compliance with RCRA requirements. EPA enforcement of LDR storage prohibition for these federal facilities is based on these plans.
	The EPA issues alternate hazardous debris treatment standards (57 FR 37194).
	The Energy Policy Act requires the EPA and NRC to issue site-specific standards and licensing requirements, respectively, for disposal of HLW at proposed DOE Yucca Mountain, NV, site.
1993	The EPA issues concentration-based treatment standards for “underlying hazardous constituents” (UHCs) in D001 and D002 wastes even if these UHCs do not cause the waste to exhibit an RCRA characteristic (58 FR 29860).
1994	The EPA issues LDR Phase II final rule, which promulgates treatment standards for newly identified organic toxicity characteristic wastes and establishes universal treatment standards (59 FR 47982).
1995	The EPA proposes the Hazardous Waste Identification Rule (HWIR, 60 FR 57747) to allow certain RCRA listed wastes and listed waste contaminated media meeting risk-based “exit” requirements to be disposed in RCRA Subtitle D (non-hazardous waste) regulated facilities.
1996	The WIPP Land Withdrawal Act amendment exempts transuranic mixed waste designated for WIPP disposal testing from RCRA LDR treatment standards and associated land disposal prohibitions.
	Land Disposal Program Flexibility Act amends Solid Waste Disposal Act to provide that LDR prohibited hazardous wastes that are decharacterized and managed in centralized CWA or SDWA regulated wastewater management systems (e.g., surface impoundments) are not prohibited from land disposed, as long as the wastes are not hazardous at the point they are land disposed.
1997	The NRC, with EPA consent, authorizes disposal of a specific commercial low radioactivity treated mixed waste containing Cs-137 at RCRA Subtitle C disposal facilities (62 FR 131-76).
	Preceding issuance of a proposed mixed waste storage and disposal rule, the EPA suspends RCRA permitting actions for certain commercial sector RCRA interim status on-site mixed waste storage facilities (59 FR 47982) [EPA 1997a].
	NRC/EPA mixed waste testing guidance is issued (62 FR 62079).
1998	For non-DOE LDR mixed wastes with no treatment/disposal options, the EPA extends to October 31, 2001, its low enforcement policy for RCRA Section 4000(j) storage prohibition (63 FR 17414 and 59989, see also 59 FR 18813 and 61 FR 18588).
	The EPA issues LDR Phase IV final rule, which promulgates new and revised treatment standards for metal-containing hazardous wastes, requires any underlying hazardous constituents in toxicity characteristic metal wastes to be treated to UTS levels, and establishes alternative treatment standards for contaminated soils (63FR 28556).

Note: Portions of table were adapted from information on the EPA Web page at http://www.epa.gov/radiation/mixed-waste/mw_pg4.htm.

Definition of Mixed Waste

Before we can understand mixed waste treatment and treatment facility requirements, we need a more complete understanding of what mixed waste is. Mixed wastes are typically produced in activities related to production of and research on nuclear power and nuclear weapons, to medical procedures and research, and to miscellaneous other research, development, and manufacturing activities that employ hazardous chemicals and use or generate radionuclides. Mixed wastes are also produced as a result of the clean-up of water, soil, and buildings contaminated as a result of these activities in the past.

Mixed waste is defined in the Federal Facility Compliance Act (FFCA) (RCRA Section 1004(41), October 6, 1992) as "… waste that contains both hazardous waste and source, special nuclear, or by-product material subject to the Atomic Energy Act of 1954." In authorizing the RCRA program, Congress in RCRA Section 1004(5) broadly defined hazardous waste to include wastes that cause or significantly contribute to an increase in serious illness or mortality or pose a threat to human health or the environment when improperly managed. Wastes that contain a hazardous waste component as designated in the RCRA implementing regulations in 40 CFR 261 and that also include a radioactive component constitute the primary mixed waste category discussed in this book (i.e., for the purpose of determining applicable treatment technologies and disposal). In addition, radioactive PCB wastes regulated under TSCA are considered to be in the "mixed waste" category for the purpose of this book. Contaminated media subject to CERCLA are also included for the same reason. The treatment required to address the RCRA/TSCA/CERCLA-regulated hazards of mixed wastes will depend on the waste categorization and classification (see also Chapter 2) under these statutes and their implementing regulations.

The radioactive component of mixed waste contains man-made radionuclides or man-enhanced concentrations of naturally occurring radionuclides that emit alpha, beta, or gamma radiation that can damage living cells and their genetic components. The statutory and regulatory requirements for treatment of mixed waste to address the hazards associated with the radionuclides also depend on how the waste is categorized: as HLW, transuranic waste, LLW, or accelerator-produced or naturally occurring radiological material (NARM). HLW is defined by the NRC in 10 CFR 60 as (1) irradiated reactor fuel, (2) liquid wastes resulting from the operation of the first cycle solvent extraction system, or equivalent, and the concentrated wastes from subsequent extraction cycles, or equivalent, in a facility for reprocessing irradiated reactor fuel, and (3) solids into which such liquid wastes have been converted. However, the EPA defines HLW as the AEA definition given in the Nuclear Waste Policy Act of 1982, which is "(A) the highly radioactive material resulting from the reprocessing of spent nuclear fuel, including liquid waste produced directly in reprocessing and any solid material derived from such liquid waste that contains fission products in sufficient concentrations; and (B) other highly radioactive material that the Commission, consistent with existing law, determines by rule requires permanent isolation." In addition to the differences regarding spent nuclear fuel and "other highly radioactive material" between the AEA and NRC definitions, "sufficient concentrations" is not defined, and the NRC had (as of late 2000) not identified in rulemaking the "other" materials that might be HLW because they require permanent isolation.

As defined by the DOE and EPA, transuranic waste exceeds a total of 100 nCi of alpha-emitting transuranic radionuclides having a half-life greater than 20 years in each gram of waste. The EPA, in 40 CFR 191, excepts from the definition of transuranic waste (1) HLW, (2) wastes that DOE determines, with EPA administrator approval, do not need the degree of isolation required by 40 CFR 191, and (3) wastes that the NRC has approved for disposal on a case-by-case basis in accordance with 10 CFR 61 (the NRC's LLW disposal licensing rule).

LLW is currently defined in the AEA, as amended, as radioactive material that: (1) is not high-level radioactive waste, spent nuclear fuel, transuranic waste, or by-product material (uranium or thorium mill tailings), and (2) the Commission, consistent with existing law, classifies as low-level radioactive waste.

The categorization of HLW based on its source, and lack of definition of radionuclide content limits, can pose issues for the categorization of wastes that may be derived from HLW or are "incidental" to HLW processing, but have characteristics more consistent with LLW or transuranic waste. The implementation guidance manual for DOE Order 435.1 on radioactive waste management establishes that, within the DOE system, wastes that are "incidental" to reprocessing are not HLW. Such incidental wastes are described in an NRC Notice of Proposed Rulemaking for revision of 10 CFR Part 50 (34 FR 8712, paragraphs 5 and 6). The DOE guidance manual establishes DOE processes and criteria for determining if these incidental wastes should be managed as HLW, LLW, or transuranic waste.

The NRC subdivides low-level radioactive waste (LLW) subject to NRC licensing and subject to NRC licensed disposal site requirements into Class A, Class B, and Class C, and Greater-Than-Class-C. Upper radionuclide content limits are defined in 10 CFR 61 for Classes A through C. NRC-defined Greater-

Than-Class-C LLW includes wastes that exceed a total of 100 nCi of alpha-emitting transuranic radionuclides having a half-life greater than 5 years per gram of waste (cf. the DOE and EPA definition of transuranic waste). The LLW classifications are generally based on the degree of overall radiological hazard after disposal, considering the type and energy of the radiation emitted by each specific radionuclide, the radionuclide concentration, the radionuclide half-life, the general potential for release of the radionuclide from the disposal site, and potential pathways to man and the environment. Class A generally presents the lowest hazard, and Greater-Than Class C the highest hazard for LLW. The NRC requires disposal of Greater-Than-Class-C LLW in a geologic repository except if it approves alternative disposal on a case-by-case basis.

Identifying a waste as "hazardous" and "radioactive" and determining the specific category and classification of the hazardous and radioactive portions of the waste as outlined in Section 2.1 is the first step in determining how the waste should be treated, what the final waste form specification should be, and what special requirements may be needed in the design, operation, and closure of the treatment facility.

Under the current RCRA regulatory framework, the Toxicity Characteristic Leaching Procedure (TCLP) is used for classifying RCRA toxicity characteristic hazardous waste, as a basis for setting leachate-concentration-based RCRA hazardous waste treatment standards, and for measuring waste form compliance with such standards. The EPA has been considering changes to its waste testing requirements and procedures and to the groundwater modeling for risk assessments used as part of the basis for its hazardous waste classification system. The considerations for changing waste testing were partly based on The Netherlands' and European Union's efforts to develop a multiple test scheme that better predicts near-term and long-term contaminant release and behavior. Congress has also given some consideration to whether it should clarify the definition of HLW (and therefore LLW). Such changes could dramatically impact the amounts and kinds of mixed wastes that must be treated, the treatment standards that must be met, final waste form testing for compliance, and, accordingly, needed U.S. mixed waste treatment capabilities and capacities.

Requirements Affecting Final Waste Form Specifications

RCRA Land Disposal Restrictions (40 CFR Part 268)

Land Disposal Restriction (LDR) treatment standards provide some of the specifications that final mixed waste forms must meet to be land disposed. Much of the RCRA hazardous waste management regulatory program was initially developed to respond to national concerns that leaching of hazardous constituents into groundwater from hazardous waste disposed on the land could significantly degrade groundwater quality. Thus, hazardous and mixed waste disposal facilities such as landfills and surface impoundments must meet minimum technology requirements (have approved liners and leak detection systems) and monitor groundwater. The EPA's LDR program added prohibitions of land disposal of each identified hazardous waste. For such LDR-prohibited wastes, the EPA also established treatment standards that the waste must meet before it can be land disposed. The philosophy behind the LDR program is to establish treatment standards that reduce the mobility or toxicity of the hazardous constituents in the waste to reduce the threat to groundwater. The LDR program also includes waste dilution and storage prohibitions, explicit requirements for final testing of wastes before disposal, and "cradle-to-grave" waste tracking and recordkeeping requirements.

LDR Treatment Standards

Over the years from 1986 through 1998, the EPA issued RCRA hazardous waste land disposal prohibitions and accompanying LDR waste treatment standards in phases to complete its response to congressional LDR mandates. Generators must adequately characterize their wastes at the original point of generation to determine the appropriate 40 CFR Part 261 EPA hazardous waste codes to be assigned and if their hazardous waste is subject to LDRs (40 CFR § 262.11; see also Section 2.1). Each EPA RCRA hazardous waste code has one or more corresponding LDR treatment standards in 40 CFR Part 268, Subpart D. If a waste is subject to LDRs at the point of generation, the applicable 40 CFR Part 268 LDR requirements will continue to apply to the waste from “cradle to grave.” For example, if an LDR prohibited waste is subsequently decharacterized or excluded from the definition of hazardous or solid waste, it may still be prohibited from land disposal until applicable treatment standards are met. As waste is treated — sometimes by a combination of on-site and off-site process steps — to meet the applicable treatment standards, the point at which compliance with the initial treatment standards is generally determined for LDR purposes is when the waste treatment processes are complete and the waste is ready for disposal. If, at this point, new codes are identified as having been added by the treatment, this would be a new point of generation for these codes. If applicable to the new codes, a new UHC determination would also be required. Additional treatment would then be required to meet the treatment standards for the newly assigned codes and UHCs (see 64 FR 25408, p. 25411, Item 8: “Treatment Residuals and Point of Generation of a New Hazardous Waste for LDR Purposes”). Because of potential changes in these requirements, it is particularly important to review the current requirements when determining treatment requirements.

If a 40 CFR 261 Subpart D listed hazardous waste to be land disposed also exhibits any hazardous waste characteristics as defined in 40 CFR Part 261 Subpart C, the LDR treatment standards for all applicable listed and characteristic waste codes must be met unless the treatment standards for the listed waste specifically include standards for the constituents responsible for causing the waste to exhibit the characteristics. In such cases, the waste can generally be treated to meet only the treatment standards for the applicable listed waste codes.

Treatment technology developers and users may participate in the development or revision of LDR treatment standards by supplying relevant data to the EPA. To develop its LDR treatment standards, the EPA first collects current technical data on available and effective treatment technologies that have been demonstrated on well-characterized wastes in each waste code category. For each waste code category, the technology that is most effective in reducing the intrinsic hazard/toxicity or mobility of the hazardous constituents in the waste is selected as the “Best Demonstrated Available Technology” (BDAT). The information used as the basis for selecting the BDAT should conform to the requirements in the EPA’s “Best Demonstrated Available Technology (BDAT) – Background Document for Quality Assurance/Quality Control Procedures and Methodology” issued October 23, 1991, as revised.

Once the BDAT is determined, the EPA establishes a waste-code-specific treatment standard based on routinely achievable BDAT performance. A treatment standard can be a concentration level (e.g., 0.025 mg/l in an extract of the treated waste or 1 mg/kg total concentration in the treated waste); or the treatment standard can be expressed as the required use of one or more specified technologies. Specified technologies, such as chemical oxidation, carbon adsorption, and high-temperature combustion, are described in general terms in 40 CFR 268.42. Examples of many of the technologies that will meet the “specified technology” treatment standard of “DEACT” to remove the characteristic of ignitability, corrosivity, or reactivity are detailed for applicable waste codes and subcategories in Appendix VI to Part 268. Incineration, which destroys hazardous organic constituents, thus removing their associated toxicity, is one example of a BDAT that has been established as a specified technology treatment standard for certain wastes and has also been used to set concentration-based treatment standards for others. Another example of a BDAT is stabilization. By chemically or physically immobilizing toxic metals, for example, stabilization can reduce the leachability (mobility) of these metals. For hazardous waste codes for which stabilization is the identified BDAT, the treatment standards can be expressed as a leachate concentration limit. Note again that the LDR treatment standards established to date are strictly technology-based standards — not risk-based standards. This is in contrast to a proposed hazardous waste identification rule that would use risk assessment methodologies to establish treated waste concentration limits for land disposal.

Because a given treatment generally performs differently on wastewaters and non-wastewaters, and different treatments altogether may be required for wastewaters and non-wastewaters, separate treatment standards are set for these two “treatability groups” within each waste code. For the purposes of RCRA LDR, 40 CFR § 268.2 defines wastewaters based on the percentages by weight of total organic carbon (TOC) and total suspended solids (TSS) in a liquid waste. Although the LDR treatment standards are assigned at the point of generation, if wastewaters are treated and produce a treatment residual that is a non-wastewater, a “change in treatability group” is said to occur that requires the final residual waste form to be tested for compliance with the non-wastewater treatment standard for the initial waste code (i.e., rather than the wastewater treatment standard). Also see the previous discussion on point of generation and potential addition of new codes and associated UHCs as a result of complete treatment of a given original waste.

To meet RCRA LDR concentration-based treatment standards, the waste can be treated by any properly permitted technology or set of technologies (not necessarily BDAT) that can achieve the given concentration level for the final waste form. Tests done to demonstrate that wastes comply with the LDR treatment standards must be performed according to regulatory agency guidance and recommendations, generally the applicable EPA SW-846 test protocols are used.

When questions arise on point of generation, change in treatability group, waste form testing, or other aspects of the LDRs, communication with the appropriate regulators may be needed to help resolve the issue.

Universal Treatment Standards

As stated by the EPA, “Use of BDAT to set treatment standards for hazardous wastes resulted in different treatment standards for the same hazardous constituent in different wastes. For example, F005 and U019 non-wastewaters both require treatment for benzene; however, the treatment standard originally set for benzene in the spent solvent was 3.7 mg/kg, while the standard originally set for unused, discarded benzene was 36 mg/kg” (EPA, 1997b; also see the LDR Phase II final rule of 9/19/94: 59 FR 47982). To achieve consistent concentration-based standards, the EPA assigned a single numeric treatment standard to each RCRA hazardous waste constituent for wastewaters and a separate single value to each such constituent for non-wastewaters. A consolidated list of these constituents and the corresponding two treatment standards (wastewater and non-wastewater) for each are given in 40 CFR § 268.48. These “universal treatment standards” (UTS) now also supply the current concentration-based treatment standards for individual RCRA hazardous waste constituents in 40 CFR § 268.40.

Treatment of Underlying Hazardous Constituents

In 1992, the D.C. Circuit Court held that the LDR treatment standards for characteristic wastes must address all the hazardous constituents of concern in the waste to be land disposed — not just the ones responsible for the characteristic. The court also ruled that dilution was ordinarily not a permissible means of treating hazardous constituents (EPA, 2000a). The additional hazardous constituents requiring treatment are called “underlying hazardous constituents” (UHCs, see 61 FR 15566, April 8, 1996). When a characteristic waste requires treatment for UHCs, the applicable 40 CFR § 268.40 treatment standards include “and meet § 268.48 standards,” that is, the UTS levels. The UHC treatment standards are thus included as part of the applicable LDR treatment standards for certain characteristic wastes, although these UHCs do not themselves cause the waste to exhibit a characteristic. When an LDR treatment standard requires UHC treatment, the identification of all UHCs reasonably expected to be present at the original point of generation of the waste is incumbent upon the waste generator. When characteristic hazardous wastes have been treated to meet the applicable treatment standards, including those for the identified UHCs, the waste can be disposed of in a nonhazardous waste landfill — a Subtitle D or Subtitle D equivalent landfill. For mixed wastes, this means that the waste would be disposed in a radioactive waste disposal facility that meets these requirements.

Dilution Prohibition

Dilution of hazardous waste does not decrease the toxicity or mobility of the hazardous constituents in the waste. Therefore, dilution of LDR hazardous wastes or the residuals from treatment of a restricted waste as a substitute for legitimate treatment (e.g., to achieve compliance with numeric treatment standards or the DEACT specific-technology treatment standard) is generally prohibited (see 40 CFR § 268.3). There are, however, certain specific cases where dilution is permissible. For example, when an appropriate treatment process, such as stabilization, results in some dilution intrinsic to the process or when wastes are aggregated for a legitimate treatment process that is appropriate for each individual waste, the hazardous constituents in the aggregated waste may be more dilute than in some of the individual wastes. To specifically address the dilution concern for toxic metals in wastes to be combusted, the dilution prohibitions require that these wastes additionally meet one of six criteria (see 40 CFR § 268.3(c)) that ensure that combustion is an appropriate technology. Under certain conditions, dilution of some characteristic wastes managed in certain CWA-regulated or equivalent wastewater treatment or pretreatment systems is allowed (see also the CWA discussion in this chapter), to meet numeric treatment standards or the DEACT technology treatment standard. In this case, the waste need only be decharacterized; UHCs are not required to be treated (see 40 CFR § 268.40).

Alternative LDR Treatment Standards

Debris is defined in 40 CFR § 268.2 as solid material exceeding a 60-mm particle size that is intended for disposal and is "a manufactured object; or plant or animal matter; or natural geologic material." The definition excludes "any material for which a specific treatment standard is provided in Subpart D, Part 268, mainly lead acid batteries, cadmium batteries, and radioactive lead solids; process residuals such as smelter slag and residues from the treatment of waste, wastewater, sludges, or air emission residues, and intact containers of hazardous waste that are not ruptured and that retain at least 75% of their original volume." A waste that is a mixture of debris and other material is subject to regulation as debris if the mixture is composed "primarily" of debris, by volume, based on visual inspection.

Alternate RCRA LDR treatment standards for debris that is contaminated with hazardous waste are given in 40 CFR § 268.45. The alternative debris treatment standards were developed for materials that are not well suited for treatment to meet the waste-code-specific treatment standards in 40 CFR § 268.40. The alternative debris treatment standards allow various surface cleaning, extraction, destruction, and immobilization treatment technologies to be used, based on the type of debris and the waste with which it is contaminated. When using these alternative treatment standards, the debris must be treated for each "contaminant subject to treatment," as defined in 40 CFR § 268.45(b), using one of the specified technologies, and the treatment process must meet certain performance and/or design and operating requirements. Debris treatment residuals must be separated from the treated debris, characterized, and meet the applicable waste-specific treatment standards. Hazardous debris that is also a PCB waste under 40 CFR Part 761 is subject to the requirements of either 40 CFR Part 761 or 40 CFR § 268.45, whichever are more stringent.

In addition to the alternative debris treatment standards, the EPA has established alternative treatment standards for soils contaminated with a listed hazardous waste or that exhibit a hazardous waste characteristic (40 CFR § 268.49). The alternative soil treatment standards require that the total or extract concentration (as applicable) of each hazardous constituent subject to treatment be reduced by 90%, with an allowance that the reduction need not be to a level lower than ten times the constituent UTS. A state must formally adopt this "less stringent" federal rule for it to be effective in that state.

Exemptions, Exclusions, and Variances that Can Affect Waste Treatment

In 40 CFR Parts 261 and 268, the EPA provides various conditional and non-conditional solid waste exclusions, hazardous waste generator exclusions, and hazardous waste exclusions and exemptions and variances from all or portions of the RCRA Subtitle C requirements and implementing regulations. These will need to be reviewed in detail when determining if and how RCRA regulates your final waste form/waste treatment, treatability study, treatment facility, and samples of waste for characterization or treatability studies.

In 40 CFR Part 261.4(e), the EPA conditionally excludes persons who generate or collect samples to be used in small-scale treatability studies from the remaining portions of 40 CFR Part 261, from Parts 262 and 263 (including Part 261 and 262 hazardous waste quantity determinations), and from the notification requirements of RCRA Section 3010. In a treatability study, defined in 40 CFR § 260.10, small samples of mixed waste are used when needed to determine the efficiency, effectiveness, and optimal conditions for a process as well as the quantity and types of secondary wastes and emissions produced. The study may also include, for example, pretreatments, process system material compatibilities, and safety- and health-related information. Additionally, 40 CFR Part 261.4(f) conditionally excludes treatability samples undergoing treatability studies and the laboratories performing the treatability studies from the remaining portions of 40 CFR Part 261, Parts 262 through 266, 268, 270, and the notification requirements of RCRA Section 3010. The authorized regulatory agency must be notified in writing at least 45 days in advance of initiating a treatability study. Specific notification requirements can vary: some regulators may want to perform a detailed review and request more information, while others may be satisfied with a simple notification. Therefore previous interaction with the regulator on these requirements is recommended. With the exception of allowed 5-year archiving of treated materials for future evaluation, unused samples or residues generated during the treatability study no longer qualify for the sample or treatability study exclusions and become subject to all applicable hazardous waste requirements 90 days after completion of the treatability study, or 1 year from the date of shipment of the sample to the laboratory or testing facility, whichever occurs first. For bioremediation studies, 2 years from the date of initial shipment are allowed. The treated waste form generally must undergo a hazardous waste determination to attach any new hazardous waste codes and associated underlying hazardous constituents added by the treatment, so that the waste can be managed accordingly when the exclusion period ends. LDR treatment standards applicable to the original waste (i.e., at its point of generation) apply to any remaining treatability study sample and to the treated waste when the exclusion period ends. Thus, these wastes must meet the treatment standards that would have applied to the original waste, as well as any new ones applicable to the waste form following treatment.

In 40 CFR § 261.4(d), the EPA also excludes small “characterization” samples of wastes and contaminated environmental media from the requirements of other Sections of 40 CFR Part 261 as well as Parts 262 through 268, 270, 124, and the notification requirements under RCRA Section 3010 when the samples are collected and shipped for the sole purpose of testing to determine hazardous waste characteristics or composition. To qualify for the exclusion, certain specific provisions related to transfer, storage, and shipping of the samples must be met. The exclusion applies until the testing is completed if the sample is not being returned to the generator. If, after testing is completed, the sample is returned to the generator, the exclusion applies until the point at which the generator receives the returned sample. At that point, the sample becomes subject to all the normally applicable requirements for RCRA hazardous waste. If, after testing is completed, the sample is stored for an “unreasonably” long time (generally longer than 1 year) before being returned to the generator, it might also become subject to all applicable RCRA hazardous waste requirements. The characterization sample exclusion is “intended to apply to small samples (typically under one gallon)” of the size needed for the laboratory to perform the testing needed for compliance with applicable regulations (not just RCRA) (EPA 2000b).

If mixed wastes are legitimately recycled, they are conditionally exempt from Subtitle C regulation once they enter the recycle process itself (see 40 CFR § 261.6). Up to that time, the wastes must be in compliance with RCRA Subtitle C regulations for hazardous wastes, including generator, transporter, and storage requirements. However, the chemicals in mixed wastes are not recycled as frequently as those in non-mixed hazardous wastes because of difficulties in obtaining products free of radioactive contaminants. Future improvements in technology may make recycling more viable for mixed wastes.

In 40 CFR Part 268, the EPA provides the means to request and obtain specific date extensions for, and variances and exemptions from, LDR prohibitions and treatment standards, including compliance date extensions and approval of replacement standards.

Mixed wastes can be land disposed in a specific disposal unit without meeting the LDR treatment standards if the disposal unit has been issued a “no-migration variance” pursuant to 40 CFR § 268.6. To obtain such a variance, a petitioner must show that health-based levels of hazardous constituents in the waste will not be exceeded outside the disposal unit boundaries for as long as the waste remains hazardous.

When a petitioner can demonstrate that applicable treatment standards and BDAT technologies are inappropriate or unachievable for a particular waste, and that the subject waste is significantly different from the wastes evaluated by the EPA in setting the standards, the agency may, generally after public review, grant a 40 CFR § 268.44 treatment standard variance. (See also 55 FR 22526; June 1, 1990).

If an applicant can demonstrate to the EPA, or in some cases to the Regional EPA Administrator, that an alternate treatment method or treatment standard can achieve a level of performance equivalent to that of an applicable specified technology treatment standard and that the alternate treatment standard is adequately protective of human health and the environment, the EPA may make a 40 CFR § 268.42(b) Determination of Equivalent Treatment and grant an equivalent treatment method variance that includes a replacement treatment standard for the specific affected waste.

There are several other limited exclusions for specific wastes otherwise subject to LDRs in 40 CFR § 261.4, as well as for remediation wastes managed in "corrective action management units" (CAMUs) in 40 CFR § 264.552, for remediation wastes managed in "temporary units" in 40 CFR § 264.553, and in 40 CFR § 268.4 for wastes generated or treated in impoundments.

Finally, if a petitioner can demonstrate to the authorized regulatory agency (generally the EPA region or state agency) that the hazards that caused the EPA to list a specific waste in 40 CFR 261 Subpart D are not associated with that waste as generated or treated at a specific facility, the agency may remove the listed code — "delist" the waste — on a waste- and facility-specific basis in a regulatory amendment per 40 CFR § 260.22. Similar determinations — "no-longer-contained-in determinations" — can be made on a site-specific basis for environmental media and debris that are contaminated by listed or characteristic hazardous waste. Listed media or debris for which a no-longer-contained-in determination is granted is generally exempt from RCRA Subtitle C regulation; however, LDR requirements can continue to apply in some cases (see 63 FR 28621 and 21622 for a recent EPA discussion of the contained-in policy).

If, in developing a new LDR treatment standard, the EPA determines that there is inadequate treatment, recovery (for recycling), or disposal capacity on a nationwide basis for waste subject to that standard, the agency may extend the effective date of the standard for up to 2 years (RCRA Section 3004(h)(2)) (National Capacity Variance). As provided in 40 CFR § 268.5, the EPA can similarly extend the effective date of the standard for a specific waste when a petitioner successfully demonstrates inadequate treatment capacity for that waste (Case-by-Case Extension).

Waste Treatment Requirements Associated with the Comprehensive Environmental Response, Compensation, and Liability Act

While RCRA emphasizes management of hazardous wastes to prevent potential threats to human health and the environment, CERCLA is aimed at remedies for existing or imminent "uncontrolled" releases of hazardous substances to the environment that pose a threat to human health or the environment. CERCLA hazardous substances are listed in 40 CFR § 302.4 and include all RCRA hazardous wastes, radionuclides, and many other substances listed by other statutes — such as TSCA, the CWA, and the CAA. CERCLA "removal" and "remediation" actions may involve hazardous wastes and contaminated environmental media that need treatment before being legally disposed.

When a waste is removed from the bounds of a CERCLA site and meets the definition of a RCRA or TSCA hazardous waste, it and its treatment facility are generally subject to all applicable RCRA and TSCA requirements. If, however, the CERCLA wastes or media are treated on-site, "substantive" "applicable or relevant and appropriate requirements" (ARARs) from any other federal or state environmental laws, regulations, or criteria must be applied to the clean-up remedy selected, to determine, for example, the CERCLA clean-up goals, the specifications that treated waste and contaminated media derived from the site must meet, and other requirements that the selected clean-up remedy must meet. Substantive requirements usually include numeric standards, monitoring requirements, and design and operating standards for treatment units, but exclude administrative requirements such as RCRA permits that would otherwise be required outside the CERCLA arena. Off-site treatment and disposal of non-RCRA, non-TSCA, and CERCLA wastes can be subject to waste-specific treatment and disposal facility waste acceptance criteria. RCRA LDR treatment standards are frequently used as ARARs for CERCLA wastes treated and disposed on-site; however, the EPA is evaluating the appropriateness of such use of these standards.

In the course of setting ARARs, the regulatory agency can also waive certain technical requirements that would normally apply outside the CERCLA arena. In addition to the process for applying ARARs, Congress also established a risk-based threshold and risk-based procedures for identifying additional requirements needed to ensure that the overall remedy and clean-up are protective. The collective requirements that must be met for the CERCLA site, including associated wastes, environmental media, and clean-up activities, are generally issued by the authorized regulatory agency or agencies in Records of Decision and in the subsequent plans and reports that the CERCLA program requires.

Waste Treatment Requirements Associated with the Toxic Substances Control Act

PCB wastes are not specifically included in the RCRA listed wastes or the RCRA toxicity characteristics. They are included, however, in the UHCs that must be treated to meet UTS for certain RCRA hazardous wastes. Aside from that, TSCA regulations in 40 CFR Part 761 govern the requirements for treatment of PCB wastes. In the TSCA regulations, the term “treatment” is rarely used explicitly, but is implicitly included in the words “clean-up” and “disposal.” The PCB clean-up and disposal requirements are partly dependent on PCB concentration and waste matrix type. The TSCA dilution prohibition, in 40 CFR § 761.1(b)(5), is similar to that in the RCRA hazardous waste regulations. PCB wastes generated from R&D activities and during chemical analysis are specifically addressed in 40 CFR § 761.60(j), 761.64, and 761.30(j).

Similar to RCRA, the TSCA requirements include both technology-based and concentration-based (total or leachate concentrations) clean-up and disposal requirements that depend on the PCB classification of the waste. This classification is generally based on the concentration of PCBs in the waste and the specific source or type of waste. For example, as of late 2000, PCB liquids that exceeded 500 ppm could only be disposed by incineration that meets 40 CFR § 761.70 requirements or a technology approved as equivalent to incineration. More flexible requirements for PCB-contaminated liquids from “incidental sources” (other than remediation waste) allow landfilling (§ 761.60(a)(3)) if they do not exceed 500 ppm PCBs and are not ignitable.

PCB decontamination standards and associated requirements for water, organic liquids, nonporous surfaces, concrete, and nonporous surfaces covered with porous non-liquid PCBs (such as in paint or coatings) are in 40 CFR § 761.79. This section also provides alternative cleaning procedures that can be used in lieu of the numeric standards for containers, equipment, tools, and other nonporous surfaces. Thermal processes to decontaminate metal surfaces are specified in § 761.72. Alternative self-implementing risk-based decontamination levels or methods may be approved on a case-by-case basis per § 761.79. Materials that meet the appropriate TSCA decontamination standards are not TSCA regulated and can be reused.

Sections 761.61 through 761.64 of 40 CFR conditionally allow land disposal of PCB remediation wastes, bulk product wastes (e.g., plastics, paints), and R&D wastes without requiring incineration or special chemical waste landfilling. Section 761.61 specifies clean-up and disposal options for remediation waste (e.g., rags, environmental media, sewage sludge, debris, and contaminated building structure debris) resulting from clean-up of any regulated PCB liquid spill or release. This waste is regulated according to the concentration of the contamination, the potential for exposure to people, and the contamination matrix (liquids, nonporous surfaces, porous surfaces, soils, sediments, dredged materials, muds, sewage sludge, and industrial sludge). The EPA has implemented a tiered system of options for PCB waste clean-up and disposal. Under some conditions, self-implementing clean-up and disposal may be allowed using the most stringent clean-up/treatment levels set by the EPA. This requires 30-day notifications of all applicable (local through regional) regulatory agencies, but no regulatory agency approval. The next tier is performance-based disposal per 40 CFR § 761.61(b) using specified approved technologies, such as destruction in a high-temperature incinerator or high-efficiency boiler, disposal in a chemical waste landfill, use of an alternate technology or permit umbrella approved by the EPA, or using the decontamination standards and methods in § 761.79. The final tier is risk-based disposal that must be approved by the EPA and state or tribal agencies as applicable. Risk-based, site-specific clean-up levels/treatment standards can sometimes be less stringent than the default levels used for self-implementing clean-up/treatment. The risk-based levels and the information that supports them generally must be demonstrated and publicly reviewed before approval.

Bulk product wastes (40 CFR § 761.62) include wastes in which the PCB contamination is or derives from manufactured products that contained only non-liquid PCBs in concentrations greater than 50 ppm when they were determined to be waste. Bulk product wastes include such things as dried paints, coatings and sealants, structures, plastics, rubber parts, and other materials in which the PCBs are contained within the material matrix. Conditional disposal options for bulk product PCB wastes include technology-based standards (e.g., incineration or protective landfilling, such as in an RCRA Subtitle C landfill), concentration-based standards based on leach testing, and waste- and site-specific risk-based standards approved on a case-by-case basis. The EPA also provides the means to apply for alternative disposal standards.

Waste Treatment Requirements Associated with the Atomic Energy Act as Implemented by the NRC and DOE

Many disposal site-specific waste specification and testing requirements are contained in the site's "Waste Acceptance Criteria" (WAC) and communicated by site staff as part of the waste acceptance process. The NRC or DOE required radiological performance assessments for the specific disposal site can be expected to be the basis for some of the physical and chemical waste form and content limitations, the radioisotopes that can be accepted and their concentration or activity limits. Radiological limits may be on a container basis or shipment basis.

General waste treatment requirements specific to radionuclides and radioactive wastes are included in NRC and DOE regulations and guidance. For example, both DOE and NRC radioactive waste disposal and transportation requirements prohibit waste that is reactive, including pyrophorics, and wastes that are capable of generating harmful quantities of toxic gases, vapors, or fumes, including hydrogen generation from radiolysis of hydrogenous materials in TRU wastes. Because liquids and chelating agents tend to allow or facilitate mobilization of radionuclides after disposal, liquids and chelating agents are generally prohibited or restricted from disposal at radioactive-waste disposal sites. When stabilizing agents are used to eliminate free liquids, some radioactive-waste disposal sites may require the use of pre-approved stabilizing agents or require submittal of test results to gain approval of any new stabilizing agents. The heat generation of the waste will also be limited, to ensure that the temperature of the waste does not contribute to release and mobilization of radionuclides. When a waste contains significant quantities of tritium, which is difficult to contain, a tritium release rate may be imposed on the waste matrix or package. Fissile material will be limited, either on a concentration basis or total quantity basis.

The NRC's 10 CFR § 61.56 gives general waste physical and chemical specifications that LLW must meet for disposal. For example, "stabilization" of NRC Class B and C LLW is required. The NRC "Technical Position Paper on Waste Form" (NRC, 1991) provides more detailed guidance for structural stability required by 10 CFR § 61.56 for Class B and C LLW. The required compressive strength testing (generally ASTM C39 [ASTM, 1980]) performed in accordance with ASTM D1074 (ASTM, 1980) for the stabilized LLW is based on the waste's being able to withstand the loading of the earthen cover for the LLW landfill without fracturing or crushing over a 300-year period. In some cases, the LLW stabilization requirements may be met by a "high-integrity" container that meets applicable specifications, rather than by the treated waste form. The NRC position paper also includes guidance for 90-day radionuclide leach testing in accordance with ANS 16.1 (ANS 1981) for Class B and C LLW.

All HLW disposal must be NRC licensed. The EPA's 40 CFR 191 standards for protection of human health and the environment apply to the management of HLW and transuranic waste, including disposal at DOE facilities that are not NRC licensed (e.g., WIPP). The NRC's 10 CFR 60 provides general licensing requirements for HLW disposal. As of late 2000, however, the congressionally mandated site-specific EPA and NRC rules governing the proposed Yucca Mountain, Nevada, HLW disposal site had not been promulgated. DOE has in the interim established acceptance criteria and specifications for HLW that is vitrified in borosilicate glass to implement the currently available requirements (DOE, 1996, 1999a). The DOE is also developing similar specifications for HLW ceramic waste forms.

In 40 CFR § 191, the EPA stipulates that NRC and DOE may decide that some transuranic wastes need the same kind of isolation as HLW. General requirements for NRC licensing of disposal of such waste in the commercial sector are specified in the 10 CFR Part 61 requirements for Greater-than-Class-C LLW as being determined by NRC on a case-by-case basis. DOE requirements for DOE transuranic waste forms to be accepted at the DOE WIPP disposal facility are provided by the WIPP Waste Acceptance Criteria (DOE, 1999b).

Final waste form requirements for LLW mixed wastes are fairly mature, although still subject to changes and inflexibilities in the RCRA regulations. Much headway has been made in the definition of acceptable final waste forms for DOE's transuranic waste and for commercial and DOE HLW disposal at the potential Yucca Mountain site. However, inflexibilities and cloudiness in the U.S. source-based definitions of HLW and LLW and in the final EPA and NRC requirements for disposal are viewed as causing corresponding issues in the selection of disposal and treatment technologies for wastes that may be "derived" from HLW but have radiological characteristics consistent with those typical of LLW or transuranic waste.

Requirements Affecting Design and Operation of Mixed Waste Treatment, Storage, and Disposal Facilities

The following discussion covers regulations that potentially govern the design and operation of treatment, storage, and disposal facilities (TSDFs) and facilities that perform treatability studies. Although many of the RCRA permitting requirements address a specific category of facility, requirements can also be "borrowed" from regulations that are not directly applicable to a facility or process if, during the RCRA permitting process, they are judged to be needed to provide adequate protection of human health and the environment. The authority to do this is contained in the "RCRA omnibus authority" provisions. With some exceptions, RCRA mixed waste TSDFs must obtain an RCRA permit according to the requirements of 40 CFR Parts 270 and 264/265.

Other major laws that may govern environmental aspects of mixed waste treatment facilities include the AEA, CERCLA, CWA, TSCA, the Safe Drinking Water Act (SDWA), the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA), and the Pollution Prevention Act (PPA). This section does not address facility closure requirements or include regulations administered by agencies other than EPA, DOE, or NRC, for example, health and safety requirements under the Occupational Safety and Health Administration (OSHA) or transportation requirements under the Department of Transportation. In addition, as noted early in this chapter, the complex requirements cannot be adequately represented here. Important subjects that are not covered are the requirements for waste tracking, recordkeeping, packaging and manifesting shipments, storing wastes, and the 40 CFR § 268.7 notifications and certifications that must be transmitted when wastes are transferred to a TSDF or between TSDFs.

Resource Conservation and Recovery Act (RCRA)

RCRA operational standards in 40 CFR Part 264 and permitting requirements in Part 270 apply to RCRA mixed waste TSDFs unless they are otherwise exempt, for example, facilities that perform only authorized treatability studies. Existing facilities that are brought under the RCRA umbrella by new rulemaking can apply for designation as an "interim status" facility subject to the applicable operational standards of 40 CFR Part 265 before they become fully RCRA permitted and subject to the standards of 40 CFR Part 264. There are a few exceptions to the applicability of the Part 264 and 265 standards to mixed waste TSDFs. RCRA TSDF facilities that manage only mixed wastes are not currently required to meet the RCRA organic emissions standards for process vents (Parts 264/265, Subpart AA), equipment leaks (Parts 264/265, Subpart BB), and cover requirements for certain hazardous waste management units (Parts 264/265, Subpart CC). The volatile organic emissions subject to these standards include an extensive list of volatile organic compounds, many more than the RCRA toxicity characteristic list of volatile organics. Additional conditional exceptions to RCRA permit requirements are material recycling facilities per 40 CFR 266, generator treatments per 40 CFR 262 and 268 within a 90-day accumulation period, and treatability studies per 40 CFR 262.

RCRA regulations allow for accumulation of hazardous wastes in temporary accumulation areas for up to 90 days without a permit or interim status designation (40 CFR 262.34). An interpretation presented in the Federal Register on March 24, 1986, clarifies that treatment of these wastes does not require an RCRA permit provided that the generator is in conformance with the requirements of 40 CFR 262.34 and Subparts J and I of Part 265. Furthermore, 40 CFR 268.7(a)(4) requires the generator to prepare, submit, and follow a written Waste Analysis Plan for treatment of such wastes.

An RCRA Research, Development, and Demonstration (RD&D) permit may be granted in lieu of a full RCRA permit for certain RD&D activities when these activities will take place in 1 year or less. The RD&D permit is renewable for a second year. Because of the time limitations, RD&D permits have not been used extensively for mixed waste RD&D, which generally takes longer than RD&D on nonradioactive hazardous waste.

RCRA TSDFs that are implementing clean-up of hazardous wastes or their constituents that have been released to the environment or are in imminent danger of being released by their operations and that pose a threat to human health or the environment are generally governed by a RCRA corrective action enforcement order or the TSDF RCRA permit, although in certain cases, CERCLA authority may be imposed for such clean-ups, particularly at federal facilities.

The EPA prohibits storage of LDR-subject RCRA hazardous waste except to accumulate a quantity needed to facilitate recycling, treatment, or disposal (40 CFR § 268.50). In the first year of storage, it is incumbent upon the EPA to prove that the waste is not being stored for the proper reasons; thereafter, the storage facility owner bears this burden of proof. In the case of RCRA hazardous waste materials that are being accumulated for recycling, 40 CFR § 260.31 requires, in addition, that at least 75% of the volume accumulated at the beginning of a year be recycled by the end of the year. Recyclable material storage that violates this “75% rule” is termed “speculative accumulation.” As of late 2000, an EPA policy that gives low priority to enforcement of the LDR storage prohibition for non-DOE mixed wastes was in effect. Time limits for storage of DOE RCRA mixed wastes at a given DOE site are tied to the demonstration of compliance with the site’s regulatory agency approved mixed waste treatment plan (Site Treatment Plan). Site Treatment Plans generally include milestones for treatment and disposal of the DOE mixed wastes.

As of late 2000, there were four exemptions to the LDR storage prohibition: (1) hazardous remediation wastes stored in a staging pile per 40 CFR § 264.554, (2) wastes being accumulated on-site for a limited time per 40 CFR § 262.34, (3) transporters storing waste at a transfer facility for 10 days or less per 40 CFR § 263.12, and (4) wastes placed in storage before the effective date of an otherwise applicable land disposal prohibition. For the latter, removal from storage for characterization or treatment, for example, triggers the storage prohibition.

Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA)

A CERCLA-subject contaminated site may have treatments applied *in situ* or waste and contaminated media derived from the site may be treated *ex situ*; the *ex situ* treatment may be within the contaminated area (on-site) or off-site. The regulatory requirements affecting the treatment facility may differ considerably among these three cases and between on-site facilities at different CERCLA sites. This is because many of the requirements set for the *in situ* and on-site *ex situ* treatments will include the substantive, but not the administrative requirements of the regulations from other authorities that would fully govern off-site treatment facilities. Examples of substantive requirements are the requirements to identify and segregate incompatible wastes, as well as CAA air emissions limits and CWA aqueous effluent limits. Substantive requirements can sometimes be waived for a specific CERCLA site or area by the authorized regulatory agency. Administrative requirements that are generally waived are the requirements to obtain formal RCRA and CAA permits for on-site TSDF activities.

The CERCLA's "off-site rule" requires that hazardous wastes taken off the CERCLA site be subject to full RCRA regulation, as applicable. The off-site rule also requires advance regulatory agency approvals for transfer of any CERCLA wastes to an off-site TSDF, laboratory, or testing facility for treatability studies. Preliminary to approval, EPA policy is to require an on-site inspection of the off-site TSDF by the regional EPA office 6 months prior to receiving the CERCLA waste (EPA 1998).

Toxic Substances Control Act (TSCA)

TSCA-regulated chemicals include asbestos, chlorofluorinated hydrocarbons used as aerosol propellants, hexavalent chromium, and polychlorinated biphenyls (PCBs). Of these, PCBs are commonly encountered in mixed wastes. The TSCA governs the uses of PCBs, clean-up of spills, PCB storage, and the disposal of PCB wastes and contaminated media. The EPA's 1998 "Disposal of Polychlorinated Biphenyls (PCBs)" rule (63 FR 35384) increased the flexibility for clean-up and disposal of PCBs, particularly for PCB remediation wastes, laboratory analysis related wastes, and certain products (e.g., paint) manufactured with PCBs.

Similar to the RCRA, most treatment and associated handling activities for PCBs and PCB-contaminated materials and media require formal regulatory approval. Operating conditions for high-efficiency boilers and scrap metal recovery ovens/smelters that feed PCB wastes are in 40 CFR § 761.71 and 761.72, respectively. These scrap metal recovery ovens/smelters may alternatively operate under a state air emissions permit that includes a PCB standard. R&D that is accomplished in less than 1 year on less than 500 gallons of liquid or 70 cubic feet of non-liquid PCB waste that does not exceed 10,000 ppm PCBs does not require agency approval. Agency approvals may be granted for R&D on larger amounts of material and for longer times.

PCB mixed waste is exempted from the TSCA 1-year storage-for-disposal limit, provided that records are kept that document disposal attempts and progress. PCB waste storage is allowed in RCRA-permitted storage facilities. PCB remediation waste, bulk product waste, and wastes stored in a facility certified under a TSCA "coordinated approval" per 40 CFR § 761.77 do not need formal storage facility approvals under § 761.65(d). TSCA coordinated approvals are EPA TSCA authority approvals of applicable storage or disposal permits issued under other authorities than TSCA that provide for the requisite control of PCBs per 40 CFR § 761.77.

Facilities performing self-implementing clean-up and disposal of PCB wastes under 40 CFR § 761.61 must notify the EPA and the applicable state or tribal agency at least 30 days before the clean-up per 40 CFR § 761.61(a)(3). If the regulatory agencies do not respond within 30 days and do not provide more stringent clean-up levels, the clean-up can proceed as in the notification and must meet PCB clean-up levels given in 40 CFR § 761.61(a)(4) or use the applicable technologies approved under § 761.60 or 761.70.

Clean Air Act (CAA)

To achieve and maintain acceptable regional ambient air quality to meet EPA National Ambient Air Quality Standards (NAAQS), states regulate certain industry categories, such as incinerators, for new point source criteria pollutant emissions using emissions standards consistent with EPA new source performance standards. Other potentially applicable CAA requirements are the EPA's Stratospheric Ozone Protection Standards and National Emission Standards for Hazardous Air Pollutants (NESHAPs). For example, source-specific NESHAPs for hazardous air pollutant emissions from hazardous (and mixed) waste combustors are found in 40 CFR § 63 and NESHAPs for radionuclide emissions are in 40 CFR § 61. Source-category-specific CAA requirements can be applied to other categories of mixed waste treatment facilities via CERCLA ARARs or RCRA permitting under RCRA "omnibus" authority to apply requirements necessary to protect human health and the environment. States may have additional requirements for smaller sources and toxic air pollutants not included in the EPA regulations.

When designing or implementing a mixed waste treatment process, air emissions that could fall under the CAA regulations must be identified and assessed to determine if a new or revised CAA Permit to Construct or NESHAPs permit is needed for the unit or possibly the entire facility, or whether similar actions for a facility-wide CAA operating permit may be needed. The CAA permits will include limitations and conditions on airborne emissions. For certain levels of radionuclide emissions, monitoring may be required even if a permit is not.

Clean Water Act (CWA)

Two Clean Water Act (CWA) goals are to achieve surface water quality that (1) “provides for the protection and propagation of fish, shellfish and wildlife,” and (2) “for recreation in and on the water.” To assist in meeting these goals, National Pollutant Discharge Elimination System (NPDES) permits are required for regulated direct discharges affecting surface waters. Mixed waste treatment facilities that discharge aqueous effluents indirectly via a publicly owned sewage or industrial waste treatment works (POTW) that has an NPDES permit are generally subject to effluent conditions and pretreatment requirements that ensure the POTW NPDES permit conditions will not be violated. The CWA also provides for regulation of non-point-source pollution, for example from outdoor storage area stormwater runoff, for facilities in areas that meet the entry criteria for being subject to the stormwater runoff requirements. A regulatory program similar to the NAAQS is under development in the states for other non-point-source discharges of pollutants to surface waters.

Wastewater treatment units are defined in 40 CFR § 260.10 as essentially a tank or a tank system, also defined in 40 CFR § 260.10, that is part of a wastewater treatment facility subject to the CWA; that is, it has an NPDES permit or legally discharges to a POTW that has an NPDES permit (40 CFR § 270.2. 264.1(g) or 265.1(c)). If such a wastewater treatment unit stores or treats hazardous wastewater, 40 CFR § 264.1 conditionally exempts the tank system unit from RCRA permitting requirements (see that CFR section for the required conditions). The unit NPDES permit, or the POTW NPDES permit, provides the treatment requirements that must be met for the discharge from the wastewater treatment unit. The POTW, the EPA Region, and the applicable state regulatory authority must be notified in writing of any discharges of what would otherwise be an RCRA hazardous waste. When such discharges exceed a given amount, information must also be included on the waste content and the annual quantity to be discharged. The POTW operator should be consulted for these and any other applicable requirements.

Safe Drinking Water Act (SWDA)

The objective of the Safe Drinking Water Act (SDWA) is to protect public health from negative impacts of contaminants in drinking water. SDWA “maximum contaminant levels” are sometimes used as clean-up levels for RCRA/CERCLA clean-up of ground and surface waters. Because this book does not include treatment or disposal by underground injection regulated by the SDWA, associated SDWA permitting requirements for underground injection control are not discussed.

Pollution Prevention Act (PPA)

The Pollution Prevention Act of 1990 (PPA) required the EPA to promote reduction of the toxicity and volume of hazardous waste generated and the recycle/reuse of certain pollutants in hazardous wastes. Regulations that implement the PPA require TSDFs that exceed certain minimum levels of releases of toxic chemicals to report the releases annually to the EPA and provide information on their pollution prevention and recycling activities for these chemicals. To encourage recycling, facilities that currently meet regulatory requirements for recycling hazardous waste components are conditionally exempted from RCRA permitting requirements that apply to other hazardous waste management facilities. The

EPA is gradually promulgating regulations that more strongly encourage pollution prevention; for example, the hazardous waste combustor NESHAPs rule (40 CFR Part 63, Subpart EEE).

Atomic Energy Act (AEA)

The NRC is authorized under the AEA to license and otherwise regulate civilian use of "by-product, source, and special nuclear materials" to ensure adequate protection of public health and safety, the common defense and security, and the environment in the use of nuclear materials in the United States. Under this authority, the NRC regulates commercial nuclear power plants and other nuclear reactors; nuclear fuel cycle facilities; medical, academic, and industrial uses of nuclear materials; and transport, storage, and disposal of nuclear materials and wastes. The NRC is authorized by the AEA to issue licenses to commercial users of the designated radioactive materials and most other federal facilities that handle these materials, with the exception of Naval Nuclear Propulsion Program facilities and most DOE facilities. The DOE regulates the excepted facilities.

Most states have signed agreements with the NRC that delegate NRC authority for regulation of radioactive "source, by-product," and small quantities of "special nuclear material" within their state. The exception to the Agreement States' authority is that "production, utilization, other fuel cycle facilities," and HLW disposal facilities are subject directly to NRC's authority and requirements per Section 274(c) of the AEA. Other than HLW disposal facilities, most DOE facilities are subject to DOE rather than NRC or Agreement State authority and requirements. While Agreement States are required to adopt programs that are adequate to protect public health and safety and compatible with the NRC program, they can also adopt more stringent requirements. In general, NRC and its Agreement States license and regulate commercial wastes and facilities, while the DOE regulates its own radioactive wastes and associated facilities. Examples of exceptions important to mixed waste management are when DOE wastes are managed at commercial NRC licensed facilities, an NRC licensed DOE spent fuel storage facility, or any HLW disposal facility.

Disposal

In general, unless a special exception or variance applies, treated RCRA listed mixed wastes that meet all applicable treatment standards must be disposed in an NRC licensed or DOE regulated RCRA Subtitle C permitted facility. If a given waste is to be disposed in a Subtitle C facility, no final waste testing is required before disposal if (1) all applicable LDR treatment standards are specified technology standards, (2) the specified technology was used for treatment, and (3) the treatment was carried out in a "well-designed and operated" RCRA permitted facility or met other RCRA requirements for legal treatment by the specified technology, such as a generator treatment in a 90-day or 180/270-day accumulation area tank or container as described in 51 FR 10168 and 57 FR 37242. Similarly, if the initial waste bore only characteristic codes for which the applicable RCRA LDR treatment standards were only specified technology standards, waste successfully treated to meet these standards may be disposed in an NRC licensed or DOE regulated RCRA permitted Subtitle C facility without being tested, provided all other requirements are met. Land disposal in an NRC licensed or DOE regulated nonhazardous RCRA Subtitle D or Subtitle D equivalent facility is allowed only for mixed wastes that initially bore only characteristic codes, that were successfully treated to meet all applicable treatment standards, and that were tested and shown to be not characteristically hazardous after treatment. The disposal site for CERCLA waste must be approved by the applicable regulatory agency for the specific waste.

As of late 2000, DOE facilities authorized for disposal of mixed LLW — in Washington and Nevada — generally were not accepting mixed wastes from out of state, although in February, 2000, the DOE issued a Record of Decision stating that it had decided to begin using these disposal facilities for off-site wastes. Certain off-site or out-of-state mixed wastes can be accepted at these sites subject to special site and state approvals. One authorized commercial facility in Utah was accepting mixed LLW from across the nation for disposal. The WIPP facility, as discussed previously, was available for TRU and mixed TRU waste disposal. An NRC licensed, DOE operated facility was in planning at Yucca Mountain for disposal of HLW. No existing or planned facility has been specifically designated for mixed HLW or mixed greater-than-Class-C type wastes, although the NRC does have a process in place for approving limited disposal of greater-than-Class-C wastes at LLW disposal sites. Such a process, which requires demonstration that the disposal method would not result in unacceptable radiological dose to members of the public or workers, could potentially be used on a limited basis for mixed greater-than-Class-C wastes.

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For Further Information

The U.S. National Archives and Records Administration Internet home page at http://www.gpo.gov/su_docs/aces/aces140.html is a source of U.S. federal laws, the Code of Federal Regulations (including all the regulations issued as of July 1 of each year), and the *Federal Register*, which is published daily and includes new proposed and final regulations as well as notices of, for example, policy, guidance, and technical regulatory support documents issued by the regulatory agencies.

Ann B. Rappaport, "Chapter 1: Laws and Regulations," in *Standard Handbook of Hazardous Waste Treatment and Disposal*, 2nd edition, Harry M. Freeman, Editor, McGraw-Hill, New York, 1997, presents the historic, economic, social, and political context for legislation and regulations that control hazardous waste management.

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EPA’s RCRA online Web site at http://www.epa.gov/rcraonline/ has selected letters, memoranda, and questions and answers that may provide insight into RCRA regulatory interpretation questions.

Chapter Two

Waste Characterization and Classification

2.1

Sample Collection Design

John P. Maney

Introduction

Mixed waste data collection activities are usually made in response to an identified need, such as a need to comply with regulations, to prepare for litigation, or to gather information for decision-making. These underlying needs have been used to define project objectives, quality criteria, and data use for thousands of data collection activities implemented by federal and state agencies and the regulated community.

Because mixed waste data collection activities for the characterization of environmental and waste matrices have been undertaken on a substantial scale for many decades, one might assume that it is a mature and refined process. Yet much interest and debate still exists regarding the data collection process. One reason for this continued interest is that the underlying needs or drivers for data collection have changed as a result of public concern regarding radioactive and hazardous waste, improved sensitivity of analytical methodologies, and more demanding health- and risk-based standards.

Another reason for the continued interest is the complexity of the data collection process itself. Data collection usually requires that a substantial number of personnel, often from different disciplines, address numerous levels of detail (refer to Table 2.1) on schedule and in an exacting manner. Likewise, the role of suppliers, data processors, validators, statisticians, engineers, project managers, QA staff, regulators, and field and laboratory staff must be understood so that the appropriate project team can be assembled for planning and implementation. An error in any of the series of details being performed by the various team members has the potential to adversely impact data quality.

The data collection process is referred to as the "data life cycle" by the U.S. Environmental Protection Agency (USEPA, 1997). The USEPA defines the data life cycle as consisting of three phases: planning, implementation, and assessment. Although these three phases of the data life cycle are separate entities, it should be emphasized that rigorous integration of planning, implementation (sampling and analysis), and assessment is necessary to optimize the data collection process for the generation of data of known and adequate quality.

Planning, the first phase of the data life cycle, should address the details in Table 2.1, among others, prior to the implementation of sampling and analysis. In general, a structured approach to planning has been the most successful in efficiently addressing project details. A structured planning process consists of a sequence of steps put into practice by persons vested in the outcome (stakeholders) and persons who have the required technical expertise. There are a number of structured planning processes, including the USEPA's Data Quality Objective planning process (USEPA, 1994), the Department of Energy's Streamlined Approach for Environmental Restoration (DOE, 1993) and the Department of Defense's Data Quality Design (U.S. ACE, 1995). While these planning processes address the same issues, their terminology and emphasis vary. The USEPA's Data Quality Objective (DQO)

TABLE 2.1.1 Examples of Project Details

Objectives	• Identification and understanding of the project “need” or “driver” (e.g., regulations, liability, protection of human health and environment)
	• Identification and participation of stakeholders
	• Identification of pertinent thresholds and standards
	• Identification of Data Quality Objectives (e.g., the decision to be made, data needs)
	• Public relations
	• End-use of data
Site/waste details	• Site or process history
	• Waste generation and handling
	• Contaminants of interest
	• Sources of contamination
	• Fate and transport/exposure pathways
	• Conceptual models
	• Population of interest
	• Adjacent properties
	• Resource constraints
Sampling details	• Health and safety
	• Representativeness
	• Logistics
	• Sampling strategy
	• Sampling locations
	• Number and types (field/QA) of samples
	• Sample volume/mass
	• Composite vs. discrete samples
	• Sampling equipment/containers
	• Sample preservation, custody and handling
Analytical details	• Subsampling
	• Optimal analytical sample volume/mass
	• Quality of reagents/supplies
	• Sample preparation/analytical method
	• Calibration and verification
	• Matrix interferences and laboratory contamination
	• Detection limits
	• Holding times and turnaround times
	• QC samples/statistical control
	• Reporting requirements
Data assessment	• Data quality objectives, data quality indicators, and performance criteria
	• Documentation of implementation activities and data quality
	• Completeness, comparability
	• Representativeness, bias, and imprecision
	• Audits, PE samples, and corrective actions
	• Chain of custody
	• Verification of assumptions and statistical treatment of data

planning process is the more widely recognized of the above planning processes and provides the basis for the following discussion of the design and implementation of sampling plans.

The planning process results in a data collection design that is documented in project plans that serve as the blueprint for the subsequent implementation phase of the data life cycle. (The data collection design is the overarching project design that includes the sample collection design and the sample analysis design.) In addition to detailing the project activities, the project plans should specify a QC and QA regime and the appropriate levels of documentation to measure and document the quality of the resulting data. These project plans are referred to by different names by different organizations (e.g., quality assurance project plans, field sampling and analytical plans, work plans, statements of work). A project plan should be made available to all project personnel and should be sufficiently complete and thorough that it facilitates implementation of the project as designed.

A successful implementation ensures that data of known quality are generated, can support decisions that need to be made, and answer project-specific questions. The appropriate use of quality control samples, quality assurance, oversight, and detailed documentation allows for a determination of data quality and data usability. Documentation and recordkeeping during the implementation phase are essential to the subsequent assessment phase.

The assessment phase of the data life cycle incorporates those activities commonly referred to as data verification, data validation, and data quality assessment. These terms, while not uniformly defined, are frequently used interchangeably. The following definitions summarize the activities that should be employed during the assessment phase. Verification is a straightforward check to determine whether project-specified activities were employed and under control, while data validation makes usability decisions on a data point by data point basis. Data quality assessment looks at usability from a project-wide perspective and attempts to answer the following questions:

- Are the samples representative?
- Are the data accurate?
- Do the data support the project decision?

Data quality assessment is the final determination as to whether the data is of known quality and of sufficient quality to achieve project objectives.

Sampling, the focus of this chapter, is an integral part of the above data life cycle — not an independent activity that culminates in the collection of field samples. Sampling must be considered in light of the analytical methods that will be applied to the samples and the ultimate use of the associated data. Although this chapter focuses on the sampling aspects of data collection design, an integrated approach to sampling plan design and implementation is thematic and critical to the following discussion. The reader is advised to consult the following “Analytical Technology” and “Statistical Inference” sections of this book for analytical and data use issues that should be considered during the design of a sampling plan.

Fundamentals

This section addresses fundamental issues and principles regarding the design of a data collection activity. A common understanding of these issues and principles between those planning, implementing, and assessing projects is necessary for success.

Accuracy

The ultimate goal of mixed-waste data collection activities is data of sufficient accuracy to support the data use. This subsection discusses the error types that impact accuracy and limit data usability. Sources of inaccuracy can be categorized into one of the following error types (EPA QA/G-5 96; Taylor, 1987).

1. *Bias*: the systematic or persistent distortion of a process that causes errors in one direction (from the true value). These systematic errors are always the same sign (e.g., use of improper calibration standards that repetitively generate data that are always too high). Bias is detected and controlled by the use of quality controls (e.g., standard reference materials) and quality assurance programs, which detail proper standard operating procedures and implement audits, assessments, and corrective actions.
2. *Imprecision*: the lack of precision, which is a measure of mutual agreement among individual measurements of the same property. The random errors that cause imprecision vary in sign and magnitude and are unpredictable on an individual basis but average out if enough measurements are taken. Imprecision is usually expressed as the standard deviation of multiple measurements, or as the relative percent difference between duplicate or collocated samples.
3. *Blunders*: mistakes that occur on occasion and produce erroneous results (e.g., mislabeling or transcription errors). Due to their infrequent occurrence, blunders are usually not detected unless a true value or reliable estimate of the true value is known. Blunders are controlled by quality

assurance programs, which detail proper standard operating procedures and implement audits, assessments, and corrective actions.

The frequent occurrence of imprecision and bias is the reason that data quality is subject to question and that there is uncertainty when using data to make decisions. Figure 2.1.1 employs targets to depict the impacts of imprecision and bias on measurement data. Because the true value, as portrayed by the bull's-eye, is 100 parts per million (ppm), ideally all measurements would be centered on the target; after collecting and analyzing a number of samples, the reported data would be 100 ppm for each and every sample. This ideal condition of precise and unbiased data is pictured in Figure 2.1.1(a). If the sampling and analytical process is very precise but suffers from a bias, the condition would be as depicted in Figure 2.1.1(b), where the data are very reproducible but express a significant 70% bias that may go undetected if the true value is not known. The opposite condition is presented in Figure 2.1.1(c), where the data is not precise and every sample yields a different concentration. However, as more samples are collected, the random nature of imprecision errors tends to cancel itself, and, lacking any systematic error, the average measurement reflects the true concentration. Figure 2.1.1(d) depicts the situation in which the sampling and analytical process suffers from both imprecision and bias, and even when innumerable samples are collected and analyzed to control the impact of imprecision, the bias would result in the reporting of an incorrect average concentration.

The data represented by each target in Figure 2.1.1 have an associated frequency distribution curve. Frequency curves are constructed by plotting a concentration value vs. its frequency of occurrence. The curves show that as imprecision increases, the curves flatten out and the frequency of measurements that are distant from the average value (Figures 2.1.1(c) and (d)) increases. More precise measurements result in sharper curves (Figures 2.1.1(a) and (b)), with the majority of measurements relatively closer to the average value. The greater the bias (Figures 2.1.1(b) and (d)), the further the average of the measurements is shifted from the true value. The smaller the bias (Figures 2.1.1(a) and (c)), the closer the average of the measurements is to the true value.

Because the combination of imprecision and bias determines how close individual or multiple measurements are to the true value, the term "accuracy" is used to capture their overall impact.

Accuracy: the closeness of agreement between an observed value and the accepted reference value (or true value). When applied to a set of observed values, accuracy will be a combination of a random component (imprecision) and of a common systematic error (or bias) component (USEPA, 1992).

The term "accuracy" as used to describe the quality of data is a function of the precision and bias of the analytical techniques/data handling as well as the precision and bias of the samples themselves. Although applicable, the term "accuracy" is not typically applied to the quality of samples. Instead, "representativeness" is the term used as the measure of the precision and bias of samples relative to a population. Representativeness is discussed in the following chapter subsection.

Representativeness

Sampling is the process of obtaining a portion of a population (i.e., the material of interest as defined during the planning process) and a necessary step in the characterization of populations that are too large to be evaluated in their entirety. The information gathered from the samples is used to make inferences whose validity reflects how closely the samples reflect the properties and constituent concentrations of the population. "Representativeness" is the term employed for the degree to which samples accurately reflect their parent population and is defined by a consensus standard (ASTM, 1996a) as:

Representativeness: a certain degree of low bias and high precision when comparing the sample value(s) to the population value(s).

The above ASTM definition and that employed in a widely recognized text on sampling theory (Gy, 1992) are encompassing definitions and unambiguously include both bias and precision as key descriptors of representativeness. Alternatively, for the characterization of waste under the Resource Conservation

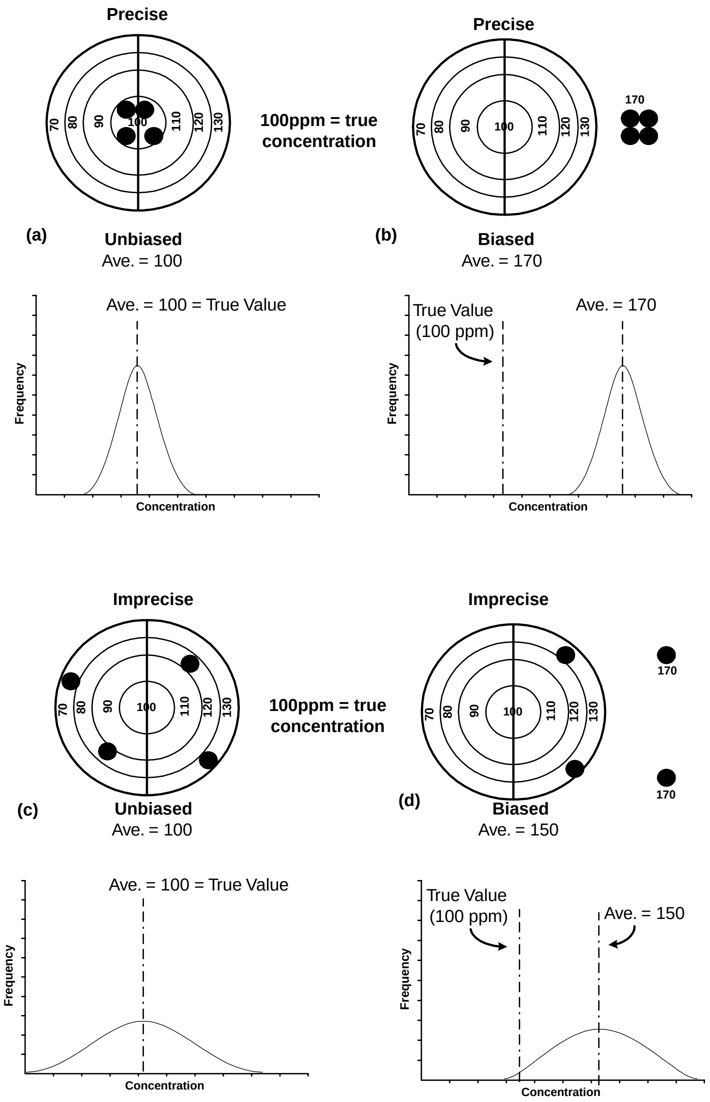

Figure 1. Error types.

FIGURE 2.1.1 Error types.

and Recovery Act (RCRA), a representative sample is narrowly defined as a sample of a population that can be expected to exhibit the average properties of the population (40 CFR 260.10). While this RCRA definition is pertinent to the characterization of radioactive wastes, when determining if the wastes express the RCRA toxicity characteristic, it is not applicable to those parts of the RCRA regulations and other data collection activities that attempt to measure other than average values. In addition to mean values, project objectives may require measurement of the mode, median, percentile, or the variance of a characteristic. Logarithmic and nominal values such as pH and ignitability are also not suitable to averaging because an arithmetic average of pH or an average of a Yes/No answer is inappropriate. The ASTM definition does not suffer from these limitations and is applicable whether the objective of the data collection activities is to collect samples that accurately reflect the mean or other statistical parameters.

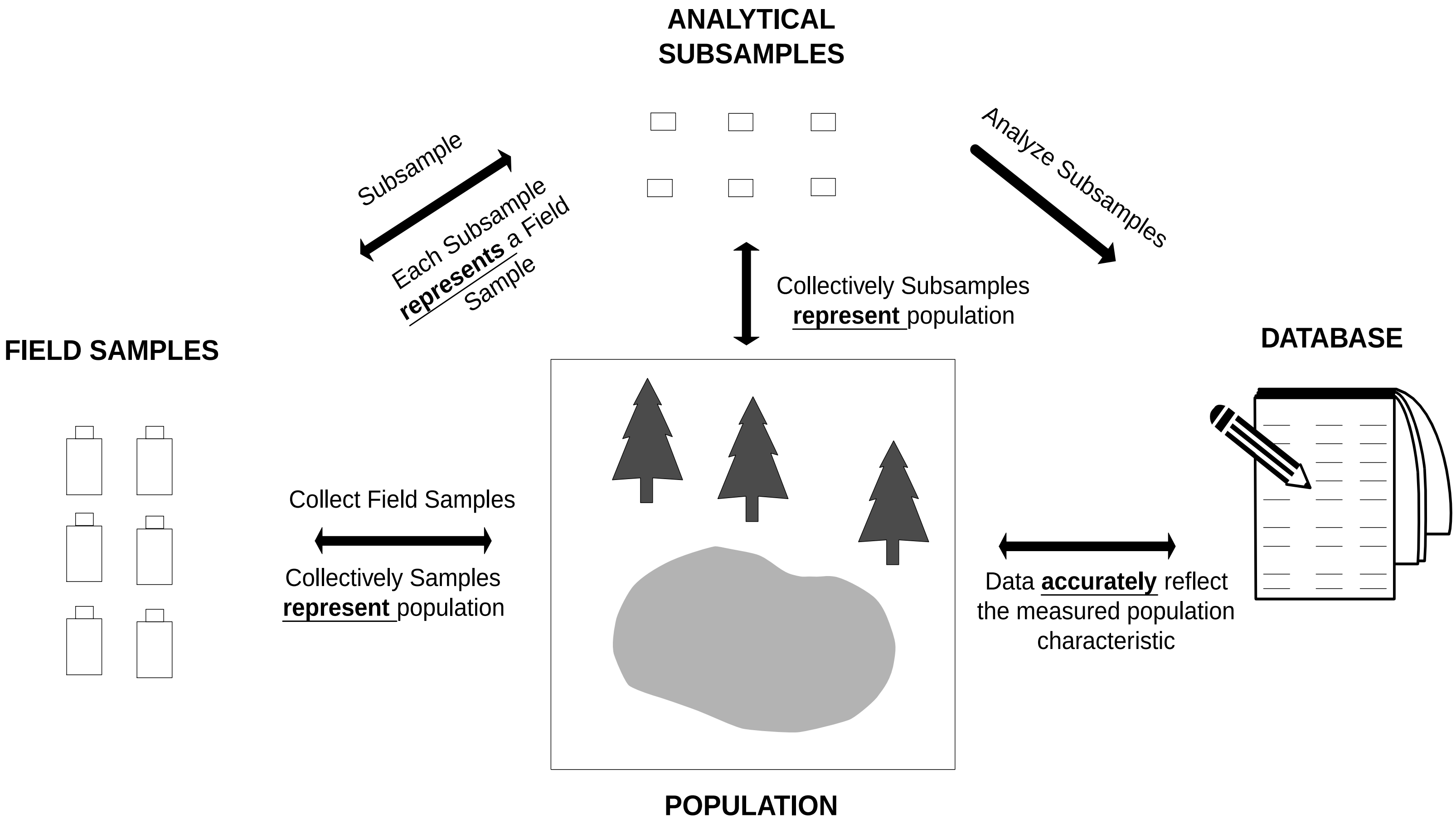

FIGURE 2.1.2 Using representative samples to measure population characteristics.

Figure 2.1.2 depicts how (1) samples collected in the field and subsamples generated in the laboratory, as a group, must physically and chemically reflect the population; and (2) data handling, measurement, and statistical analysis must be appropriate to ensure the data accurately reflect the characteristic of interest. A flaw in any portion of the sample collection or sample analysis design or their implementation can impact sample representativeness, the accuracy of data, and the correctness of associated decisions.

Heterogeneity

Heterogeneity is generally the single greatest impediment to optimizing a data collection design and is typically the greatest source of uncertainty in the decision-making process. This chapter subsection discusses homogeneity and the different types of heterogeneity that can be encountered during data collection activities. The following definitions, taken from the consensus standard ASTM D5956, should facilitate this discussion (ASTM, 1996b).

Component: an easily identified item such as a large crystal, an agglomerate, rod, container, block, glove, piece of wood or concrete.

Heterogeneity: the condition of the population under which all items of the population are not identical with respect to the characteristic of interest.

Homogeneity: the condition of the population under which all items of the population are identical with respect to the characteristic of interest.

Population: the totality of items or units under consideration.

Practical homogeneity: the condition of the population under which items of the population are not identical, but for the characteristic of interest, the differences between individual physical samples are not measurable or significant relative to the project objectives. That is, for practical purposes, the population is homogeneous.*

According to the prior definitions, sampling of a population such as an abandoned site would be a simple task if it were homogeneous. In theory, all items of this homogeneous site would be identical for the characteristic of interest and no differences in spatial distribution would be detectable. Thus, sampling and measuring any item would allow for evaluation of the entire site. Unfortunately, actual populations do not consist solely of identical items. At times, however, the difference between individual items is not measurable and/or is not significant relative to the project objectives. In this situation, the degree of heterogeneity is so minor that for practical purposes the material is considered homogeneous (practical homogeneity).

Homogeneity is diametric to heterogeneity. Homogeneity is a unique state of zero differences between population items, while heterogeneity is a continuum of increasing differences between items of the population. Because heterogeneity is the norm in practice, the items of a population such as an abandoned site are dissimilar to some degree. In addition to the magnitude of heterogeneity, the different items of heterogeneous populations can be distributed to create distinctly different types of heterogeneity.

Random heterogeneity: occurs when dissimilar items are randomly distributed throughout the population.

Non-random heterogeneity: occurs when dissimilar items are non-randomly distributed, resulting in the generation of strata.

Stratum: a subgroup of a population that is (1) separated in space, time, component, or some combination of the three from the remainder of the population, and (2) being internally consistent with respect to a target constituent or property of interest but different from adjacent portions of the population.

Differences in the composition or properties of the individual items of a population result in heterogeneity. One of these properties, item size (i.e., particle size), deserves special consideration due to its

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potential impact on sampling design and implementation. The issue of sampling and particle size are discussed in the next subsection.

Figure 2.1.3 depicts homogeneous and heterogeneous populations. The drum-like populations portray different types of spatial distributions, while the populations being discharged through the waste pipes represent different types of temporal distributions. No spatial or temporal distributions are identifiable between the identical items of a homogeneous population (Figure 2.1.3(a)). Identifiable spatial and temporal distributions are present in the heterogeneous populations (Figure 2.1.3(b)), with the existence of strata in the non-randomly heterogeneous populations (Figure 2.1.3(c)). The type and magnitude of heterogeneity should be considered during sample collection design because it will impact the representativeness of samples.

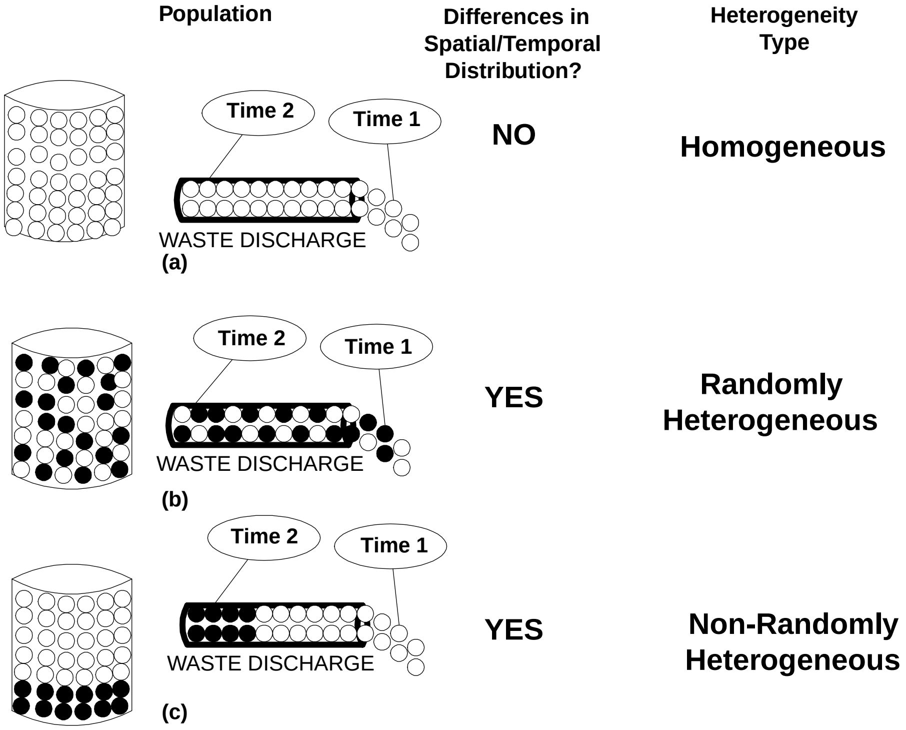

FIGURE 2.1.3 Types of heterogeneity.

Figure 2.1.4 is a graphical representation of different types of strata that may be present in non-random heterogeneous populations. Different strata, which result in different distributions and different average concentrations and properties, are the result of different origins. Stratification over time (e.g., 1000 times higher lead in wastewater during the day shift than during the night shift) or space (e.g., 1000 times higher lead concentrations at one portion of the property than at others) are common and well understood. Although prevalent, stratification by component is poorly understood. Some populations are heterogeneous while having no identifiable spatial or temporal stratification. When these populations contain components such as large crystals, blocks, gloves, or pieces of wood or concrete, then it may be advantageous to consider the population as consisting of a number of component strata. A component stratification approach simplifies the sampling and analytical process and facilitates making inferences from samples to stratified populations. Component stratification is appropriate for the characterization of complex wastes that consist of many and diverse component strata that are not separated in space or time (e.g., auto fluff). Component stratification is analogous to the age, gender, and socioeconomic

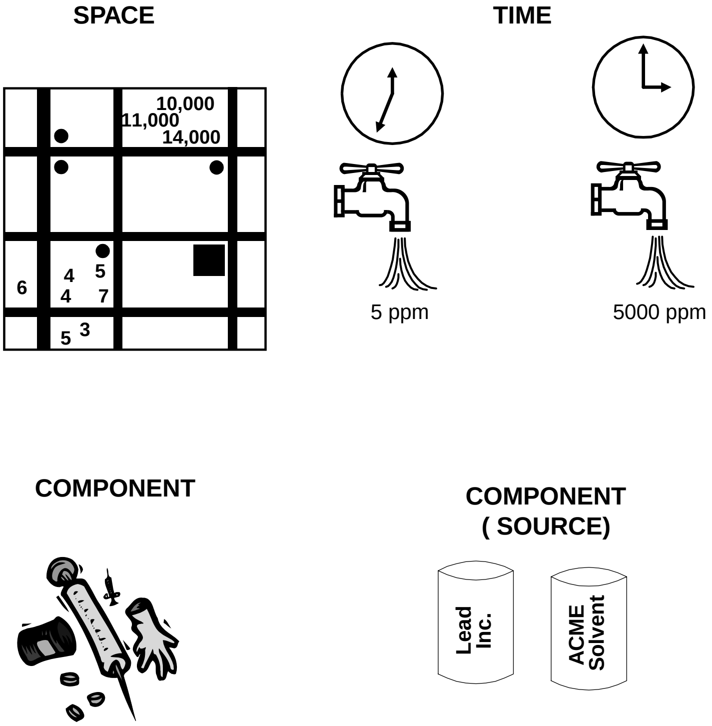

FIGURE 2.1.4 Types of strata.

stratification of persons into specific strata, which statisticians and pollsters apply to demographic data, regardless of where those individuals may live.

Although heterogeneity is an issue when sampling gases and liquids, it is typically a more confounding source of uncertainty when dealing with solids. The following chapter subsection summarizes "particulate sampling theory," a proven approach to managing the heterogeneity of solid materials.

Sampling Theory

The heterogeneity of a population results from two factors: (1) the difference in composition of the items that constitute the population, and (2) the manner in which these different items are distributed across the population. To properly characterize a contaminant or property of interest, heterogeneity must be accounted for by the sample collection design.

Gy's sampling theory has been found to be an important tool for improving sample collection designs because of its ability to offer better understanding and control of heterogeneity. The work of Pierre Gy (Gy, 1992) and Francis Pitard (Pitard, 1993) originally focused on the mining industry; however, the principles are equally applicable to the environmental and waste sampling of particulates. Gy's sampling theory manages heterogeneity during sample collection and sample preparation by considering seven sources of variance and errors that contribute to sampling inaccuracy.

1. *Fundamental error.* This source of error is a function of the varying composition between particles (items) of different size. This varying composition is a source of sampling imprecision that should be controlled. This error is smaller as the sample mass contains a larger number of particles. Fundamental error increases as the size of the particles increases relative to the sample mass, and is controlled by increasing the sample mass or by decreasing the size of the largest particles (e.g., by grinding) prior to collecting a sample or subsample.
2. *Grouping and segregation error.* This source of error is a function of the short-range heterogeneity within and around the area from which a sample is collected and the fact that the collected sample

usually consists of a group of particles (as opposed to a single particle). If there is a tendency for particles to associate into groups of like particles because of gravity, shape, magnetism, or electrostatic charge, the resulting non-random heterogeneity can decrease the accuracy of a sample. This source of variance is controlled by the use of many small increments to make a sample and by proper mixing and subsampling.

3. *Long-range heterogeneity.* This source of variance is similar to the grouping and segregation error, but is on a much larger scale. Long-range heterogeneity is responsible for non-random heterogeneity and the existence of strata. This error is controlled by the selection of the appropriate sampling design.
4. *Periodic-range heterogeneity.* This source of variance is a type of long-range heterogeneity, except that the non-random nature of heterogeneity is periodic or cyclic in nature. For example, a landfill cell being alternately filled with day- and night-shift production wastes, resulting in cyclic deposition of alternatively similar strata. This error is controlled by the selection of the appropriate sampling design.
5. *Increment delimitation error.* This error occurs when the shape of the sample is such that it excludes or discriminates against certain portions of the material to be sampled. For example, a sampling device that samples only the top portion of a waste as it leaves a discharge pipe, leaving a portion of the material unsampled. This type of error is eliminated by the correct choice of sampling equipment.
6. *Increment extraction error.* This error occurs when the sample is not extracted properly, so that portions of the chosen sample are lost or extraneous materials are included in the sample. For example, the coring device is too small to accommodate a large item and the large item is pushed aside as the coring device penetrates the material. This error type is controlled by choosing properly sized and designed sampling equipment and ensuring its proper use.
7. *Preparation error.* This error results from the incorrect preservation, handling, mixing, grinding, and subsampling that can result in loss, contamination, or altering of the sample, so that it is no longer representative of the material being sampled. The proper choice and implementation of preparation methods control this error.

All of the preceding errors and sources of variance should be considered during the design of sampling plans. While the above terms may be unknown to someone unfamiliar with sampling theory, most of the concepts, except for fundamental error, should be familiar to those experienced in the design and implementation of sampling plans. Fundamental error is a key driver when determining the appropriate sample mass to be collected,and is directly proportional to the size of the largest particle and inversely proportional to the sample mass. Table 2.1.2 compiles the maximum particle size allowed for a given sample mass to achieve the specified fundamental error. A quick review of this table is simultaneously informative and alarming. The data indicates that a 1-gram (g) sample, a mass typical for a metals digestion, can accommodate only a maximum particle size of 0.1 centimeter (cm) if a fundamental error of 16% RSD is desired. Pitard has generated graphs (referred to as nomographs) that allow for the choice of optimum sample size under varying conditions (Pitard, 1993) Table 2.1.2 also indicates that a 1000-g sample must be collected and analyzed in its entirety to maintain a fundamental error of 16% when a population contains a maximum particle size of 1 cm.

The typically larger sample masses recommended by sampling theory, as compared with sample sizes that are driven solely by analytical requirements, can result in increased costs, logistical, and possibly health and safety issues. There are situations when strict adherence to sampling theory is not necessary (e.g., when the largest particles in a population are artifacts such as rocks or bricks, whose contribution to contamination is known or can be estimated), and it may be possible to base the sampling on less-demanding sample mass requirements. Nonetheless, any such divergence from sampling theory should be based on verifiable knowledge of the material being sampled and how the contaminant of interest is contained within and distributed throughout the population.

TABLE 2.1.2 Maximum Allowable Particle Size (cm) for a Given Sample Mass per Various Fundamental Errors

	Maximum Allowable Particle Sizes Per Different Fundamental Errors				
Sample Mass (g)	5% RSD	10% RSD	16% RSD	20% RSD	50% RSD
0.1	0.02	0.04	0.05	0.06	0.10
1	0.05	0.08	0.10	0.12	0.22
2	0.06	0.10	0.13	0.15	0.28
3	0.07	0.11	0.15	0.17	0.32
4	0.08	0.12	0.17	0.19	0.35
5	0.08	0.13	0.18	0.21	0.38
10	0.10	0.16	0.22	0.26	0.48
20	0.13	0.21	0.28	0.33	0.61
30	0.15	0.24	0.32	0.38	0.69
40	0.16	0.26	0.36	0.41	0.76
50	0.18	0.28	0.38	0.45	0.82
75	0.20	0.32	0.44	0.51	0.94
100	0.22	0.35	0.48	0.56	1.04
500	0.38	0.61	0.83	0.96	1.77
1000	0.48	0.76	1.04	1.21	2.23
5000	0.82	1.30	1.78	2.07	3.82

If a population contains a maximum particle size that is not listed in Table 2.1.2, then the minimum sample mass to control the fundamental error to 16% can be approximated from the following equation (Pitard, 1993):

$$M_S = 1000{*}d^3 \qquad (2.1.1)$$

d = Diameter of the largest particles, in centimeters
M_S = Mass of the sample, in grams

Or, the maximum particle size that can be accommodated by a given sample can be approximated from:

$$d = \sqrt[3]{M_S/1000} \qquad (2.1.2)$$

Fundamental error and the other aspects of sampling theory are reconsidered in subsequent portions of this chapter.

Terminology

Data collection activities are multidisciplinary efforts and require experts from different areas to communicate clearly to ensure that data of known and useful quality are generated. Lack of a commonly understood terminology is one of the greatest impediments to effective communications. Problems with terminology are not restricted to esoteric and discipline-specific topics; some of the more frequent miscommunications occur as a result of different meanings assigned to commonly used terms such as duplicate samples, field blanks, and sample size. In these latter cases, there is a mistaken belief that planning team members have a common understanding of terms, which is found to be false only after implementation. This problem is further complicated with mixed wastes, where for decades, hazardous waste and radioactive waste expertise in sampling and analysis developed somewhat independent of each other.

To develop effective communications, in addition to establishing a documented channel of communications that keeps all stakeholders and experts informed, it is important to identify a common terminology early in the planning process by referencing a consensus standard or by developing a glossary of terms and definitions. The agreed-upon terminology should be documented in project plans and distributed to all members of the planning and implementation team.

Health and Safety

This chapter does not attempt to address the health and safety issues associated with mixed waste because such issues are organization-, project-, regulatory-, and waste-specific. This chapter does, however, recognize that health and safety issues have significant impact on the design and implementation of mixed waste sampling plans. A necessary goal of all mixed waste sampling designs is to ensure that individual and collective exposures are as low as reasonably achievable (ALARA). It is also recognized that compliance with ALARA guidance can result in significant design changes that may increase costs and/or increase the uncertainty in project decisions.

Applications

This subsection is based on the seven steps of the USEPA's DQO planning process (USEPA, 1994). The first six steps of the DQO process are briefly reviewed from a sampling perspective, while the seventh step, optimization of design, is explored in more detail regarding issues that should be considered when optimizing a sampling plan design.

The DQO process was developed in the mid-1980s by the USEPA Quality Assurance Management Staff (QAMS), partially in response to the costly and embarrassing generation of unusable data for projects such as Love Canal. The DQO planning process, in part, is based on the principles of Total Quality Management. The DQO process is to a large degree common sense, with its greatest advantage being that it adds structure to the planning process. This structure and organized way of approaching the planning process increases the likelihood that important issues will be considered and that the underlying details necessary for success will be addressed.

Structured planning processes such as the DQO process do require an up-front investment of effort to address issues, review assumptions, make decisions, and plan. It should be noted that when a structured planning process is not followed, decisions are still made regarding issues such as project drivers, data inputs, and population boundaries, but, lacking a planning structure, these decisions might be made by default, or in the field by personnel who may not be familiar with the project objectives. A structured approach increases the likelihood that critical issues will be given a level of attention that reflects their importance.

To supplement this brief discussion, more detail on the DQO process can be found in EPA guidance (USEPA, 1994; USEPA, 2000), ASTM standard D 5792-95 (ASTM, 1995), (note that the ASTM standard defines the term "action-level" differently than the USEPA guidance), and MARSSIM (NUREG, 1997).

Step 1: State the Problem

This initial step of the DQO process describes the history and identifies the needs and drivers, which are the reasons for undertaking the data collection activity. The driver may be for compliance with regulations, support of litigation, or a need for site or waste information so that a decision can be made or a question answered.

A detailed understanding of the rationale for sampling is necessary for plan design. For example, not only is it important to know that sampling will be done in support of the RCRA, but it is also important to know if the sampling for toxicity contaminants is done for compliance with the 40 CFR 261 RCRA regulations or the 40 CFR 268 RCRA regulations. Compliance with the 40 CFR 261 regulations is concerned with average concentrations and allows for the use of composite samples, while the 40 CFR 268 regulations are typically interested in point-in-time or space concentrations and require the use of grab samples for many wastes. A thorough understanding of the drivers behind sampling will allow for the identification of all stakeholders, necessary experts, pertinent conceptual models, limitations (e.g., can access only a portion of the waste pile), and constraints (e.g., sample the sewer effluent within 1 hour of a rainfall), and will facilitate the remainder of the DQO planning process.

The outputs for this step, as agreed upon by the stakeholders, include:

- Documentation of the drivers for sampling
- Identification of all stakeholders and required expertise
- Documentation of the history and pertinent regulations or requirements
- Documentation of all deadlines, limitations, and constraints
- Identification of available resources
- Development of a conceptual model, if appropriate

Step 2: Identify the Decision

This step is closely related to Step 5 of the DQO process but approaches the decision from a more qualitative or generic perspective; Step 5 addresses the specifics of the correct statistic and its relationship to the action level. The identification of the decision follows from a detailed understanding of the project drivers as defined in Step 1. It is critical to document the decision statement early in the planning process, because it requires the stakeholders and experts who make up the planning team to come to a consensus not only on what the decision is, but also on what will be done once a decision is made.

More complex problems or sites may require that a series of decisions be made. Each of these nested decisions should be defined with consideration for their role in the overall project.

Some planners may consider some data collection activities to be information gathering activities that will answer a particular question. The use of the term "decision statement," however, was chosen to force the stakeholders to think further down the process and to identify what action will be taken once a question (e.g., Is the radioactive material also a hazardous waste?) is answered. It is important to identify and document the actions (e.g., dispose in landfill X if not hazardous) and alternate actions (e.g., dispose in landfill Y if hazardous) because they have the potential to significantly impact data needs and the sampling plan design.

The outputs for this step, as agreed upon by the stakeholders, include:

- A documented decision statement that addresses the alternate actions that will be taken in response to decision outcomes

Step 3: Identify Inputs to the Decision

This step determines what information is needed to make the decision defined in Step 2. The type of data, the required frequency of the data, and data constraints and limitations identified in this step will influence the final sampling plan designed in Step 7 of this planning process. The frequency and amount of data will be refined during the optimization of the sample design, when the number of samples will be chosen to meet the acceptable decision error rates.

In addition to needed sampling/analytical data, information such as risk, health, and state and federal regulatory thresholds may be required and are to be identified during this step of the planning process.

As previously mentioned, regulatory drivers can require specific data inputs. For example, the Toxic Substances Control Act (TSCA) has specific requirements for wet- and dry-weight concentrations and requires phase specific data for multi-phasic materials, while certain RCRA land disposal regulations require that the phases of surface impoundment wastes be analyzed separately.

The outputs for this step, as agreed upon by the stakeholders, include:

- Listing of data inputs (e.g., chemical, physical, toxicological, regulatory data) needed to make the decision
- Identification of sources for data inputs
- Determination as to whether needed data already exist, or sampling is required

Step 4: Define the Study Boundaries

From a sampling design perspective, defining the study boundaries is a critical step. Statisticians commonly refer to the "study area" as the "population." Gilbert (1987) further discriminates between the sampled population and the target population. Ideally, the population that is subjected to sampling (sampled population) is the same population for which a decision is to be made (target population). If the sampled and target populations are not identical, then the assumptions or site/process/waste knowledge used to justify extrapolation from the sampled population to the target population should be evaluated. These assumptions (e.g., the waste generation process and raw materials will not change, so wastes generated today also represent future wastes) should be documented during this step.

While the boundaries of the proposed sampled population may change later during Step 7 (the optimization of design), the target population must be defined at this time to proceed with the planning process.

Success in defining the population boundaries will be determined, in large part, by how well the decision has been defined. For example, does the decision to determine if a radioactive waste expresses hazardous characteristics apply to a single drum generated today, or is data from the sampled population to be used to make inferences to all historical waste? Will the decision be applied only to waste generated under certain operation conditions? Will inferences be made from the sampled population and applied to all future wastes? The population boundaries must reflect the project objectives as defined by the decision statement and data inputs.

The choice of temporal and spatial boundaries can influence project outcomes. For example, increasing the boundaries of a decision unit could result in the dilution of a hot spot compared with boundaries that capture the hot spot with little or no dilution. (*Note*: A decision unit is that portion of the overall population, as defined by spatial, temporal, or component boundaries, for which data will be used to make a decision. The decision unit could be the entire population [e.g., all surface impoundment contents, the waste effluent for a 24-hour period] or a portion of the population [e.g., only the northwest quadrant of an impoundment, or only the day shift's effluent].) In consideration of this fact, USEPA guidance (USEPA, 1994) suggests that the boundaries be chosen to define "the scale of decision-making to the smallest, most appropriate subset." For example, determining the appropriate scale can be accomplished when evaluating the hazardous characteristics of a radioactive waste by estimating the smallest reasonable mass of material that would constitute a significant hazard if that mass expressed the characteristic of interest. The size of this decision unit can be small (e.g., a single drum) if one is concerned with ignitability, or large (e.g., 5000 cubic yards) if concerned with leaching from a low concentration waste pile.

Defining the decision units requires that the support (i.e., length, width, height, depth, orientation, and temporal boundaries) of the decision unit be identified. Once the decision unit and its support are defined, then during the optimization step a determination can be made as to whether a subset or all decision units will be sampled. For example, if there is little likelihood that any of a population of 100 drums are ignitable, it may be appropriate to sample only a few randomly selected drums to verify that the drums are not ignitable.

When the objectives of the data collection activity focus on qualities of the entire population (e.g., mean, median, 99th percentile), then the decision unit will be equal to the target population. When hot spots or subsets of the population (e.g., remediation or exposure units) are of concern, then the decision unit upon which a determination will be made is smaller and different from that of the population. If a population is to be subdivided into smaller exposure or remediation units (i.e., decision units), the boundaries of the exposure or remediation units and their relationship to the overall population should be documented.

The outputs for this step, as agreed upon by the stakeholders, include:

- Description of the spatial and temporal boundaries of both the target and sampled populations
- Identification of any assumptions or process knowledge employed to justify use of a sampled population that is different from the target population
- Identification of pertinent population characteristics such as strata, hot spots, exposure units, remediation units, and areas of different use
- Identification of decision unit support (i.e., length, width, height, depth, orientation, and temporal boundaries)

- Identification of constraints, such as time or space constraints as to when, where, or how samples can be collected

Step 5: Develop the Decision Rule

This step refines the decision rule that was identified in Step 2 of the planning process by incorporating (1) the statistical parameter that will be compared with the decision point into the “if” portion of the rule; (2) the resulting action into the “then” portion of the “if … then” rule; and (3) the outputs of Step 3 (data inputs) and Step 4 (population boundaries).

> *Example*: If the 90% UCL of the mean concentration for toxicity characteristic leaching procedure (TCLP) metals for a remediation unit exceeds the RCRA limits, then the radioactive waste must be disposed at a mixed waste facility; otherwise the radioactive waste will be disposed at a radioactive waste facility.

The specifics of how a decision will be made are identified during this step. The statistical parameter (e.g., mean, median, 99th percentile, or upper confidence limit) or a data point itself (e.g., ignitablility, corrosivity data) is typically compared with a decision point. The statistical parameter is chosen to reflect the characteristic of importance for the project decision (e.g., average value or hot spot) and whether a decision will be based on less than, equal to or less than, equal to or greater than, or greater than the decision point.

This step encourages stakeholders to consider the detailed mechanism for implementing a decision and to come to consensus. Incorporation of the actions into the decision rule forces the planners to explore how the data will be used, which may require earlier steps of the planning process to be revisited to ensure compliance with project objectives.

The outputs for this step, as agreed upon by the stakeholders, include:

- Identification of statistical parameters
- Identification of the decision point
- Detailed specification of the actions that will be taken once a decision is made
- Documentation of the “If … Then” rule.

Step 6: Specify Limits on Decision Errors

Data collection projects generally make inferences from a few samples to large populations. Because only the samples — not the entire population — are subjected to analysis, there is uncertainty in decisions as information gleaned from the samples is extrapolated to the population. This uncertainty can result in decision errors. Statistics is the branch of mathematics used to manage uncertainty and to estimate the potential for these decision errors.

The potential for decision errors will be a function of imprecision that, in turn, will be a function of the number of samples, the size and heterogeneity of the population, and the imprecision of sampling and analytical methods. Statistics can be employed to optimize sampling plan designs so that these sources of imprecision are controlled and potential decision errors are managed to within acceptable limits. This process requires that stakeholders have an estimate of data imprecision and reach a consensus on what would be an acceptable rate of decision error as the decision point is approached. This application of statistics to the decision-making process is covered by Section 2.3 of this handbook, which should be referenced for more detail.

As discussed in the “Accuracy” subsection, data quality and the associated decisions can suffer from three types of errors: bias, imprecision, and blunder. The impact of bias and blunders on decisions is controlled through the implementation of quality assurance programs that require the use of quality controls samples, SOPs (standard operating procedures), audits, and assessments. If quality assurance programs encounter bias or blunders, it is assumed that the source of the bias will be addressed and the data corrected prior to use. Bias and blunders are not incorporated into the tolerable limits of decision error generated by this step of the planning process. Bias and blunders, however, must be considered during Step 7 of the planning process, and quality assurance requirements must be incorporated into project plan documents. This step of the planning process employs statistical techniques to focus on decision errors resulting from imprecision.

The outputs for this step, as agreed upon by the stakeholders, include:

- Tolerable limits for Type I (false positive) decision error rates
- Tolerable limits for Type II (false negative) decision error rates

For the remainder of this chapter, which focuses on the optimization of design, the assumption is made that the outputs from Step 6 are available.

Step 7: Optimize the Design for Obtaining Data

The objective of this final step is to identify the most resource-effective data collection design that satisfies the DQOs specified in the previous six steps. The DQOs for a data collection activity include, among others, deadlines; logistical constraints; contaminants of interest; the type, quality, and quantity of data inputs; the spatial and temporal boundaries of the population; statistical parameters; decision points; and the desired confidence in decisions. These DQOs are used to select and optimize the final data collection design, which should address all pertinent sampling and analytical issues. Table 2.1.3 depicts the components of a data collection design that should be considered during optimization.

TABLE 2.1.3 Hierarchy of Data Collection Design

Data Collection Design	
Sample Collection Design	Sample Analysis Design
Sampling Design	Analytical SOPs
Sampling SOPs	Data handling
Sampling QA/QC	Analytical QA/QC

The data collection design is the overall project design and incorporates two separate but interdependent designs: the sample collection design and sample analysis design.

The sample collection design consists of:

- *Sampling design*: the strategy or scheme for selecting the type, number of samples, location, time or components for sampling. Simple random, stratified random, systematic and judgmental sampling, are examples of sampling designs.
- *Sampling SOPs*: the detailed and documented standard operation procedures (SOP) that describe the steps to be followed when implementing a sampling activity (e.g., equipment preparation, sample collection, decontamination of equipment, subsampling). Refer to EPA QA/G-6 for guidance on suggested content and format for SOPs (USEPA, 1995).
- *Sampling QA/QC*: the project-specified quality controls (e.g., collocated samples, equipment, ambient and trip blanks) and the associated quality assessments (e.g., audits, reviews) and assurances (e.g., corrective actions, reports to management) that constitute the activities used to document, measure and control data quality.

The sample analysis design consists of:

- *Analytical SOPs*: the detailed and documented SOPs that describe the steps to be followed when implementing an analytical activity (e.g., sample preparation, separations, instrumental analysis, data generation, review and handling).
- *Analytical QA/QC*: the project-specified quality controls (e.g., method replicates, method spikes, calibration check standards, and blanks) and the associated quality assessments (e.g., audits, reviews) and assurances (e.g. corrective actions, reports to management) that constitute the activities used to document, measure, and control data quality.

An optimized data collection design incorporates sampling and analytical SOPs, QA, QC, and a sampling design (e.g., random sampling) that are capable of managing heterogeneity, accommodating project limitations and constraints such that samples are sufficiently representative and data are sufficiently accurate to achieve project DQOs.

Although an optimized data collection design is usually capable of achieving project objectives with fewer samples than a less-efficient design, the efficiency of a design cannot be measured solely in terms of the minimum number of samples or analyses. A design is usually not efficient if it does not incorporate an appropriate margin of replication for critical samples, which would therefore jeopardize completeness and increases the likelihood of incurring re-sampling costs. A design that decreases its demand on resources by skirting health and safety or ALARA requirements is also not an efficient data collection design.

Figure 2.1.5 is a graphical depiction of the optimization process. During optimization, the sampling design is chosen and methods and SOPs are selected along with quality assurance, quality controls, and performance criteria. Quality assurance activities and quality control samples are used to monitor the implemented design and to document the quality of data. Performance criteria are chosen for quality control samples by allocating to sampling and analytical activities portions of the overall allowable-decision error, as identified in the previous DQO Step 6, (e.g., if a 50% overall imprecision would still allow project decisions to be made with acceptable certainty, then a 20% performance criteria can be established for collocated sample data). As indicated by Figure 2.1.5, optimizing the sample collection design involves many design decisions. Table 2.1.4 summarizes key design decisions and identifies the population characteristics and DQO inputs that influence these decisions. This table and the remainder of this chapter discriminate between population and sample decisions because the impact of heterogeneity, the complicating factor for sample collection design, is typically different for samples and the populations from which they are collected.

The sample collection design decisions listed in Table 2.1.4 are often interrelated and complex. For example, while short-range heterogeneity can impact decisions regarding sampling design, sample type, the number of samples, sample mass, and subsampling procedures; it is only one of nine inputs that should be considered when deciding on the number of samples. Table 2.1.4 also recognizes subsampling as a key part of the data collection design and a part that must be properly designed to ensure that sample representativeness is maintained when only a portion of a sample is subjected to analysis.

In summary, the output of Step 7 of the DQO planning process is the development of a data collection design that will generate data of known and sufficient quality to achieve project objectives. A prerequisite for quality data (i.e., unbiased and precise data) and the focus of this chapter is that samples be representative of the population of interest. This chapter focuses on the sampling aspects of the data collection design and those issues critical to a sampling plan design. References to analytical and data handling issues are only with regard to their impact on the sampling plan design. The reader is advised to consult the analytical technology section of this handbook for analytical issues that should be considered during optimization of data collection design.

Managing Population Heterogeneity (Large Scale)

This subsection addresses the impact of long-range heterogeneity on sample collection design. Long-range heterogeneities are those that express themselves across the target population and result in the generation of strata and linear and cyclic trends. As indicated in Table 2.1.4, long-range heterogeneity influences decisions regarding sampling design, sampling location/timing, and the number of samples.

Sampling Design. In general, the selection of a sampling design will be determined by project objectives and by what is known about the heterogeneity of the target population. Prior to choosing a strategy, the characteristic of interest (target compounds), population boundaries, decision rule, acceptable decision errors, and budgets must be known. The chosen design should accommodate the spatial and temporal distribution of contaminants, be practical and cost-effective to implement, and generate data that allow objectives to be met. When budgets are the controlling factor, the most effective sampling plan for the available dollars should be designed. When the need to make a decision with a specified amount of

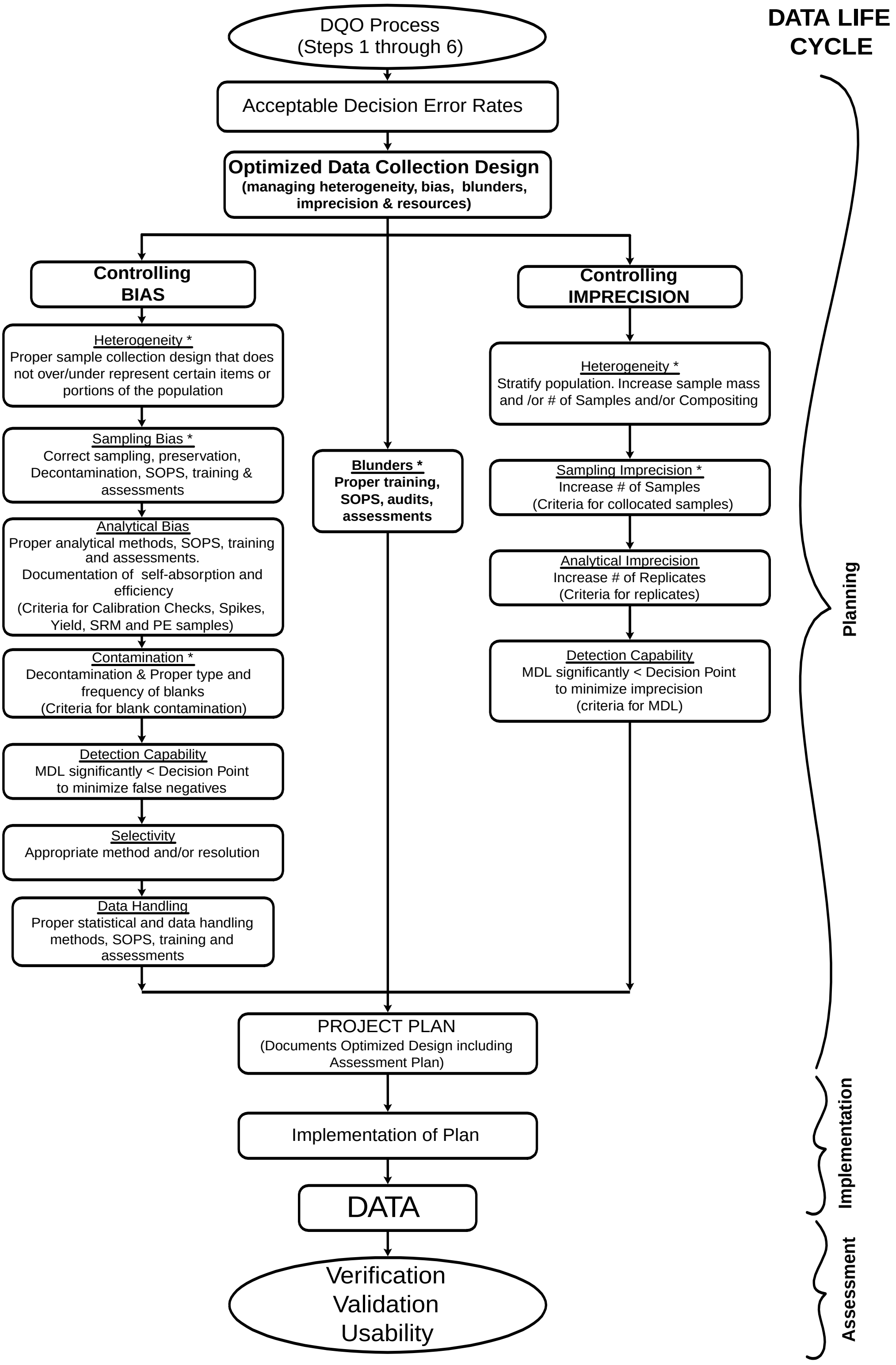

FIGURE 2.1.5 Optimization of the data collection design. *denotes those design issues that impact sample collection.

TABLE 2.14 Influence of Inputs on the Sample Collection Design

	Influence on Sample Collection Design Decisions[a]						
	Population Decision				Sample Decisions		
Inputs to Sample Collection Design Decisions	Sampling Design[b]	Sampling Location/ Timing	Composite or Discrete Samples[c]	# of Samples	Sample Mass/ Volume	Sampling Device	Subsampling
Overall objective (e.g., estimate a statistical parameter, detect hotspot, etc.)	X		X	X			
Acceptable decision error			X	X			
Proximity to action level			X	X			
Sampling & analysis variance[d]				X			
Population & strata boundaries	X	X		X			
Short-range heterogeneity[e]	X		X	X	X		X
Long-range heterogeneity (strata)[f]	X	X		X			
Accessibility	X	X				X	
Item size/matrix[g]					X	X	X
Analyte[h]			X			X	X
Analytical requirements[i]					X	X	X
QC samples[j]				X	X		
Budget[k]	X		X	X			

[a] Health and Safety and ALARA issues are determinative factors in data collection design that can override other factors when making design decisions.

[b] The choice of sampling design (e.g., simple random, stratified random, systematic, and judgmental) can be impacted by the type of heterogeneity (i.e., stratification) and the need for improved precision for statistical decision-making (e.g., some sampling strategies can yield more precise estimates of the mean). Other than when accessibility problems exist, the sampling design will be the determinative factor for sampling locations.

[c] Composite samples can be employed to control variance resulting from population heterogeneity when mean concentrations are of interest or when heterogeneity across the area being sampled is not of interest. Composite samples are used to increase confidence in decisions when analytical costs are high and limit the number of analyses.

[d] For the purposes of this table, “Sampling & analysis variance” is the expected variance resulting from only the sampling collection and analytical process and does not reflect variance contributions from population heterogeneity

[e] Short-range heterogeneity is the heterogeneity encountered within a sampling location (e.g., an individual grid). This type of heterogeneity can be averaged by taking larger sample mass/volumes, composite samples or by taking more discrete samples within the sampling location. If the sampling location has the same mass/volume as the sample mass/volume (i.e., the entire sampling location is sampled), then short-range heterogeneity is not an issue.

[f] Long-range heterogeneity, or non-random heterogeneity, is the type of heterogeneity that results from the non-random distribution of the analyte of concern across the population such that strata exist. Stratified random sampling, which is used to sample strata individually, is generally the preferred sampling design for these stratified populations.

[g] Item size and fundamental error will influence sample mass, the minimal opening of sampling devices, and subsampling. The type of matrix (e.g., viscous liquids, cementitious solids) will influence sampling device and subsampling decisions.

[h] The sampling device must be compatible with the analyte such that it does not result in loss of the analyte through adsorption or contamination by leaching. Properties of the analyte (e.g., volatility) will influence the choice of subsampling procedures, sampling devices and whether compositing is viable.

[i] Analytical requirements such as the minimum analytical sample size will impact the choice of sample mass/volume, which in turn may impact the choice of sampling devices.

[j] The mass/volume of a sample often needs to be increased if it will be subjected to additional quality control analyses (e.g., matrix spike/matrix spike duplicate analyses). For other QC samples, the sample mass/volume may not change but the number of samples may increase (e.g., collocated samples).

[k] Budget constraints can have a significant impact on sample collection design from decreased numbers of samples to a change in sampling strategy (e.g., judgmental sampling of a limited area in lieu of the entire population). If analytical costs are more significant than sampling costs, then compositing may be a cost-effective means of achieving certain project goals.

certainty is the driver, the chosen strategy should be the most cost-effective strategy for achieving the specified levels of certainty (Gilbert, 1987).

A lack of knowledge of how contaminants are distributed spatially, or of how concentrations change over time, is often the greatest challenge in choosing the optimum sampling strategy. When little is known about contaminant distributions, preliminary sampling may be advisable or needed prior to choosing a sampling design.

The decision process for choosing a sampling design is diagramed in Figure 2.1.6. Although this figure cannot address the myriad of sampling designs and project-specific issues, it does address the common sampling designs and typical project objectives that drive the design selection. A key driver for sampling design selection is whether sampling errors are to be estimated. If the decision-maker needs to estimate the uncertainty in data and associated project decisions, probabilistic sampling will be required. Simple random, stratified random, and systematic sampling are familiar examples of probabilistic sampling designs. Non-probabilistic designs (i.e., authoritative sampling designs) typically use process or site knowledge to focus sampling on a portion of the population, such that the probability of being sampled varies for different portions of the target population. Typically, authoritative sampling is not used if the resulting data is to be used to support a decision that will be reviewed by others (e.g., regulators) or is of a contentious nature (e.g., litigation), because the innate bias of authoritative sampling can be difficult to defend. The use of probabilistic sampling not only allows for an estimate of decision errors resulting from imprecision, but also minimizes the chances for the intentional and unintentional introduction of bias by those who collect the samples.

Selection between the different probabilistic sampling designs will be determined by the DQOs (e.g., need to detect hot spots, or need to measure mean concentrations) and knowledge of population heterogeneity (e.g., existence of strata or trends). The decision process depicted in Figure 2.1.6 is limited to the common sampling designs; however, these designs typically constitute the underlying structure of more complex designs. The remainder of this subsection presents an overview of these common sampling strategies and summarizes their advantages and disadvantages. If these common sampling strategies are not cost effective or applicable to the population of interest, a statistician should be consulted to identify other strategies that may be more appropriate.

It is important to note that the nomenclature for sampling designs are not uniformly used and understood. Unfortunately, some commonly used terms are assigned different meaning by different people and texts (e.g., multiple terms for authoritative sampling).

Authoritative sampling. Authoritative sampling is a non-probabilistic sampling design because it precludes each and every portion of the population from having an equal probability of being selected and sampled. Authoritative sampling is also known as:

Judgmental sampling
Biased sampling
Non-probability sampling
Non-statistical sampling
Purposive sampling
Subjective sampling

These terms can elicit different meanings for different members of a planning team; thus, it is important that the terms are defined clearly, preferably in writing, at the beginning of the planning process. The term “authoritative sampling” as used in this context is not a type of haphazard sampling, by which samples are collected without any thought or planning. Authoritative sampling designs rely upon a person’s judgment, or a decision rule, to decide which portions of a population will be sampled. Authoritative sampling designs can be appropriate for certain populations or for certain times in a sampling program. Authoritative sampling may be appropriate under circumstances such as the following;

- Preliminary information is required about a site to facilitate planning
- A spill of an unknown chemical has been encountered

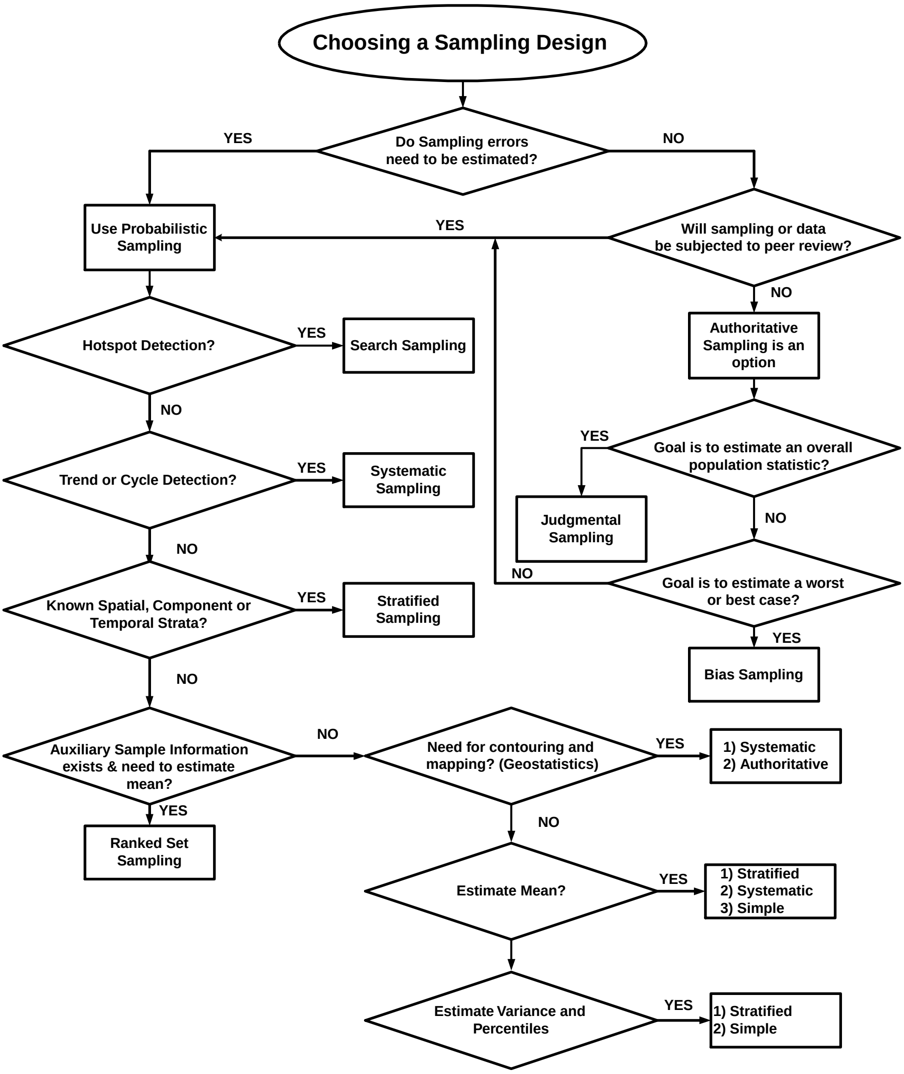

FIGURE 2.1.6 The decision process for choosing a sampling design.

- Limited access to small portions of the population
- Use of a field screening technique to select a limited number of samples for laboratory analysis

While authoritative sampling can generate useful data, its subjective method of sample selection makes it difficult to prove that bias has not been introduced and precludes an accurate estimate of the population variance. Because of its subjective nature, the use of authoritative sampling in support of high-visibility or contentious projects is usually not advisable.

It is important not to confuse authoritative sampling with the use of historical information during sampling design. For example, if one area of a site is known to be heavily contaminated while another area is not believed to be contaminated, this information can be used to defensibly divide the sites into strata. Use of information such as this, in conjunction with statistical sampling strategies, should generate unbiased, representative and defensible data.

Two types of authoritative sampling are specified by ASTM D 6311 (ASTM, 1998a): judgmental and biased sampling. The goal of judgmental sampling is to use process or site knowledge to choose one or more sampling locations that will be representative of the average concentration or typical property.

Judgmental sampling designs can be cost effective if the people choosing the sampling locations are objective in their selection of sample locations and if their knowledge of the population is correct. If the person choosing the sampling locations intentionally distorts the sampling by a prejudiced selection, or if that person's knowledge is wanting, judgmental sampling can lead to incorrect and sometimes very costly decisions. The chances of judgmental sampling's generating accurate and useful data increases as the population becomes more homogeneous and as the existence of any strata and their boundaries becomes more obvious.

Biased sampling is a type of authoritative sampling, the intent of which is to estimate worst or best cases. At times, it may be best to employ both "best-case" and "worst-case" biased sampling approaches for the same site. For example, if process/site knowledge can be used to locate the lowest and highest contamination levels, these two limits could be sampled and used to estimate the range of contaminant concentrations.

Simple random sampling. Simple random sampling is the least complicated of the statistical sampling strategies. The basic tenet of simple random sampling is that every portion of the population has an equal chance of being sampled. Simple random sampling is an established strategy that is suitable for determining average concentrations and variance. It is a valuable strategy when little is known about the targeted population. A major limitation is that, relative to other strategies, a large number of samples are required or significant portions of the target population can go unsampled. Stratified random sampling is usually preferable to simple random sampling (Gilbert, 1987; ASTM, 1998a).

Stratified random sampling. Stratified random sampling will yield a more precise estimate of mean concentrations when the population is divided into strata that contain similar concentrations and spatial distributions. Once the strata boundaries are established, each stratum is subjected to simple random sampling.

Stratified random sampling can also be used when budgets limit the number of samples and little is known about the population heterogeneity. Under this limited budget/limited sample scenario, the sampling team ensures that all areas of the site are represented by dividing the population into topographical or temporal strata, each of which is subjected to simple random sampling.

Stratified random sampling can yield a more precise estimate of mean concentrations and total amounts (inventories) of a contaminant than simple random sampling. Stratified random sampling also provides useful information about each individual stratum, which can decrease the need for further sampling, if the individual strata will be managed differently. Although substantial numbers of samples are required to thoroughly investigate an area, stratified sampling is more efficient and should require fewer samples than simple random sampling (Gilbert, 1987; ASTM, 1998a).

Waste can be stratified over space, time, and component. Component stratification is a powerful tool when a very heterogeneous population consists of easily identifiable components (e.g., bricks, gloves, porous and non-porous materials) and the contaminant of interest is not associated to the same degree with all components (Maney, 1993; ASTM, 1996b).

Systematic random sampling. Systematic random sampling provides a uniform coverage of the site and is usually easier to implement than simple or stratified random sampling. It is well suited for detecting concentration trends over time and space, and under certain circumstances can yield a more accurate estimate of mean concentrations.

The major limitations of systematic random sampling include:

- Substantial bias can result if unknown concentration cycles coincide with the systematic sampling locations. Thus, prior to employing a systematic strategy, historical or waste generation information should be investigated to determine the likelihood of cyclic patterns in the population.
- Inaccurate variance estimates occur when the heterogeneity is not random.
- Substantial numbers of samples are required.

Systematic random sampling is applied to a two- or three-dimensional population by choosing a random starting time or location with the aid of random number tables or a random number generator.

The initial starting point is where a grid of equally spaced sampling locations is initiated. A second random number can be chosen to determine the orientation of the grid over the population. (Alternatively, the grid structure can be optimally aligned to the population boundaries and a random location selected within a grid, such that all grids are systematically sampled at the same relative position.) The grid dimensions or the distance between sampling locations is often determined by the budget, which will determine how many samples can be collected and analyzed. The sampling process is greatly facilitated by the fact that field personnel can easily measure to adjacent sampling locations. The fact that the first location and the grid orientation are chosen in a random manner ensures that operator bias does not impact the choice of sampling locations.

Systematic random sampling can also be applied in a similar fashion to a temporal population. Consider a wastewater effluent that is to be evaluated for daily trends in radioisotope concentrations. Assume the stakeholders allocated enough funds to collect and analyze 24 effluent samples. A systematic random sampling effort would be initiated by selecting a time of day with the use of a random number table. A sample would be collected at this randomly chosen time and at subsequent hour periods until a total of 24 samples had been collected.

Systematic sampling can also be applied in the same methodical manner to a line or transect (Gilbert, 1987; ASTM, 1998a).

Search sampling. Search sampling is not employed to measure population characteristics such as mean values or variance, but is typically used to locate areas of high concentrations called “hot spots.” Prior to implementing a search sampling effort, the planning team must (1) estimate the likely shape and size of the hot spot, and (2) determine the acceptable risk of not detecting the hot spot. Using this information, the shape of the sampling grid units (e.g., square or triangular) is chosen and the distance between sampling locations is calculated (Gilbert, 1987).

Ranked set sampling. Ranked set sampling (RSS) is a design that exploits quantitative (e.g., field screening data) and qualitative (e.g., coloration) auxiliary data to more precisely estimate mean concentrations. It is advantageous to employ RSS when auxiliary data can be used to rank the range of concentrations in potential samples and when the cost of acquiring auxiliary data and implementing the RSS ranking is less than the cost of collecting and analyzing samples for the primary contaminant. RSS uses a simple random sampling design to choose multiple sets of potential sampling locations from across the target population. (If the cost of sampling is small or if sample collection is required for generating the auxiliary data, then the samples will be collected prior to ranking. If sampling is costly and not necessary for generating auxiliary data, then sample collection can be restricted solely to those samples that were selected by RRS.) Auxiliary data such as field measurements or contaminant staining is used to rank the sampling locations within each set of samples. After selecting a sample from each rank from each set of samples, the rank-selected samples are collected and analyzed for the primary contaminant (Gilbert, 1997).

Geostatistical sampling. Geostatistical sampling is done in accordance with the chosen geostatistical model for a population. The actual sampling could be probabilistic, authoritative, or systematic in nature. Whatever the sampling design, the coordinates of sampling locations need to be documented for the subsequent geostatistical assessment. Geostatistics, as applied to environmental problems, typically attempts to correlate contaminant concentrations with spatial locations within a population, such that the measured and estimated concentrations are overlaid on a population map to generate contours and isopleths. To generate these maps, geostatistics employs different interpolation methods to estimate concentrations between points of known concentration. Kriging, which employs a linear-weighted approach, is one of the more common interpolation methods. Geostatistical techniques estimate average contaminant concentrations and total mass of contamination, and discriminates between areas that do and do not need remediation (Myers, 1997).

Sample Type. For purposes of this discussion, there are two types of samples: discrete and composite samples. A discrete sample is also referred to as a “grab,” or “increment.” (For probabilistic sampling, the population is conceptually divided into sampling units that are of the same mass/volume and dimensions as the discrete samples.) Once collected, no other materials other than preservatives are added to or subtracted from discrete samples until analysis or subsampling/preparation prior to analysis.

A composite sample is a combination of two or more discrete samples. Compositing, the process of generating composite samples can occur simultaneously with the act of sample collection (e.g., sampling of liquid effluent with an autosampling device into a single sample container over a specified time period), or a number of subsequent steps (e.g., homogenization, particle-size reduction, subsampling, combining of aliquots) may be required to generate a composite sample. Composite samples can be used to:

- Decrease analytical costs with the intentions of decreasing overall project costs
- Yield more precise estimates of mean values
- Efficiently identify the existence of infrequently occurring hot spots
- Increase the sample mass/volume available for analysis when individual discrete samples would be too small to meet objectives

The disadvantages of compositing include the loss of information on intersample variance and any extreme values, as well as a loss of sensitivity when higher concentrations are diluted by mixing with less contaminated discrete samples. These disadvantages discourage the use of compositing when information on intersample variance or extreme concentrations are required or when the measured concentrations approach the analytical method detection limit. In addition, compositing is usually not advantageous when:

- Regulations require the use of discrete samples (e.g., RCRA land disposal restriction requirements for grab samples when evaluating nonwastewaters).
- Sampling costs are greater than analytical costs.
- Analysis is a greater source of imprecision than sampling and population heterogeneity.
- Discrete samples are incompatible and may react when mixed.
- Properties of discrete samples such as pH or ignitability change qualitatively upon mixing.
- Discrete samples contain or will be analyzed for volatile analytes that could be lost during the compositing process.
- Analytical holding times would have expired if retesting of discrete samples is required.
- Sample matrix impedes homogenization and/or subsampling.
- There is a need to evaluate if the concentrations of different contaminants are correlated.

The remainder of this subsection discusses issues to be considered when designing and implementing a compositing strategy. A detailed discussion of the advantages and disadvantages of compositing and guidance on the mixing and subsampling of discrete and composite samples is also presented in ASTM Standard D 6051(ASTM, 1996c).

More-Precise Estimates of the Mean. If the analysis contributes insignificantly to imprecision as compared with the population heterogeneity and sampling, then composite sampling can be a resource-efficient mechanism for increasing the precision of the estimates of the population mean. Under these circumstances, properly prepared composite samples will result in increased precision because the composite sample is a physical average of its discrete samples. The precision of this physical averaging process is proportional to the number of discrete samples in a composite sample (i.e., the more discrete samples, the more precise the mean estimate); and when more than one composite sample is collected and analyzed the imprecision is further reduced by the number of composite samples.

Central Limit Theorem. The central limit theorem states that, regardless of the type of the original distribution, as repeated measurements of a mean value are made, the distribution of the mean measurements will be approximately normal. This tendency toward a normal distribution facilitates statistical interpretation of mean data by parametric statistics. Non-normal data must undergo evaluation by non-parametric statistics or the data must be subjected to transformation prior to evaluation with parametric statistical tests. Because the mixing, subsampling, and combining steps used to generate composite samples are, in effect, a physical averaging of discrete samples, the analysis of samples composited across the target population yield repeated estimates of mean values, whose concentration distribution tends toward normality. This tendency toward normality makes composite samples more suitable for evaluation by parametric statistics.

Hierarchy of Decision Units, Composite Sample Boundaries, and Discrete Samples. Composite sampling can be applied to practically homogeneous, randomly heterogeneous, or non-randomly heterogeneous populations as well as individual temporal, spatial, or component strata. Discrete samples can be chosen from these populations and from within strata using various random or systematic sampling designs. When composite samples are to be employed, the DQO process should specify the decision unit, the composite sample boundaries, and the mass/volume of discrete samples that will be used to achieve DQOs.

The composite sample boundaries are the spatial, temporal, and component boundaries over which discrete samples are composited. The dimensions of the composite sample boundaries are less than or equal to those of the decision unit. Figures 2.1.7 demonstrates the interrelationship of decision units, sample composite boundaries and discrete samples under four different and typical conditions:

1. In Figure 2.1.7(a), the decision unit boundaries are equivalent to the composite sample boundaries with one composite sample containing nine systematically chosen discrete samples collected and analyzed to generate a datum for making the decision that pertains to the decision unit. One composite sample yields an estimate of the mean concentration but lacks an estimate of variability.
2. In Figure 2.1.7(b), the decision unit boundaries are equivalent to the composite sample boundaries and three composite samples containing three randomly chosen discrete samples are collected and analyzed to generate data for making the decision that pertains to the decision unit. The collection and analysis of three composite samples yield both an estimate of the mean concentration and an estimate of the variability of the mean. As more samples are collected, the distribution of the mean should become normal.
3. In Figure 2.1.7(c), the decision unit is larger than the composite sample boundaries, and four composite samples, each containing five randomly chosen discrete samples from the same quadrant, are collected and analyzed to generate data for making the decision that pertains to the decision unit. This compositing design generates a mean estimate and the ability to estimate whether there are concentration differences between geographical areas (i.e., stratification). This design can also yield estimates of variability if the discrete samples are independent and the concentrations are not correlated.
4. A fourth design is a combination of Figures 2.17(b) and (c) in that the population is divided into quadrants as depicted in Figure 2.17(c), with five composite samples consisting of one discrete sample from each strata. This approach ensures that each quadrant is represented in each composite sample and that the mean and variability can be estimated and the mean distribution will tend toward normality.

The following issues should be considered when defining or evaluating decision units, composite sample boundaries, the number of discrete samples per composite, and which discrete samples are combined to generate a composite sample.

- Do discrete samples come from different areas of the population, between which there may be a need to discriminate (e.g., different component strata, such as lead bricks and soil that may be handled differently during remediation; a heavily contaminated area vs. a less contaminated area; old waste from recently generated wastes or effluent from day shift vs. effluent from the night shift)?
- Will the physical mixing of discrete samples result in some reaction or change that will alter the concentrations/properties of interest (e.g., mixing of acidic and basic discrete samples that result in neutralization and generate a composite sample that masks the corrosive nature of a portion of the population)?

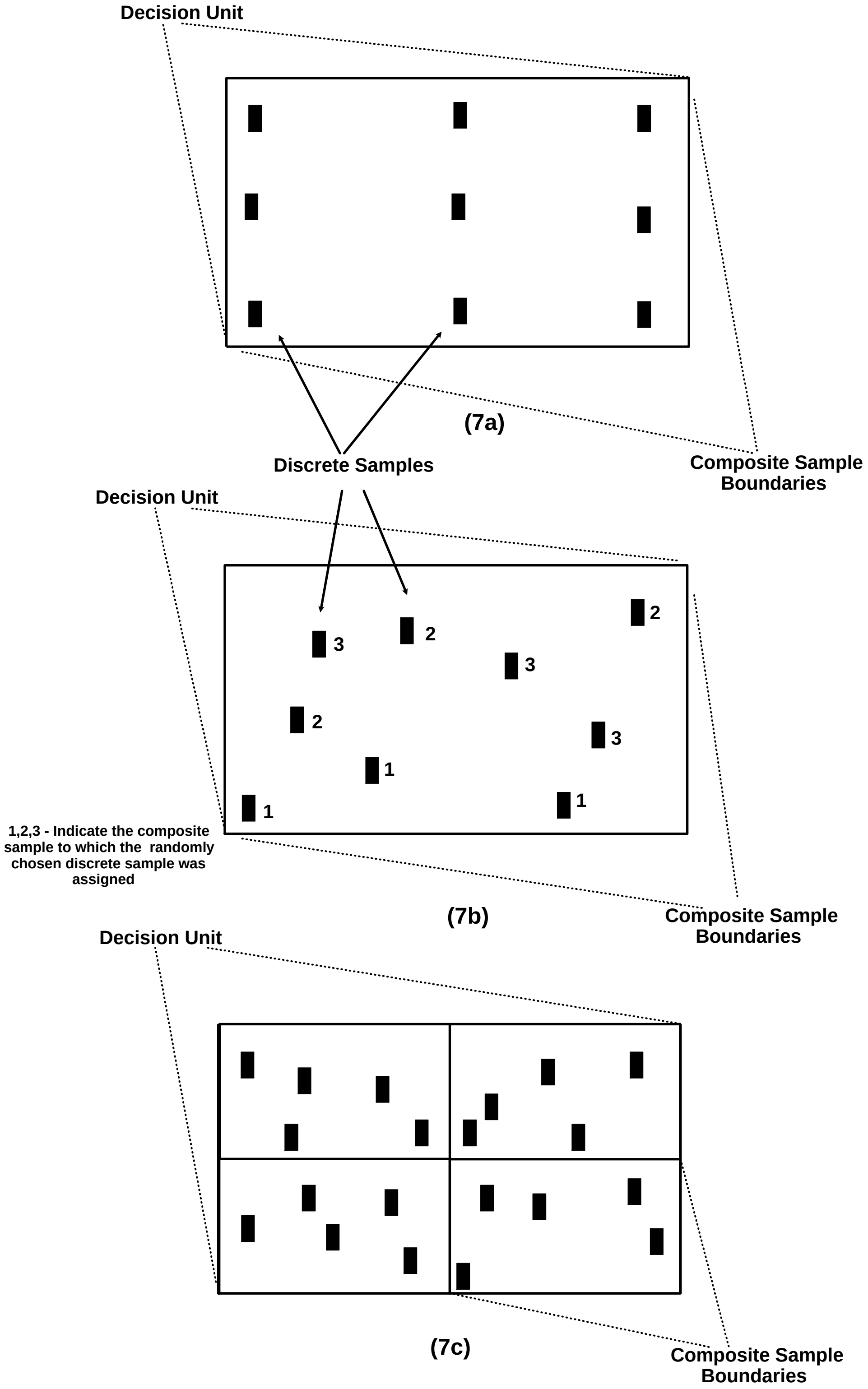

FIGURE 2.1.7 Hierarchy of decision units, sample composite boundaries, and discrete samples.

- Is there a scale of concern (e.g., a 10-cm^3 portion of a large waste population being above a decision point may not be a problem, while a 1-m^3 may be enough to constitute a significant hazard) that can be used to define boundaries within which a decision should be made and for which compositing will meet DQOs?
- Is the number of discrete samples per composite so large that the concentration/property represented by an individual discrete sample can be diluted and a hazard masked?
- Will the composite samples be used to generate continuous or discrete data?

Consideration of the above issues when defining decision unit and composite sample boundaries should increase the usability of composite sample data and increase compliance with DQOs.

Number of Samples. As indicated in Table 2.1.4, the number of samples specified by an optimized sample collection design is a function of many inputs (i.e., overall objectives, acceptable decision errors, heterogeneity, variance, boundaries, quality control, and budget). In general, as the allowable decision error and proximity of the measured values to the decision point decrease and as the heterogeneity, sampling, and analytical variances increase, the number of samples will necessarily increase to meet the project DQOs.

The number of samples specified by a sample collection design are based on assumptions regarding typical concentrations, decision points, heterogeneity, and sampling and analytical imprecision. Once these assumptions are made, then the planners can use the budget, statistics, and an understanding of the sources of variability to choose the optimum number of discrete or composite samples and analytical replicates. The accuracy of these underlying assumptions will determine the success and efficiency of sample collection designs.

The multiple sources of variability present in most data collection activities offer options for optimizing the number of samples. For example, if sampling is expensive, then there may be incentive to decrease analytical imprecision by employing a more precise analytical method or by increasing the number of analytical replicates. If sampling is not expensive, then more samples could be collected as a means of managing imprecision. For a given situation, there may be many options for controlling imprecision. The greatest gains in decreasing imprecision are typically obtained by addressing the greatest source of variability, which is usually the heterogeneity of the population. Heterogeneity can be managed by stratification of the population, collecting more samples, larger samples, and composite samples.

After acquiring an understanding of the sources of imprecision, statistical methods are employed to estimate the actual number of samples to be incorporated into the sample collection design. The statistical methods are chosen to accommodate the sampling design (e.g., stratified random sampling), the null hypothesis, and the assumptions made during planning (i.e., the concentration for the contaminant of interest is log normally distributed). Because of the critical roles that statistics play during planning and after data collection, it is essential that a statistician or someone experienced in the application of statistics be included in or accessible to the planning team.

For further discussions of the role of statistics in data collection refer to ASTM D 6311 (ASTM, 1998a), ASTM D 6250 (ASTM, 1997), MARSSIM, and Chapter 2.3 in this handbook.

Managing Sample Heterogeneity (Small Scale)

Sample Mass/Volume. As indicated by Table 2.1.4, decisions regarding sample mass/volume are impacted by the heterogeneity and particle size of the material being sampled and by analytical requirements. Sample volume/mass may also be impacted and need to be increased if a sample will be subjected to additional quality control analyses. Safety issues associated with hazardous and radioactive materials can be the determinative factor for sample mass/volume when increased sample mass/volume might put field and laboratory personnel at risk. (Note: The mass/volume of a sample, the shape of the sample (length, width, and height dimensions) and the timing and orientation from which the material is sampled are sometimes referred to as the sample support.)

The choice of mass/volume for samples of practically homogeneous liquids and gases is usually driven by the mass/volume required for analysis. In choosing the optimum sample mass/volume for particulate materials, the concerns raised by Gy's sampling theory [Gy, 1992] must also be considered. Sampling theory has identified fundamental and grouping and segregation errors as those that should be considered and addressed when choosing a sample mass/volume.

The collection and analysis of the large samples that are sometimes recommended to address fundamental error can result in increased costs, logistical issues, and possibly health and safety issues associated with the increased exposure. However, when the largest particles in a population are artifacts whose contribution to contamination is known or can be estimated, then it may be possible to base the sampling on less demanding sample mass requirements. Nonetheless, any such divergence from sampling theory should be based on a verifiable knowledge of the material being sampled and how the contaminant of interest is contained within and distributed throughout the population (Maney, 1993).

Grouping and segregation errors resulting from the sampling of particulate materials (short-range heterogeneity) can be addressed by the use of numerous increments per sample (ten or more) or large masses/volumes that minimize the impact of these errors.

Sampling Devices/SOPs. When selecting sampling devices and methods (SOPs), the following performance factors should be considered:

1. *Health and safety.* The risk and exposure to personnel when using a given sampling device should be evaluated in terms of an institution's ALARA and health and safety requirements.
2. *Representativeness.* The sampling device as implemented should be capable of accommodating the largest particles (i.e., the opening to the sampling device should be at least three times the diameter of the largest particle and never less than 10 mm [Gy, 1992]), and should not result in the loss of certain fractions of the sample (e.g., fines or volatiles) or expose the sample to contamination.
3. *Usability and adaptability.* Are the sampling device and associated procedures suitable for the range of working and environmental conditions that are likely to be encountered in the field? Ideally, the sampling device should allow access to all portions of the population. A device that is difficult to employ can increase costs and/or negatively impact sample representativeness.
4. *Compatibility with analytes and sample matrix.* The sampling device should be made of a material that is compatible with and will not react with the sample matrix, the analytes of interest or any cleaning and decontamination solutions. The sampling device should not adsorb or leach the analytes of interest. The device and its implementation should be capable of accommodating the required sample mass/volume, the range of particles sizes, and the consistency of the material being sampled.
5. *Acceptance of methodology.* The context of the data collection activity can also impact the choice of sampling devices. If the context is contentious or subject to litigation, then it may be advisable to use generally accepted practices, as opposed to less widely used techniques whose representativeness can be questioned. Consensus standard organizations such as ASTM and federal and state guidance documents can be sources of accepted sampling devices and uses.
6. *Manual and automatic sampling.* Samples can be collected manually or with automatic samplers. Automatic samplers can be cost-effective when there is a desire to minimize personnel exposure, when a long-term sampling project is to be undertaken, or when a portable automatic sampling system can be employed. The viability of the automatic sampling devices must be evaluated in terms of representativeness, holding times, and preservation. If automatic samplers are used, sample custody must be addressed for those times during which sampling equipment will be left unattended.
7. *Cost-effectiveness.* A holistic approach must be employed when evaluating the cost-effectiveness of sampling devices. For example, the cost of disposable sampling equipment may be justified in light of decontamination costs. Likewise, a more expensive device may be more durable, simpler to use, or result in the collection of a more representative sample. Cost-effectiveness of sampling devices should be based on their overall cost/benefit to the project.

Numerous sources, including the following, have compiled and discussed the advantages and limitations of sampling devices.

ASTM Standards on Environmental Sampling, 2nd edition, 1987. PCN: 03-41 8097-38, ASTM 100 Barr Harbor Drive, West Conshohocken, PA 19428-2959.
ASTM D 6232 — Selection of Sampling Equipment for Waste and Contaminated Media Data Collection Activities, (ASTM, 1998b).
Technical Project Planning Guidance for HTRW Data Quality Design, EM 200-1-2, July 1995.
Index to USEPA Test Methods, EPA Region I Library/LIB, JFK Building , Boston, MA 02203 (Also includes index to USEPA sampling documents).
Test Methods for the Evaluation of Solid Wastes — Physical/Chemical Methods, SW-846, 3rd edition.
Subsurface Characterization and Monitoring Techniques, A Desk Reference Guide, EPA/625/R-93/003a and b, May 1993.
NIOSH Manual of Analytical Methods, 4th edition, National Institute of Occupational Safety and Health. August 1994. NIOSH Publication No. 98-119
Compendium of Methods for the Determination of Air Pollutants in Indoor Air, EPA/600/4-90/010, April 1990.
Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, EPA/600/4-89/017, June 1989.
Pitard (1993).
Gy (1992).

If the material being sampled is particulate or contains particulates, then prior to selection, all sampling devices and procedures should be evaluated in light of the error sources described by sampling theory (Gy, 1992; Pitard, 1993) and as previously summarized in this subsection.

Sample Handling/Shipping. Shipping requirements vary according to the type of contaminants, and their concentration and requirements differ depending on whether the waste contains radioactive, hazardous, or mixed wastes.

Shipment of mixed waste samples must comply with:

- U.S. Nuclear Regulatory Commission regulations
- U.S. Department of Transportation regulations
- International Air Transportation Association Dangerous Goods regulations
- U.S. Postal Service regulations

Shipments of mixed wastes can also be subject to RCRA regulations if they do not meet the 40 CFR 261.4(d) exemption for samples. Refer to MARSSIM for a further discussion of shipping requirements NUREG, 1997.

Subsampling. The generation of an analytical sample from a larger field sample is a step critical to sample integrity, yet subsampling is not typically addressed in project plans. Additionally, many environmental laboratories do not have adequate standard operating procedures (SOPs) for subsampling. Because subsampling is subject to the same biases and imprecision that complicate sampling, the representativeness of subsamples is questionable if proper subsampling procedures were not specified and followed.

Unless information indicates otherwise, the analyst should assume that the field sampling sample as received at the laboratory accurately represents the sampling location from which it was collected. If the field sample mass is equal to or less than the specified analytical size, then the field sample can be analyzed in its entirety, subsampling is not required and an additional source of potential preparatory error is avoided. If the mass of the field sample is greater than the specified analytical sample size, then subsampling will be required. If subsampling is required, the analyst attempts to generate a subsample that is representative of the entire field sample and a subsample that is suitable for analysis.

Subsampling is straightforward when sampling a relatively homogeneous liquid or gas. Dealing with multi-phasic liquids is not as straightforward but usually can be addressed by:

- Mixing the sample such that all phases are homogenized, and then decanting a subsample
- Allowing all of the phases to separate, then subsampling and analyzing them separately
- Using an opened tube or composite liquid waste sampler (COLIWASA) to collect a sample that representatively captures the vertical heterogeneity

If the sample is a mixture of liquids and solids, subsampling usually requires that the phases be separated. The individual phases are then subsampled separately. Subsampling of the liquid phase can be accomplished as described above; subsampling of the solid phase should be done according to sampling theory. It may be possible to homogenize and representatively subsample a suspension of fine particles within a liquid, but the testing necessary to prove the efficiency of this approach is typically not justified unless there is an ongoing project.

Solids should be subsampled according to sampling theory, which predicts that for a given material the larger the sample mass subjected to analysis, the smaller the fundamental, grouping, and segregation errors. The size of the subsample must also comply with the analytical requirements, which typically specify a sample mass/volume. The initial step complying with sampling theory requires an estimate of the particle sizes that constitute the solid sample. The largest particle size contained within the field sample must be compared with the maximum particle size that is allowed for the specified analytical sample mass (refer to Table 2.1.2) . For example, if a field sample were to be subsampled to generate a 1000-g subsample, Table 2.1.2indicates that for a 16% fundamental error rate, the maximum allowable particle size is 1.04 cm in diameter. If the largest particle size in the field sample is less than 1.04 cm, then the analytical subsample can be collected and meet the 16% fundamental error constraint. If the largest particle size in the field sample is greater than 1.04 cm and the analytes of interest are not volatile, then the options for generating a subsample are:

- Subjecting the field sample to particle size reduction (PSR) prior to collection of the analytical subsample. If the PSR is successful in reducing all particle sizes to less than 1.04 cm, then collection of 1000-g subsamples would result in a maximum fundamental error of 16%.
- If it is known that the largest particles are free of significant amounts of the analyte of interest, then it may be possible to exclude the large particles from the subsample, omit PSR, and still collect a subsample that complies with the 16% fundamental error constraint.
- Extract or digest a larger mass of sample or perform a number of extractions or digestions until the required sample mass for the existing particle size is processed. Analyze a small portion of the relatively homogeneous extract/digestate to accommodate instrument sensitivity. If multiple extractions/digestions are required, combine the extract/digest before analysis or generate a mathematical average following analysis of the individual extracts/digestates.

If the largest particle size of the field sample exceeds the allowable size for maintaining a 16% fundamental error rate and the analyte of interest is volatile, the use of PSR is precluded and the options are fewer:

- Determine if the largest particle sizes in the field sample are free of the volatile analyte and, if so, estimate fundamental error and acceptable sample sizes using the largest particle sizes that contain the analyte.
- Collect the sample size suggested by Table 2.1.2 into a solvent such as methanol and analyze a portion of the relatively homogeneous extract.
- Employ the specified analytical sample size and accept a larger fundamental error.

It is important to verify assumptions (e.g., large particles lack significant amounts of a contaminant) through sound knowledge or preferably by testing. When assumptions cannot be confidently made, the minimum sample sizes as defined by sampling theory should be used.

If PSR is required because the field sample is large and the largest particle size in the field sample is significantly larger than that allowed in the analytical sample, a multi-step PSR procedure may be advantageous because it avoids the inefficient process of grinding large sample masses to small-particle sizes. The multi-step process involves an initial grinding of the entire large sample to some intermediate particle size at which a subsample is collected. The smaller subsample is then subjected to grinding to the desired particle size. It is important to note that the fundamental error is additive for each subsampling step.

ASTM Standard D 6323 lists a variety of PSR equipment (i.e., cutting mills, jar mills, disc mills, dish and puck mills, mortar grinders and jaw crushers) and tabulates their uses and limitations (ASTM, 1998b).

Subsequent to PSR and prior to subsampling, many analysts subject their samples to homogenization. The goal of homogenization is to mix the sample such that the grouping and segregation error becomes insignificant as the various items of the population are randomly distributed through the sample. If homogenization is successful, collection of a subsample is simplified because any portion of the sample accurately represents the average properties of the sample. It is important to note that even when homogenization is successful, due to gravity it is only a temporary state. Pitard has dedicated two chapters to homogenization (Pitard, 1993).

Splitting is employed when a field sample is significantly larger than the required analytical sample and when fundamental error and the particle size are not the controlling factors. The goal of splitting is to control grouping and segregation error to achieve an aliquot of the field sample that reflects the average properties of the original field sample. Sample splitting is similar to homgenization in that one of its goals is to decrease the grouping and segregation error. Unlike homogenization, splitting has a second goal of reducing the mass of the retained sample. Gy (1992) suggests use of alternate or fractional shoveling procedures.

The issues regarding the subsampling of particulate-containing materials are identical to those considered when collecting the original field samples and are as follows:

- The tool used to collect the analytical sample must be correct and not discriminate against any portion of the sample (control of increment delimitation and increment extraction errors). Rectangular scoops are a preferred subsampling tool (Pitard, 1993).
- The mass of the subsample must be enough to accommodate the largest of the particles contained within the field sample (control fundamental error). It is recommended that the opening to the sampling device be a minimum of three times greater than the largest particle size (Gy, 1992).
- The sample mass and the manner in which it is collected must accommodate the short-term heterogeneity within the field sample (control of grouping and segregation error by collecting at least ten increments to form the subsample [Pitard, 1993]).

Upon completion of representative subsampling, a defensible groundwork is completed for subsequent physical and chemical analyses as described in Chapter 2.2.

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For Further Information

As emphasized by the above references, the federal government and consensus standard organizations such as ASTM have and continue to produce valuable sampling guidance. The USEPA and the ASTM joined forces to write needed standards at an accelerated rate. This section has referenced a number of the standards that have resulted from this cooperation. Other accelerated standards relevant to data collection activities are presently being written and will become available. A number of federal agencies have drafted a detailed document, the Multi-Agency Radiation Laboratory Analytical Protocols (MARLAP), which addresses relevant radiochemical and planning issues. The USEPA has also drafted relevant and significant guidance (e.g., updated RCRA sampling), which are under peer review as of this writing.

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2.2

Analytical Technology

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Introduction

Characterizing environmental samples has been exhaustively adressed in the literature for most analytes of environmental concern. One of the weak areas of environmental analytical chemistry is that of radionuclides and samples contaminated with radionuclides. The analysis of samples containing high levels of radionuclides can be far more complex that that of non-radioactive samples. This chapter addresses the analysis of samples with a wide range of radioactivity. The other areas of characterization examined are the hazardous components of mixed waste, and special analytes often associated with radioactive materials.

Characterizing mixed waste is often similar to characterizing waste components in non-radioactive materials. The largest differences are in associated safety precautions to minimize exposure to dangerous levels of radioactivity. Radiological dose must be kept as low as reasonably achievable (ALARA). This chapter outlines recommended procedures to safely and accurately characterize regulated components of radioactive samples.

Background

The U.S. Department of Energy (DOE) through various agreements with local, regional, and federal organizations[1] has led a massive effort to clean up radioactive waste from our nation's highly contaminated sites. As a result, the DOE is a key leader in the development and application of mixed waste and environmental radionuclide characterization technology. This effort has greatly expanded our understanding of the technology needs for detecting and quantifying radionuclides in waste and environmental samples. Some of the contamination at DOE sites contains levels of radionuclides several orders of magnitude greater than what had previously been examined in environmental samples. These newly regulated levels of radionuclides created a need to expand our ability to analyze samples with fallout levels and those containing radioactive waste from reactor fuel and fuel processing. In addition, there are now needs to analyze intermediate levels of radionuclides found at sites of nuclear accidents (Chernobyl). Waste from radiological processing varies in complexity, from simple fallout levels in typical environmental matrices to cauldrons of organic/inorganic materials mixed with highly radioactive waste in tanks. For example, some waste tanks contain material from many years of processing nuclear fuel.

Throughout the world, there are related waste problems that will benefit from better analytical techniques. These include problems from all non-DOE sources of mixed waste, including nuclear medical, university research, nuclear power, etc. The need to create more-stable waste forms, or put waste into more acceptable locations, has resulted in efforts to better understand these waste materials.

In many cases, the analysis of mixed waste could be almost as simple as the analysis of non-radioactive waste. However, radioactive samples pose special hazards such as dose and matrix issues. Shielding is often necessary, and special equipment such as a hot cell is sometimes required. Coordinating sampling and analysis activities so that hold times are met can be difficult. Also, refrigeration or other means of maintaining sample integrity are often compromised. These unique problems make it difficult for standard methods to provide accurate information.

Since the onset of the clean-up effort, researchers have developed improved analytical methods, analytical equipment, and sample preparation methods. The DOE has helped resolve many of the needs through funding of various programs and the subsequent development of related documents. This review summarizes many of the successful projects that have resulted in methods now used throughout the world to analyze radioactive samples.

Initial efforts to characterize radioactive samples focused on existing EPA techniques designed for non-radioactive samples. These methods often failed when high levels of radionuclides were present. Some of the best examples of this failure are in organic analyses. This is seen in reports of early efforts to analyze organic components in radioactive material from waste sites using EPA methods.[2] This study involved the analysis of samples from two radioactive sites. In one case, 94.9% of the total organic material was identified. In contrast, only 1.2% of the organic carbon was identified in samples from the second site. In these investigations, standard protocols provided by the EPA were used. The EPA methods were not designed to identify all organic species, and the low mass balance in the second site was cause for concern. It was not clear whether the remaining organic components were hazardous or the analytical methods simply failed due to sample complexity. These and other analytical chemistry challenges, combined with the concern for exposure to excessive radioactivity, led to the development of new or modified (EPA/standard) methods for mixed waste. Some radiochemistry methods were subsequently developed by regulatory agencies. Many of these were relevant to fallout or nuclear plant effluents, but were not appropriate for high levels of contamination. Additional analytical methods were needed for not only radioanalytical chemistry, but also for inorganics, organics, sample digestions, and sample preparation. Unmet technology needs in the analysis of mixed waste were summarized in 1994.[3]

Several radioanalytical and other methods exist that were developed independently at several DOE sites through the 1980s. Many of these methods differed greatly from one another because they were largely developed in secrecy. When they were made publicly available, it was clear that they represented a tremendous variety of approaches, levels of quality control, and quality assurance.

As clean-up at DOE sites progressed, it was necessary that analytical methods be made available in writing and be reviewed, verified, and tied to appropriate quality assurance. An effort to document all of these analytical chemistry methods resulted in books of procedures from Hanford, Los Alamos, Oak Ridge, Savannah River, and other sites.[4] The book produced from Hanford consisted of six volumes, each containing approximately 50 procedures. One site, LANL, assembled an electronic database of its procedures. Procedures from the various DOE sites were compared and consolidated from the national labs when possible and placed into a book of methods.[5] This book also contains both guidance on the use of a performance-based approach to analyzing radioactive waste and protocols for sampling radioactive samples.[5]

The book generated for the DOE contains a number of new developments in the analyses of highly radioactive complex waste. One is the ability to more fully characterize organic components in tank waste using derivatization techniques.[6] Another valuable advance is the development of methods to analyze headspace components from tank waste.[7,8] One area not well covered by the DOE manual is the development of field methods.[9] Additional noteworthy progress has been made in the fields of process analytical chemistry.[10] Process, or online, analyses have evolved for the quantification of some specific radionuclides.[11-14] These and similar methods will become more important as radioactive waste processing becomes more common.

The greatest analytical chemistry needs for the DOE at the onset of the clean-up effort dealt with the characterization of highly radioactive samples, such as materials contained in the Hanford, Idaho, Savanna River, and Oak Ridge waste tanks. The analysis of environmental samples containing much less radioactivity than that found in tank waste can be carried out using either modifications of the methods designed for tank waste, or using methods designed for environmental samples.[15] Shielding and sample size can usually be adjusted accordingly to obtain both the desired detection limits and to minimize exposure. However, other challenges are meeting published hold-times and preservation conditions. Missing these times and disregarding common preservatives (such as keeping the sample at 0°C) could result in sample degradation or loss of volatile components. It was previously thought that hold times were unimportant for waste that had been stored underground for decades. However, some of these old samples have been shown to contain volatile components,[7] indicating a need to meet stringent preservation and hold-time criteria. An approach to meeting these criteria has not yet been developed for highly radioactive wastes, but work is under way to address this issue.

This section focuses on methods developed for the analysis of radioactive samples as developed and provided by the DOE. Many of the methods developed within the DOE labs describe deviations from EPA or other standard protocol.[16] This section does not exhaustively review commonly used procedures for non-radioactive samples. Those are available from several other sources (e.g., EPA-SW-846, NIST, AWWA, etc.).[16]

A final note before listing and describing individual methods is to state that methods are often needed for special, non-regulated analytes, such as chelators and organic acids in radioactive waste. These and other organic species in radioactive samples can degrade in high-radiation fields. When this happens, a large variety of products can form which otherwise would not have been expected from process knowledge. An example is the high diversity of compounds from the radioactive waste tank 241-C-103 at Hanford.[7] Numerous organic species are present, including some highly volatile species, all of which should have evaporated over the many decades of storage, yet continue to persist.[17]

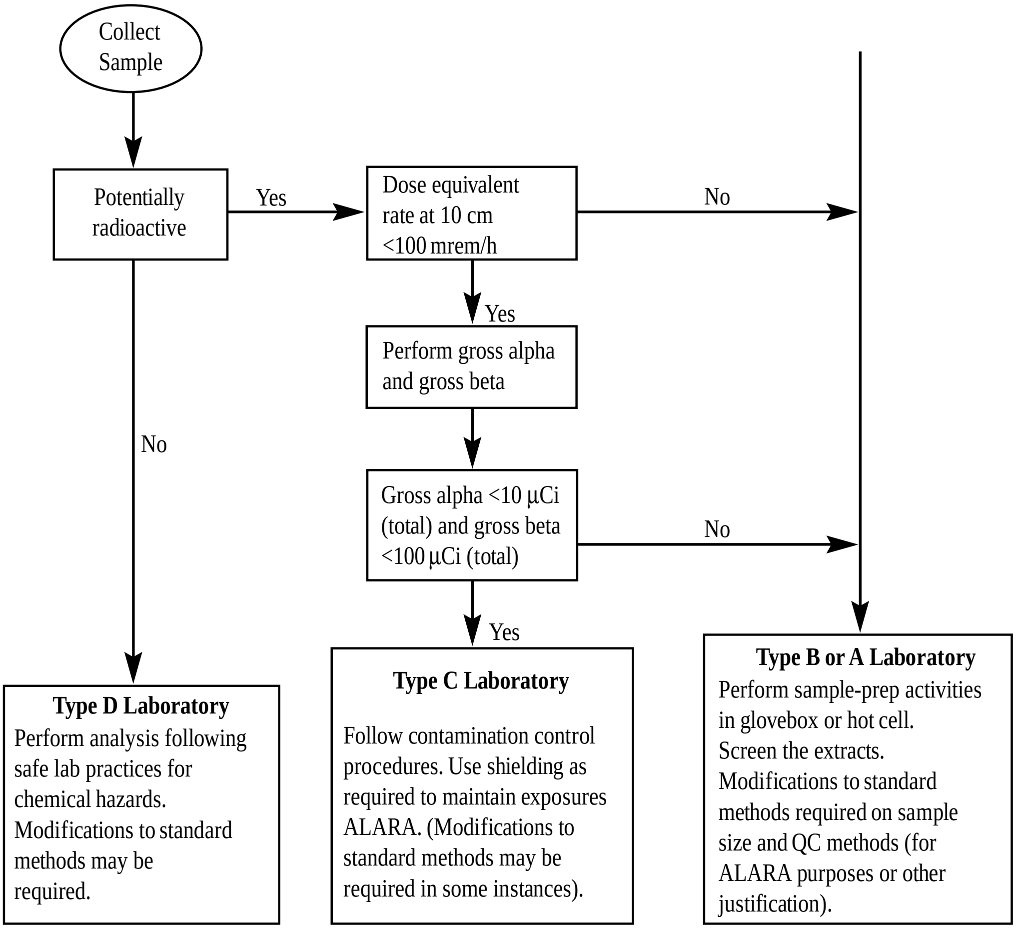
How to Analyze Radioactive Samples

Radioactive samples can be segregated by the level of alpha, beta, and gamma emissions. There is no clear universal distinction between samples that are highly radioactive and handled with protective equipment or shielding vs. those that can be handled with minimal protection at the lab bench. An attempt to differentiate low- from high-level samples has been published and is shown in Figure 2.2.1.[5] It is safe to consider all samples as radioactive if they have been located in a radioactive material area such as a contaminated field location or a laboratory where radioactive samples are processed. It is also common to treat samples as radioactive if they are even potentially radioactive (see Figure 2.2.1). Consult local safety guidelines and the sample provider before determining handling procedures for radioactive samples.

In this section, analytical methods have been divided into the three main categories: radionuclides, inorganic, and organic. As in all analytical techniques, there should be clear agreement among the analyst, project manager, and regulator(s) before any methods are used on any regulated samples.

Radionuclides

Radionuclides can often be analyzed either by their mass (or mass to charge ratio), via inductively coupled plasma/mass spectrometry (ICP/MS), ICP, or by their chemical and radioactive decay properties (radioanalytical chemistry). Both decay- and mass-based techniques are described in this chapter. Radionuclide analyses require that the isotope be measured free of interference. Interferences are both matrix and method dependent. Means of freeing the analyte isotope from interferences vary. When ICP/MS is used, the main matrix effects can be removed either on the plasma or through separation technologies. The dissolution approach typically includes acid dissolution and dilution, followed by ion chromatography to separate components with identical chemical behavior. Isobaric interferences can sometimes be determined and corrected. Traditional radiochemistry methods require counting (alpha, beta, gamma, X-ray). Counting techniques remove the non-radioactive matrix effects as appropriate for attenuation/absorption concerns. Classical radioanalytical methods also require the removal of interfering alpha/beta/gamma- and X-ray-emitting components, typically through various separation technologies.



Type D Laboratory
Perform analysis following safe lab practices for chemical hazards. Modifications to standard methods may be required.

Type C Laboratory
Follow contamination control procedures. Use shielding as required to maintain exposures ALARA. (Modifications to standard methods may be required in some instances).

Type B or A Laboratory
Perform sample-prep activities in glovebox or hot cell. Screen the extracts. Modifications to standard methods required on sample size and QC methods (for ALARA purposes or other justification).

Note: When aliquots of a sample are taken, the facility requirements will be based on the radiological quantitation associated with that aliquot.
Laboratory Types:
Type A – Radiochemical laboratory equipped with gloveboxes and hot cells with nonabsorbent floors and working surfaces. Designed specifically for handling high-activity radioactive materials. Laboratory should be isolated from surrounding offices or laboratories by change facilities or air locks. Contamination-zone clothing, such as coveralls and shoe covers, should be used. Personnel dosimetry (including extremity dosimeters as required), portable Geiger Müller (GM) and ionization survey instruments, air samplers, and other appropriate monitors should be available.
Type B – Intermediate radiochemical laboratory equipped with approved chemical hoods with high-efficiency particulate air (HEPA) filters and gloveboxes. Laboratory should be isolated from surrounding offices or laboratories by change facilities or air locks. Contamination-zone clothing, such as coveralls and shoe covers, should be used. Personnel dosimetry (including extremity dosimeters as required), portable GM and ionization survey instruments, air samplers, and other appropriate monitors should be available.
Type C – Radiochemical laboratory equipped with approved chemical hoods that are vented through HEPA filters. Face velocities at hood openings should have a minimum velocity of 100 cfm. Lab coats and personnel dosimetry should be worn. Labs should be equipped with GM survey meters and should offer other appropriate monitors.
Type D – Chemistry laboratory equipped with approved chemical hoods. The radioactivities of samples will present no external exposure or internal concern. Most procedures for handling hazardous waste samples should provide sufficient protection for employees.

FIGURE 2.2.1 Operating guide for RMW samples. (From Reference 3. With permission.)

Mass (or mass-to-charge) measurements are typically more sensitive for those components that have longer half-lives (assuming there are no isobaric interferences). Short half-life species may be more easily quantified by radioanalytical chemistry methods. However, methods such as ICP/MS and ion chromatography (IC)/ICP/MS may soon become popular alternatives for analysis of most, if not all, radionuclides because they can be automated and can analyze a large number of components simultaneously.[18]

Radioanalytical methods have been published for low levels of radioactivity for several years. Much of the technology traces back to methods developed by the Environmental Measurements Laboratory (EML).[15] A similar document was later developed at the Radiological and Environmental Sciences Laboratory (RESL).[19]

Table 2.2.1 summarizes many currently available radioanalytical chemistry methods. The table differentiates between techniques used to measure environmental and high level samples. Method numbers are shown in Table 2.2.1 with footnotes to reference their origin.

The radioanalytical chemistry methods are shown in a number of different categories. One division is field and laboratory methods. In this table, only a few field methods are indicated. These include methods for gamma spectrometry, thorium in breath, ^{99}Tc in water, and alpha emissions from a surface. Other field screening tools are available, but are less often used for quantitation, such as beta/gamma monitors, alpha monitors, hand-and-shoe counters, etc.

Laboratory methods for radioanalysis of soil and waste samples are numerous. Many of these methods are designed for environmental levels, but high-level samples can usually be diluted so that standard separation and counting procedures can be performed. Several high-activity radiochemistry methods have been developed for the analysis of tank waste. These methods either use a streamlined analysis (less rigorous chemistry for matrix removal), or more effectively address radionuclide interference from various components inherent in the processing used to create the waste.

Inorganic Components

The analysis of most inorganic species is outlined in a number of standard references.[12] This section focuses on the analysis of inorganic components of radioactive samples. These analyses are most often carried out by methods similar to those used for non-radioactive samples. Most exceptions are in three areas. The first is when common methods are inadequate due to interferences in complex matrices. The second is when radiation levels are so high that remote methods are necessary and it is difficult to meet holding times or preservation requirements. The third is for inorganic analyses of radioactive species, such as by ICP/MS. This category of analyses is awkward because radionuclide analyses seem to belong in the radionuclide category. The difference is in the methods of analysis. Radioanalytical methods measure the decay of the analyte. Inorganic analysis of radionuclides measures the mass of the analyte and some non-energy-producing parameter such as conductivity in ion chromatography or abundance by mass spectrometry. Because these methods typically measure radionuclides as if they were inorganic components, they have been put in the category of inorganic components. Another type of inorganic analytical methods includes the analysis of special components. One example is [OH^-] in highly alkaline waste (Karl Pool, unpublished results).

Methods designed to address some of the challenges of analyzing inorganic species in radioactive samples are listed in Table 2.2.2.

Some waste samples contain high levels of uranium and/or thorium and this can interfere with ICP or gas furnace atomic absorbance (GFAA) analyses. Method MP100R was developed by Swaford and Keller from Oak Ridge. This method reduces the levels of uranium, thorium, and plutonium without influencing concentrations of most other metals.[5] Similarly, method MP110R from the same authors uses a different approach to remove uranium and/or thorium from waste. The first method (MP100R) uses a solvent extraction process. The second method (MP110R) uses a membrane that specifically removes U and Th.[5]

Cyanide can sometimes be highly concentrated (>0.12 w/w) in radioactive wastes. Method MU012R was developed by Karl Pool at Pacific Northwest National Laboratory. It provides a technique to accurately

TABLE 2.2.1 Available Standard Radiochemistry Methods

	Field		Laboratory	
	Soil	Soil	Aqueous	Tank/High Level
Sample Preparation		C999[a]		
Screens				
Alpha		RP710[b]	900.0[c], 7110[d], D1943[a], RP710[b]	RP710[b]
Beta		RP710[b]	900.0[c], 7110[d], D1890[a], RP710[b], RP720[b]	RP710[b]
Tritium			RP720[b]	
Actinides		RP735[b]	RP725[b], RP735[b]	RP725[b]
Gamma spectrometry				
Ge(Li) or HPG	RS100[b]	RI010[b]	D3649[a], RI010[b], 901.1[c]	
Na(Ti)		RP730[b]	D4962[a], 901.1[c], RP730[b]	
Chemical Separations				
For alpha analysis				
Pu		C1001[a], Pu-02[c], Pu-03[c]	D3865[a], RP800[b]	RP800[b]
U		C1000[a], U-02[e]	908.0[c], 7500-U[d], D3972[a], U-02[e]	
Th	4C.1[f]			
Am/Cm		Am-01[c], Am-02[c]	Am-03[c], RP800[b]	RP800[b]
Ra		Ra-02[e], Ra-04[e]	903.3[c], Ra-03[e], 903.1[c], Ra-05[c], 7500-Ra[d], D2460[a]	
For beta analysis				
Tritium		RP580[b]	906.0[c], 7500-^{3}H[d] D4107[a], RP580[b], ^{3}H-01[e], ^{3}H-02[e]	RP580[b]
^{59}Ni, ^{63}Ni			RP300[b]	RP300[b]
^{79}Se			RP530[b]	RP530[b]
^{89}Sr, ^{90}Sr			905.0[c], Sr-01[e], RP501[b], RP515[b]	
^{90}Sr		RP510[b], RP520[b] Sr-02[e]	RP500[b], RP510[b], RP501[a], 7500-Sr[d], Sr-02[e], RP515[b], RP520[b]	RP501[b]
^{99}Tc	RS551		RP550[b], Tc-01[e], RS551[b]	
^{210}Pb			Pb-01[e], RP280[b]	
^{228}Ra			904.0[c]	
For LEPS/gamma analysis				
^{94}Nb, ^{93m}Nb			PR330[b]	RP330[b]
^{129}I			RP230[b]	RP230[b]
^{131}I			D4785[a], 7500-I[d], 902.0[c]	
Non-specific Methods				
Electrodeposition		G-01[e], G-02[c]		
Co-precipitation			G-03[e]	
Instrumental Analysis				
Gamma spectroscopy		D3649[a]		
Alpha spectroscopy				
Gross beta analysis				RP710[b]
Gross alpha analysis				RP710[b]
Beta spectroscopy (LSC)				RI100[b]
Miscellaneous				
Surface analysis				
Alpha emission rate	RA010[b], RA020[b]			

Note: This table was largely reproduced with permission from [3]. A few updated references have been added.

[a] Reference 16.

[b] Reference 4.

[c] Reference 17.

[d] Reference 18.

[e] Reference 11.

[f] Reference 9.

TABLE 2.2.2 Analytical and Preparative Methods for Inorganic Components of Radioactive Samples

Method Number	Title
MP100R	Solvent Extraction of Uranium and Thorium from Radioactive Liquid Wastes
MP110R	Clean-up of Transuranic Liquid Wastes using Extraction Chromatography
MU012R	Total Cyanide by Remote Microdistillation and Argentometric Titration
MM100	Inductively Coupled Plasma-Mass Spectrometry for Radionuclide Analysis
MM210	ICP-MS of ^{99}Tc, ^{230}Th, and ^{234}U using Flow Injection Preconcentration
MM800	Ion Chromatography and ICP-MS of Uranium Isotopic Abundance in Water
MM810	Separation and Analysis of Rare Earth Elements using IC-ICP/MS

From Reference 3. With permission.

measure these high concentrations remotely in radioactive waste.[5] The detection limit for this procedure is approximately 20 µg per sample.

The other methods in Table 2.2.2 use ICP/MS to analyze radionuclides. Similar methods designed to analyze high levels of radionuclides have been reported elsewhere.[18] One advantage of using ICP/MS for the analysis of radionuclides is their effectiveness for both waste and environmental levels. Another advantage of ICP/MS for analyzing radionuclides is in the ability to quantify several species simultaneously. The biggest disadvantage is the cost of the equipment.

Special inorganic method needs also exist for some mixed waste sites, such as for hexavalent chromium in soil (Ref. 3, Method MU016). However, most of these needs are addressed in standard references such as SW-846 (7000 series methods).

Organic Components

Most of the organic analytical methods used for either slightly or highly radioactive matrices are similar to standard regulatory methods (such as those provided in SW-846 or elsewhere[16]). The greatest exceptions are in the sampling, transport, and subsampling processes. Sampling strategies for radioactive materials can be significantly different from that of non-radioactive materials, resulting in both time and temperature differences that could influence sample integrity. Another common variable is pressure and headspace. Volatile components should be sampled in tightly sealed containers without any headspace. However, many highly radioactive samples are taken remotely with significant headspace, sometimes venting into the atmosphere. Such samples are highly suspect, but can often be analyzed for non-volatile species, especially if adequate controls have been included. One final variable of concern is the sample size. The most commonly used environmental analytical procedures can require large samples, up to several hundred milliliters per sample. When radiation levels are high, smaller sample sizes are typically used, potentially compromising detection limits.

Otherwise, when a standard method applies and can be followed safely, it should be used. Some contracts and regulatory agencies require compliance to specific published methods despite the above complications.

A few organic species are difficult to analyze because they are highly reactive, or will not extract effectively. When environmental levels of radionuclides are present, standard protocols perform well. For wastes found with high levels of radioactivity, such as in underground storage tanks at Hanford, special methods are needed to handle and process the samples. Often, changes to standard protocol are as simple as changing the sample size. This section describes some of the more complex adjustments to standard protocols that have been used at various DOE sites. One example is a method using a remote purge and trap system in a hot cell. Other methods are described for analyzing non-regulated analytes such as chelators and organic acids. These are of special interest in radioactive waste sites for two reasons: (1) their ability to complex with radionuclides and carry them through the soil more easily than the uncomplexed metal ion; (2) their contribution to the chemical processes in the waste tank. Methods are also available for analyzing headspace components of highly radioactive waste tanks,[7,8] which use SUMMA™

canisters or sorbent tubes for sampling and gas chromatography coupled with mass spectrometry (GC/MS) for analysis. These headspace components are typically low in radioactivity such that traditional methods are adequate. However, for some headspace analytes, enough heat is generated by the waste to volatilize species that are normally in the condensed phase. Under these circumstances, special laboratory techniques are needed to avoid sample condensation in the analytical apparatus.

Table 2.2.3 describes some of the methods that have been generated to extract or quantify organic species in highly radioactive samples.

TABLE 2.2.3 Analytical Methods for Organic Components of Radioactive Samples

Methods	Title
OC010R	Preparation and Cleanup of Hydrocarbon Containing Samples for the Analysis of Volatile Organic Compounds
OP010R	Remote Purge and Trap Gas Chromatography of Volatile Organics in High-Level Radioactive Wastes
OP020R	Ultrasonic Solvent Extraction for Analysis of Volatile Organic Compounds in Solid Radioactive Mixed Wastes
OP030R	Purge and Trap in a Glovebox
OP040R	Reduced-Scale Zero Headspace Extraction for TCLP Volatiles in Shielded or Containment Conditions
OP100R	PCBs in Aqueous Radioactive Mixed Wastes Using Solid Phase Extraction Disks and GC-ECD
OP120R	Reduced-Scale Liquid–Liquid Extraction of Semivolatile Organic Compounds
OP130R	Analysis of TCLP Semivolatiles and Pesticides in Radioactive Mixed Waste Sludges
OG015R	Major Nonhalogenated Volatile Organics in Radioactive Aqueous Liquids Analyzed by Direct Aqueous Injection Gas Chromatography
OG100R	Analysis of Polychlorinated Biphenyls in Solid Radioactive Mixed Wastes
OH100R	Direct Analysis of TCLP Acidic Semivolatile Compounds in Radioactive Liquid Wastes or Leachates Using HPLC with Ultraviolet Absorbance Detection
OM100R	Analysis of Semivolatile Organic Compounds Using Capillary Gas Chromatography with Ion Trap Mass Spectrometric Detection
OM500R	Qualitative Analysis for Low Molecular Weight Organic Acids in Mixed Hazardous Waste Samples by Thermospray LC-MS
OM510R	Determination of Chelators and their Degradation Products in Mixed Hazardous Waste Samples by Derivatization GC-MS

From Reference 5.

The first method listed in Table 2.2.3 (OC010R) was developed at Pacific Northwest National Laboratory (PNNL) by Rich Lucke and co-workers. This method removes long-chain hydrocarbons (normal paraffin hydrocarbons) from samples in which they interfere with analysis by purge and trap GC. A methanolic extraction of the sample is followed by clean-up with an 18-carbon alkyl chain solid-phase sorbent cartridge. Sample radioactivity has been found to decrease significantly when this clean-up method is used. The method is suitable for any sample matrix, such as waters, sorbents, or soils, containing excessive quantities of normal paraffin hydrocarbons.

Once the samples have been cleaned up, volatiles may need to be analyzed remotely if radiation levels remain high. Method OP010R[3] describes remote purge-and-trap procedure followed by thermal desorption GC to analyze volatile organic compounds in high radioactive liquid wastes. This method was developed by Christensen and co-workers at Idaho National Engineering Laboratory (INEL) and describes a modified purge-and-trap apparatus for use in a hot cell.

The next method (OP0Z0R) was developed at Oak Ridge National Laboratory (ORNL) by Schenley and Griest. It uses an ultrasonic extraction process to separate volatile organics from solid radioactive wastes. The method is suitable for hot cell, glovebox, or radiochemical hood use. Sample radioactivity decreases significantly when this approach is used. The method OP030R was also developed at ORNL by Thompkins, Schenley, and Griest.[23] This method describes an apparatus used in a glovebox to measure volatile species by purge and trap, similar to method 5030 in the EPA's SW-846.

A reduced-scale zero headspace extraction method is described in method OP040R.[5] This method was developed by the same group that developed the volatile analysis methods described above. It is used to analyze volatile organic compounds in solid wastes that are too radioactive to be handled under the conditions found in SW-846 Method 1311. A prototype tumbler and syringe holder was constructed for use in a glovebox or hot cell. This method should be performed only in cases where the direct analysis suggests that TCLP regulatory limits may be exceeded.

Polychlorinated biphenyls are quantitatively determined in extracts from radioactive aqueous matrices by Method OP100R.[5] Sample radioactivity is significantly decreased during extraction with solid-phase extraction disks, which also minimize laboratory waste generation. The method was developed at ORNL and is suitable for use in a glovebox or hot cell.

A reduced-scale liquid–liquid extraction method is described in Method OP120R.[5] This method (also developed at ORNL) is for the analysis of semivolatile organic compounds in aqueous samples that are too radioactive to be handled outside a hot cell or glovebox in the 1-L volumes required by SW-846 Method 3510. Sample radioactivity has been found to be significantly decreased during this extraction process.

Semivolatile organic (nonacidic) compounds and pesticides from radioactive mixed waste sludges are extracted by sonication and analyzed by GC-ECD (electron capture detector) in Method OP130R.[5] The method (from ORNL) is suitable for glovebox and hot cell operations.

Sample aliquots are taken in a radiochemical glovebox or hot cell in Method OG015R, developed at ORNL.[5] Analytes are major nonhalogenated volatile organic compounds in radioactive aqueous liquids that cannot be analyzed in a conventional laboratory. This method utilizes direct aqueous injection-gas chromatography (DAI-GC) to provide data on highly polar, water-soluble organic compounds that are not readily determined by purge and trap.

In Method OG100R,[5] waste samples are weighed and extracted in a radiochemical glovebox or hot cell and then subjected to a modified standard GC-ECD method for quantification of PCBs. Sample radioactivity is greatly reduced in extracts, which facilitates analysis. This method was also developed at ORNL and is similar to a combination of SW-846 Methods 3550, 3665, and 8081.

Leachates and aqueous liquid wastes are directly injected into a reverse-phase HPLC column in Method OH100R.[5] This method (from ORNL) is for the analysis of acidic semivolatile compounds, and minimizes both operator exposure to sample radioactivity and laboratory waste generation.

Method OM100R (developed at ORNL)[5] is similar to SW-846 Method 8270B in that it describes the determination of semivolatile organic compounds in extractions from solids, soils, and groundwater. It differs in that it provides performance data from mixed waste and includes alternate detection methods.

Low-molecular-weight organic acids, including formic, acetic, propionic, glyoxylic, glycolic, gluconic, citric, and tartaric acids, are qualitatively determined in Method OM500R. The method was developed at PNNL by Jim Campbell and co-workers and uses thermospray liquid chromatography-mass spectrometry (LC-MS).[24] Derivatization is not required. The method is suitable for hot cell, glovebox, or lab bench use and is applicable to tank waste samples. Sample radioactivity is significantly decreased by cation exchange before analysis by LC-MS.

Methylation followed by GC-MS is used in Method OM510R[5] to analyze chelators and their degradation products, including EDTA, HEDTA, ED3A, NTA, citric acid, oxalic acid, and succinic acid. The method was developed by Jim Campbell and co-workers at PNNL. It is suitable for hot cell, glovebox, or lab bench use and is applicable to tank samples.[25]

Other Characterization Methods

Numerous other characterization methods address both the physical and chemical condition of the waste. These include pH testing, hardness, density, viscosity, flammability, etc. Most of these methods are not used for regulatory purposes, but rather to determine how to handle the waste. For example, removing waste or transporting it to another site for treatment may require substantial knowledge of its physical characteristics. These procedures are outside the scope of this section, but can often be obtained from specific-site-standard operating procedures.

Conclusion

Analytical methods are being used worldwide on radioactive samples. Most of these analytical methods are provided by the regulatory community through the USEPA or similar agencies. The exception is in situations where radionuclide levels are much higher than in typical environmental samples. For these, the DOE has extensive information. This review summarizes much of the current technology in this area. However, newer technologies are constantly being developed as needed. Many of these remain unpublished but may someday be widely distributed.

The analytical methods being used for radioactive samples continue to evolve. Better technology is the result of an evolutionary process, creating new tools to address the analytical challenges of the nuclear industry. It is expected that, eventually, radioactive samples will be easily and quickly characterized with as much ease as more commonly encountered samples.

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2.3

Statistical Inference

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Introduction

When there is an environmental problem and the stakeholders desire to solve it using data, statistical inference is a tool that can be used for this purpose. Ideally, the stakeholders would like to measure the entire population that contains the problem of interest. In that case, everything the stakeholders want to know about the population is measured and the conclusions about it involve no uncertainty. However, such measurement of the entire population is often impractical or impossible, largely because of the high costs involved in such an approach. An alternative to this approach is to take a sample of this population and infer from the sample data necessary information about the population.

Statistics is such a tool for observing a subset of the population, or samples, and using the sample data to make inference or conclusions about the population. For this inferential process to work, there are two requirements: (1) the inference must be valid, and (2) the uncertainty of the inference must be quantified.

First, the validity of this sample-to-population inference depends largely on the degree to which the sample data is representative of the population. Representativeness is likely to occur when there is a proper sampling and measurement design that describes the spatial and temporal boundaries of the population; where or when the samples are to be taken and how many; how the physical samples are to be taken, handled, and preserved; and then how the samples are to be measured. These elements do, in fact, contribute to imprecision (or precision) and bias of the data. The degree or extent of precision and bias define the degree of representativeness. Bias probably cannot be entirely eliminated in practice. However, when the size of the bias becomes too large, it can invalidate the sample-to-population inference. Thus, it is highly recommended that the potential sources of bias be well understood and that steps be taken to prevent them from taking place or that their effects be minimized.

Second, the precision of the data can be used to quantify the uncertainty of the inference. Data-based inference involves uncertainty because (1) the samples are only a subset of the population, and (2) the samples may be taken and measured with error. Statistics can be used to identify and quantify the sources of error. Quantification of these errors can be used to make statements about how confident one is about the conclusions regarding the population using the sample data.

Statistical inference can be about estimation of a population parameter (e.g., the mean concentration of a contaminant in the population), or about a test hypothesis about a population parameter (e.g., whether the population concentration is above or below a regulatory limit). Because environmental applications tend to focus on test of hypothesis, the following discussions are made in that context.

This section discusses the fundamentals in making statistical inference from sample data, in particular the importance of representative samples, how to set up a test of hypothesis, the presumption implicit in the hypothesis, how to quantify the uncertainty of the test, and ways to increase confidence in making conclusions.

Basic Concept of Representative Samples

The concept of representative samples is the foundation for a valid statistical inference. ASTM(ASTM, 1996a) defines a representative sample as: "a sample collected in such a manner that it reflects one or more characteristics of interest (as defined by the project objectives) of a population from which it is collected."

A sample or a set of samples can properly reflect its population only when the samples, collectively, have high precision and low bias, relative to the characteristic(s) of interest in the population.

Two typical sources of imprecision and bias emanate from the sampling and measurement processes. Sampling can result in imprecision because the population may not be totally homogeneous. Heterogeneity in the population will lead to random differences among the samples taken, and these random differences are a source of imprecision. A second type of sampling error is of a systematic nature, such as consistently higher or lower concentrations of a contaminant in the samples than in the population. This is a source of bias. Statistical inference deals only with random error. Systematic error can be controlled or minimized by attention to the design and implementation of the sampling protocol and quality assurance procedures.

Similarly, imprecision and bias can be present in the measurement process. Measurement bias often results from instrument drift, defective standards, or analytical interference.

When significant sources of errors are suspected to exist, an experiment can be conducted and statistics can be used to quantify the random variance components (but not the systematic bias). If they are too large, they can be controlled or reduced either by improving the sampling and measurement processes or by taking more samples and making more analytical measurements for each sample. Optimization techniques can be used to balance between reduction in random errors and increases in sampling and analytical costs (ASTM, 1998).

In most environmental applications, imprecision from sampling is often much greater than that from analytical measurement. One way to reduce sampling error (or imprecision) is to obtain composite samples by combining individual samples. Details of some efficient sampling approaches are given in later subsections.

Elimination or minimization of bias in sampling, measurement, or any other part of the processes is a significant issue. Bias is usually difficult or impossible to measure because the true value is rarely known. Thus, minimization of bias to a very large extent depends on a well-designed protocol and its proper implementation. This includes a well-defined population, a statistical design that specifies the population boundary and sampling locations, proper choice of sampling equipment, proper use of the equipment to collect the physical samples, proper handling and preservation of the samples before analysis, and a proper measurement process to translate the physical samples into unbiased data.

There have been questions about whether a single sample can be representative of a population. A single sample can be representative under the following conditions:

1. *When the population is highly homogeneous with respect to the characteristic of interest* — In this case, random differences among the samples are likely to be very small or negligible. Thus, a single sample is often sufficiently representative of the population.
2. *When the sample is a composite of individual samples randomly collected from the population, under the condition that each sample is collected without bias (or negligible bias)* — In this case, the composite sample would be essentially free of bias and with much higher precision than an individual sample.

When these conditions are not met, a single sample may be biased. Biased sampling can be useful in determining whether a contaminant is present at the location of sampling, but it should not be used to infer to the general population.

Process in Statistical Inference

The ASTM (ASTM, 1995) and the USEPA (USEPA, 1994) have a data quality objectives (DQO) process for planning and solving environmental problems. According to the USEPA, the DQO process has the following steps:

1. State the problem.
2. Identify the decision.
3. Identify the inputs to the decision.
4. Define the study boundaries.
5. Develop a decision rule.
6. Specify tolerable limits on decision errors.
7. Optimize the design.

These steps are similar to steps for statistical inference. For example, Gilbert (1987) outlines a 12-step approach for planning an environmental sampling study, which is somewhat parallel to the DQO process, but with different emphasis. All these steps can be re-stated as follows:

1. *Solving the right problem* — corresponding to "state the problem" in the DQO process.
2. *With the right kind of data* — corresponding to the DQO steps in "define the study boundaries" and "identify the inputs to the decision."
3. *Using an appropriate decision rule* — related to DQO steps in "identify the decision," "develop a decision rule," and "specify tolerable limits on decision errors."
4. *Doing it optimally* — corresponding to the DQO step in "optimize the design."

We discuss statistical inference for solving environmental problems in the context of these four steps.

Solving the Right Problem

Stating the problem is the first step in solving the right problem. Solving the right problem minimizes re-work and allows resources to be directed toward more productive uses.

The problem statement typically needs to have the following elements:

- Nature and location of the problem
- Suspected or known contaminants and their adverse effects
- Regulations involved
- Stakeholders
- Whether emergency measures are needed
- The required resources and their constraints
- Project objective(s) and how and when a decision is to be made

The statement needs to be very clear about the project objectives and criteria for determining when the objectives have been achieved and the problem has been solved. There are times when reiteration of the process is needed. However, the iteration should be a result of new information and not of a poorly stated problem at the outset.

Right Kind of Data

The data used for statistical inference come from physical samples collected from a population and measured by a chosen analytical method. Thus, planning for the collection of the right kind of data needs to address: the population, collection of the physical samples, handling and preparation of the samples, and the measurement process.

The spatial and/or temporal boundaries of the problem area define the boundaries of the target population. A population can be a waste site, a pile, or a drum, depending on the situation. When all the materials in this population are available for sampling, then the sampled population and the target population are identical. When the sampled population is only a subset of the target population (e.g., only a portion of the population is accessible for sampling), potential bias can arise. When such a difference exists, it is up to the stakeholders to decide whether the sampled population is a sufficient approximation to the target population for decision-making purposes and whether any qualifications need to be attached to the conclusion.

It is often assumed that the entire population is the decision unit for inferential purpose. When this is the case, samples are collected from this population and a decision is made for the entire population. There will be times when it makes sense to divide the population into smaller decision units. For example, a population may consist of a highly contaminated ditch, an overflow basin, and a generally uncontaminated area (except perhaps hot spots). In this case, the population can be divided into three decision units. Each unit may have its own problem statement, objective, and decision rule. For example, using process knowledge, authoritative samples can be used to confirm or characterize suspected contamination of the ditch and to make decisions regarding immediate treatment and clean-up. For the basin, a simple random sampling design can be adopted and the decision can be based on whether the sample mean concentration is significantly higher than a certain regulatory limit. For the third area, a grid sampling design can be used for the detection of hot spots.

The collection of physical samples deals with the identification of sampling locations and how the sample is to be taken at each location. The notion of "representative sample(s)" has two meanings: (1) each sample needs to be collected in such a manner that it is representative of the materials at the sampling location; and (2) the samples collected from all the locations must collectively reflect the population at large.

Sample representativeness at the location of sample collection depends on the proper choice of sampling equipment as well as its proper use. It is especially important that the sampling equipment be able to accommodate the largest particle size of interest and allow all the materials at that location equal probability of selection. The use of equipment that preferentially selects certain parts of the materials will lead to biased results. Further details are provided by Pitard (1989).

Each sample may be representative of its sampling location, but all the samples together may not be representative of the population. This can happen when all the samples are taken from a certain area of the population while ignoring the rest. For example, samples may be collected only from the rims of a contaminated basin. While these samples, collectively, might be representative of the rims of the basin, they might not be representative of the entire basin. For the samples to be representative collectively, a sampling plan must be designed so that all the possible sampling locations in the population have an equal chance of selection. A simple random sampling design has this property. Advantages and disadvantages of other sampling designs are discussed in ASTM (1998).

Proper sample handling and preservation to prevent bias is a well-known subject. They also may affect precision of the data. Sample handling and preservation are not issues of a statistical nature, but are mentioned here because they are part of the process toward obtaining representative sample data.

The measurement process is also important in obtaining the right kind of data. Apart from control of instrument drift and analytical interference to prevent bias, there is also an issue of laboratory subsampling prior to analysis. When a sample is not analyzed in total and a subsample is used, the same principles in sampling are applicable to subsampling. The sample is simply regarded as the population, and the subsample(s) is to be taken so that it is representative of the sample.

Test of Hypothesis and Decision Rule

A statistical test of hypothesis is often used to determine where the true value of a population is likely to be. A test of hypothesis is framed by two hypotheses: a null hypothesis and an alternative hypothesis. The null hypothesis is the presumed hypothesis of choice before the data are collected. If the sample data is judged to be consistent with this hypothesis through a statistical test, this null hypothesis is accepted. On the other hand, if the data is judged to be inconsistent with the null hypothesis, then the null hypothesis is rejected and the alternative hypothesis is accepted.

In this framework, there are two likely errors. One is called Type I error, the error of rejecting the null hypothesis (and accepting the alternative hypothesis) when the null hypothesis is true. A second kind of error is called Type II error, the error of rejecting the alternative hypothesis (and accepting the null hypothesis) when the alternative hypothesis is true. These two errors have different interpretations, depending on how the null and alternative hypotheses are stated in applications. For example, when the null hypothesis is that the true population value does not exceed a regulatory limit and the alternative hypothesis is that it does, the Type I error is a "false positive" error and the Type II error is a "false negative" error. These two types of errors are decision errors. Stakeholders must often specify how large an error is acceptable, based on the seriousness of the consequence of such an error.

Each of the two hypotheses (null and alternative) is associated with an action as a result of its acceptance. The decision rule in the context of a statistical test of hypothesis is simply about how the result of the statistical test is to be used to accept or reject a hypothesis and what consequent action to take.

Implicit in the test of hypothesis is a presumption used to set up the null hypothesis (H_0). Choosing an inappropriate presumption has very serious consequences. For example, in testing whether the mean concentration (μ) of a contaminant in a population exceeds a regulatory limit (L), the null hypothesis and its alternative hypothesis (H_a) can be set up in two different ways:

$$1.\ H_0\text{: } \mu < L \text{ vs. } H_a\text{: } \mu \geq L \tag{2.3.1}$$

$$2.\ H_0\text{: } \mu \geq L \text{ vs. } H_a\text{: } \mu < L \tag{2.3.2}$$

These two null hypotheses have very different underlying presumptions and consequences. The null hypothesis in Eq. (2.3.1) presumes that the mean concentration of the population does not exceed the regulatory limit. The consequence of this presumption leads to the statistical comparison of the lower confidence limit (LCL) against the regulatory limit, where LCL is calculated by:

$$LCL = m - t_{1-\alpha,\, n-1}s/\mathrm{Ð}n, \tag{2.3.3}$$

where

m = Sample mean
s = Sample standard deviation
n = Number of samples
α = One-sided significance level
$t_{1-\alpha,\, n-1}$ = tabled t-value corresponding to 100(1–α)% confidence level with (n–1) degrees of freedom

The decision rule here can be stated as follows:

1. If LCL < L, then the material is judged to be non-hazardous. The material can be disposed of by shipping to a landfill.
2. If LCL ≥ L, then the material is judged to be hazardous. The material needs to be treated before disposal.

Note that the second part of the decision rule, when read in conjunction with Eq. (2.3.3), implies that:

$$m - t_{1-\alpha,\, n-1}s/\mathrm{Ð}n \geq L\text{; or}$$

$$m \geq L + t_{1-\alpha,\, n-1}s/\mathrm{Ð}n$$

Because the quantity ($t_{1-\alpha,\, n-1}s/\mathrm{Ð}n$) is always non-negative, it means that the sample mean concentration of the material can be somewhat higher than the regulatory limit L and not trigger any regulatory action. In other words, as long as the sample mean concentration is not statistically significantly higher than the regulatory limit, no regulatory action is required.

This kind of null hypothesis is often appropriate when comparing the concentration of a certain material against the background (Gilbert and Simpson, 1992). It may be appropriate as well when the consequence of a false positive error is more serious than the consequence of a false negative error. The stakeholders need to weigh these factors when deciding whether a particular presumption in the null hypothesis is reasonable.

The null hypothesis in Eq. (2.3.2) presumes that the mean concentration of the population exceeds the regulatory limit. Consequence of this presumption leads to the statistical comparison of the upper confidence limit (UCL) against the regulatory limit, where UCL is calculated by:

$$\mathrm{UCL} = m + t_{1-\alpha,\, n-1} s/\sqrt{n} \tag{2.3.4}$$

The decision rule here can be stated as follows:

1. If UCL < L, then the material is judged to be non-hazardous. The material can be disposed of by shipping to a landfill.
2. If UCL ≥ L, then the material is judged to be hazardous. The material needs to be treated before disposal.

Note that the first part of the decision rule, when read in conjunction with Eq. (2.3.4), implies that the sample mean concentration of the material needs to be significantly lower than the regulatory limit L so as not to trigger any regulatory action.

It is important that stakeholders understand the presumption underlying the test of hypothesis and its effect on how the decision is made. The choice of a presumption depends primarily on what the regulations allow and the relative consequence of false positive and false negative errors in the decision-making.

The hypotheses in Eqs. (2.3.1) and (2.3.2) are for testing the mean of a population. Tests for quantities such as the medians and proportions are discussed in USEPA (1995).

The quantity ($t_{1-\alpha,\, n-1} s/\sqrt{n}$) in Eqs. (2.3.3) and (2.3.4) is a quantification of uncertainty in the decision-making. It indicates the margin of error required by the decision-maker(s) for specified decision error α. The term ($s/\sqrt{n}$) indicates how reliably the population mean is estimated by the sample mean.

In summary, the steps for setting up the hypotheses and carrying out the decision rule for a typical case are:

1. Determine the choice of presumption underlying the null hypothesis.
2. State the null hypothesis H_0 and the alternative hypothesis H_a.
3. Specify a decision error for α.
4. Collect and measure the samples to obtain the sample data, according to a sampling and measurement design. This step provides the value of n, the number of samples collected.
5. If the null hypothesis is Eq. (2.3.1), use Eq. (2.3.3) for the decision rule. If the null hypothesis is Eq. (2.3.2), use Eq. (2.3.4) for the decision rule. The various quantities in Eq. (2.3.3) or Eq. (2.3.4) can be calculated using the sample data and statistical table.

The optimal number of samples to collect is addressed in the next chapter subsection.

Doing It Optimally

Society has limited resources. When environmental testing is done efficiently, the same number of resources can be directed to addressing more environmental problems. Statistics can often be used to optimize the sampling and measurement design and reduce the costs of sampling and analysis.

The choice of sampling design is case specific. For a population known to be fairly homogeneous in the distribution of the concentrations of a contaminant, a simple random sampling design may be appropriate. If there is knowledge that the population has areas of high concentrations and areas of low concentration, a stratified random sampling design is more efficient. In this case, the population is divided into strata of high and low concentrations, and random samples are then taken from each of the strata. When the entire population is the decision unit, the methods of calculating its mean and standard error and the test of hypothesis are covered in most statistics textbooks. Discussions on the advantages and disadvantages of some commonly used designs are given in ASTM (1998).

Once a sampling design is chosen, the next question is to determine the number of samples to collect. The ASTM (1998) and USEPA (1995) have extensive discussions on the optimal numbers of samples to collect under various situations. When too much data is collected, the additional data provide marginally less information. When there is too little data collected, the decision errors, in terms of false positive and false negative errors, can become too large.

For example, when it is desired that the absolute deviation of the sample mean from the population mean be within a prescribed limit d with 100(1–α)% probability, then the optimal (minimum) number of samples, n, is:

$$n = (Z_{1-\alpha/2}\sigma/d)^2 \tag{2.3.5}$$

where

$Z_{1-\alpha/2}$ = The $(1 - \alpha/2)$ percentile point of standard normal distribution
σ = Standard deviation of the population
d = $|m - \mu|$
m = Sample mean
μ = Population mean

Because it is often easier to estimate the coefficient of variation (CV) than the standard deviation σ, a more useful formula for calculating the needed sample size is:

$$n = (Z_{1-\alpha/2}CV/d_r)^2 \tag{2.3.6}$$

where

CV = s/μ
s = Sample standard deviation
d_r = $|m - \mu|/\mu$

Note that a guess of the population mean is needed for these formulae. This can be done based on historical data or process knowledge.

When it is necessary to consider both the false positive error and the false negative error, Eq. (2.3.5) can be revised as follows:

$$n = (Z_{1-\alpha/2} + Z_{1-\beta/2})^2\sigma^2/d^2 \tag{2.3.7}$$

where α = False positive error rate
β = False negative error rate

It should be noted that determination of the optimal number of samples or measurements depends on the sampling design, and also on the sources of error. In a simple random sampling design, samples can be analyzed in replicate. In this case, there will be two sources of error: sampling error and analytical error. Optimization here has to do with choosing the optimal combination of the number of samples and the number of replicate analyses per sample. This topic is discussed in ASTM (1998). For more complicated situations, such as the stratified random sampling design, a statistician can be consulted.

When samples can be combined without loss of materials and when analytical cost is higher than sampling cost, composite sampling is often a very effective way of reducing analytical costs. Composite sampling has the following advantages:

1 A composite sample is unbiased when the individual samples going into the composite are unbiased.
2. A composite sample is more precise than an individual sample. Assuming that the composite sample can be analyzed in total or is highly homogeneous, the variance of a composite sample is

approximately the variance of the individual sample, divided by the number of individual samples going into the composite.

3. A composite sample tends toward normal distribution as the number of individual samples going into the composite becomes large. Therefore, statistical methods under normal distribution assumption can be applied.
4. Composite sampling also may allow for greater spatial coverage of the population, when compared between the same number of composite samples and individual samples.

Because of increased precision of the composite samples, fewer composite samples are needed than individual samples to achieve the same level of precision. This leads to a reduction in analytical cost. The extent of cost reduction is a function of the number of individual samples going into the composite. Under the assumption discussed above, some examples of cost reduction are given in Table 2.3.1.

TABLE 2.3.1 Approximate Reduction in Analytical Cost Due to Composite Sampling

Number of Individual Samples[a]	% Reduction in Analytical Cost
2	50
3	67
4	75
5	80

Note: Assuming that the composite sample is analyzed in total or is highly homogeneous.

[a] Individual samples going into the composite.

Alternatively, one can take advantage of the increased precision of composite samples to increase the confidence level of the statistical test. Increased precision of composite samples means that the term $(t_{1-\alpha,\, n-1}s/\text{Ð}n)$ in Eqs. (2.3.3) and (2.3.4) are smaller, leading to tighter LCL and UCL for comparison against a regulatory limit.

One concern regarding sample compositing is the potential loss of volatile materials. A procedure to combine the samples directly into methanol can be used to address this problem. A discussion of these advantages and potential limitations of composite sampling is given in ASTM (1996b).

Another approach to reducing analytical cost is the method of ranked set sampling. This is a method of using information of a quick or inexpensive measurement to stratify the population *at the sample level* and reduce the number of samples needed for analysis of a primary variable of interest while achieving the same level of precision. Details of the method are discussed by Pacific Northwest Laboratory (1995) and an application is given by Nussbaum et al. (1997).

Statistical Inference and Making a Conclusion

Statistical inference is often used to make a conclusion based on the result of a statistical test. Statistical tests provide a mathematical framework for a data-based decision on whether an objective has been reached. This kind of conclusion is a statistical conclusion using only the sample data. In any real-world applications, the decision-makers should incorporate site-specific information and knowledge to ensure that the proper decision is made.

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2.4

Mixed Waste Characterization

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Introduction

Methods and technologies used to characterize mixed waste depend on the end-use of the exercise. In examining mixed waste, one should first identify the likely answers to a number of questions, including:

1. What kind of mixed waste requires characterization? Is it environmental contamination of soil or groundwater; an ongoing process or waste stream; contents of an abandoned tank; or some other mixed waste?
2. Will radiation exposure levels allow normal laboratory processing or must remote-handling methods be employed?
3. Is characterization being conducted *in situ* or *ex situ*?
4. Will data be used for risk assessment, selection of management or treatment options, or waste disposal?
5. Are data being collected to support regulatory processes such as the Resource Conservation and Recovery Act (RCRA) or the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), a separate state-authorized clean-up action, or as part of routine process control?

Chemical and radiological data generated during characterization must, at a minimum, meet the ultimate goals of the project. A selection of methods and technologies must work within any limitations imposed by circumstances of the situation and the waste form. From the answers to these questions, clearly identified data needs, data quality objectives, and situational limitations, determination of how to best characterize a mixed waste can begin.

New methods and technologies for characterization of mixed waste have been developed in the past decade, primarily by and for the Department of Energy (DOE) but also the Department of Defense (DOD), universities, and private laboratories and businesses. These include both *in situ* and *ex situ* methods applicable to high- and low-radiation fields. However, standard methods of chemical and physical analysis remain primary characterization tools. This section focuses on the characterization of chemical constituents, with only minor discussion of radiological constituents, because these methods are generally better defined and implemented. In addition, while the term “mixed waste” specifically refers to a waste that is both radioactive and a hazardous waste under the RCRA, this section assumes the broader interpretation that mixed waste is any material that is radioactive and requires characterization for chemical constituents.

In all cases of mixed waste characterization, careful consideration must be given the end use of the data and of the quality level associated with the data to achieve those end uses. Sometimes quick, simple, and inexpensive analyses are all that is required. Sometimes analytical data of both high accuracy and high precision are required. When studying environmental contamination, this process is often iterative, beginning with “quick-and-dirty” methods and progressing to more detailed and more expensive analyses as the nature and extent of contamination require better definition. In all cases, characterization of mixed waste should be governed by an appropriate Quality Plan. Discussions of Quality Plans can be found in several sources, including EPA Guidance for Quality Assurance Project Plans–EPA QA/G5, EPA/600/R-98/018, February 1998.

Define the Waste Requiring Characterization

Environmental Media

The reasons for characterization of environmental media (e.g., soil or groundwater), are often different from those for process wastes. When characterizing environmental media, the goal is usually to define the nature and extent of any mixed waste contaminants that might be present. These wastes may have originated from discharges to surface water, groundwater, surface impoundments, soil, or from stack emissions. Mixed waste constituents may be as diverse as metals confined to a thin layer of surface soil or a dense non-aqueous-phase organic liquid pooled in a fractured-rock aquifer several hundred feet below the ground surface. Details of the individual circumstance will drive decisions on characterization.

Several guidance documents are available to assist in characterizing environmental media. An excellent compilation can be found on a CD-ROM distributed by the U.S. Environmental Protection Agency, National Exposure Research Laboratory (NERL) – Las Vegas: Site Characterization Library, Volume 1 (Release 2), EPA/600/C-98/001, April 1998. These guidance documents include those written by private authors, the American Society for Testing and Materials (ASTM), and the USEPA.

Additional information and guidance on site characterization can be found on another CD-ROM compilation: USEPA Technology Innovation Office: Information Sources for Innovative Remediation and Site Characterization Technologies, EPA 542-C-98-003. This CD focuses on site characterization and potential remediation technologies.

Depending on the media and types of waste involved, a number of technologies or methodologies are available for field-oriented analytical and characterization studies. These are summarized in Table 2.4.1 and Section 3. A more detailed discussion of strengths and weaknesses of each method is presented in Field Analytical and Site Characterization Technologies, Summary of Applications; EPA-542-R-97-011, November 1997.

Ongoing cooperative efforts between industry and the USEPA to develop and verify methods for characterization of environmental media are conducted through the Consortium for Site Characterization Technology and are documented at: http://www.epa.gov/swertio1/programs/scmt/verstate.htm.

Chemical Technologies

Biosensor (Number of Sites: 1)

Biosensors are analytical tools in which the sensing element is an enzyme, antibody, deoxyribonucleic acid, or microorganism; and the transducer is an electrochemical, acoustic, or optical device. The technology was used to detect explosives (trinitrotoluene [TNT]; cyclo-1,3,5-trimethylene-2,4,6-trinitramine [RDX]; and cyclotetramethylenetetranitramine [HMX]) in soil, groundwater, and compost residues.

Reported Advantages	Reported Limitations:
• Potentially cost-effective	• None identified
• Real-time data	

TABLE 2.4.1 Available Technologies for Field-Oriented Analytical and Characterization Studies

Technology	Site Screening	Site Characterization	Cleanup Monitoring	Compliance Monitoring	Confirmation Sampling	Enforcement	Health and Safety Monitoring	Waste Characterization	Risk Assessment
Chemical Technologies									
Biosensor	✓		✓	✓					
Colorimetric test strip	✓	✓	✓	✓					
Cone penetrometer mounted sensor	✓	✓							
Fiber-optic chemical sensor	✓	✓							
Fourier-transformed infrared spectrometry		✓	✓	✓			✓		
Gas Chromatography	✓	✓	✓		✓				
Immunoassay	✓	✓	✓	✓	✓			✓	
Mercury vapor analyzer		✓					✓		
X-ray fluorescence	✓	✓	✓	✓	✓	✓			✓
Geophysical Technologies									
Bore-hole geophysical		✓							
Direct-push electrical conductivity	✓								
Electromagnetic induction		✓							
Ground penetrating radar	✓	✓							
Magnetometry		✓							
Seismic profiling	✓	✓							
Radionuclide Technologies									
Gamma-radiation detector	✓	✓							
Passive alpha detector		✓	✓					✓	
Sampling and Sampler Emplacement Technologies									
Closed-piston soil sampling		✓							
Direct-push prepacked well screen		✓		✓					
Low-flow groundwater pumping	✓	✓		✓					
Soil gas sampling		✓							✓
Vertical groundwater profiling		✓		✓					
Vibrating well installation	✓	✓							

Colorimetric Test Strip (Number of Sites: 3)

Colorimetric test strips are a single-measurement, portable technology that uses a wet chemistry non-immunoassay test to detect analytes in soil or water. The intensity of the color formation can be determined visually or with a spectrophotometer. Colorimetric test strips have been used to detect nitrates, TNT, RDX, and HMX in soil and groundwater.

Reported Advantages	Reported Limitations:
• Potentially cost-effective	• Possible interference caused by nitrite
• Easy to use	• Creation of soil slurry necessary to use test strips
• Real-time data	

Cone Penetrometer Mounted Sensor (Number of Sites: 34)

Cone penetrometer mounted sensors are real-time, *in situ*, file screening methods for petroleum hydrocarbons and other contaminants, as well as lithologic parameters. The method includes use of the Site

Characterization and Analysis Penetrometer System Laser-Induced Fluorescence (SCAPS-LIF) cone penetrometer mounted sensor technology. The SCAPS-LIF technology was developed through a collaborative effort of the U.S. Army, Navy, and Air Force, under the auspices of the Tri-Services SCAPS Program. The method uses a fiber optic-based, laser-induced fluorescence sensor system, deployed with a standard 20-ton cone penetrometer. Cone penetrometer mounted sensors have been used to perform field screening and site characterization for PAHs and total petroleum hydrocarbons (TPH) such as diesel and jet fuel, gasoline, waste oil, heating fuel, and kerosene, in soil and groundwater, as well as the lithologic parameters (pH, redox potential, conductivity, soil type, and other factors).

Reported Advantages:

- Potentially cost-effective
- Continuous, real-time data
- Accurate measurements
- Three-dimensional mapping possible
- Contaminant fingerprinting capability
- Enhanced delineation of contaminant (2-inch vertical resolution)
- No soil cuttings
- Quick decontamination
- Data allowed selection of optimal confirmation soil boring locations

Reported Limitations:

- Expensive for a limited number of sample locations
- Naturally occurring fluorescent material can lead to false positives
- Limited by rough terrain
- Difficult to maneuver in tight spaces
- Subsurface cobbles cause probe refusal

Fiber-Optic Chemical Sensor (Number of Sites: 3)

Fiber-optic chemical sensors are coating-based sensors on fiber optics that detect contaminants by monitoring the change in the refractive index on the coating of the fiber optics that alters the amount of light transmitted to a detector. The technology has been used to measure concentrations of TPH; benzene, toluene, ethylbenzene, and xylene (BTEX); and halogenated VOCs, such as trichlorethylene (TCE), in groundwater and soil gas.

Reported Advantages:

- Potentially cost-effective
- Can be used *in situ*
- Easy to use
- Portable
- Quick turn-around time

Reported Limitations:

- Possible interference from other chlorinated VOCs
- Results affected by bailing method and amount of water bailed
- Concentration of contaminants affects response time

Fourier-Transformed Infrared Spectrometry (FTIR) (Number of Sites: 3)

This method is an air monitoring technique that identifies compounds by fingerprinting spectra. A sample's molecular constituents are revealed through their characteristic frequency-dependent absorption bands. The technology has been used to measure the concentration of VOCs in air for health and safety, compliance, and clean-up monitoring.

Reported Advantages

- Adequate detection levels
- Portable
- Real-time data

Reported Limitations:

- Interference caused by water vapor
- QA/QC methods not fully developed
- Not appropriate when a high degree of spatial resolution is required

Gas Chromatography (Number of Sites: 24)

Gas chromatography (GC) is an analytical technique used to separate and analyze environmental matrices for contaminants. Gas chromatography has been widely accepted as a primary analytical tool for site characterization because of its capability to separate, detect, identify, and quantify target analytes in a complex mixture. The technique is suitable only for the analysis of thermally stable organic compounds. Gas chromatography, with the use of various detectors (photoionization, flame ionization, electron capture, electrolytic conductivity, nitrogen-phosphorus, mass spectrometer, and others), and with various sample extraction and introduction methods (headspace, purge and trap, solvent extraction, solid-phase extraction, thermal desorption, and others), has been used to measure concentrations of halogenated and non-halogenated VOCs, SVOCs (including polychlorinated biphenyls [PCBs], polynuclear aromatic hydrocarbons [PAHs], and pentachlorophenol [PCP]), TPH, pesticides, and dioxins in soil, soil gas, sediment, groundwater, and air.

Reported Advantages:

- Potentially cost-effective
- Low detection limits (able to measure maximum contaminant level [MCL] concentrations)
- Quick turn-around time
- High-quality data generated
- Portable
- High sample throughput
- Good correlation with EPA's Contract Laboratory Program (CLP) laboratory data
- Ability to perform simultaneous analysis for BTEX and other hydrocarbon compounds

Reported Limitations:

- Experienced operator required
- Learning curve associated with use of equipment
- Library of components limited for mass spectrometer
- Petroleum carrier solvent caused interference with analysis for PCP
- Modification of extraction time required to improve consistency of results
- Poor extraction of diesel fuels from soils with high organic matter
- Co-elution of three types of contaminants hindered ability to meet detection limits

Immunoassay (Number of Sites: 43)

Immunoassay is a technique for detecting and measuring a target compound through the use of an antibody that binds only to that substance. Quantitation is performed by monitoring color change, either visually or with a spectrophotometer. The technology has been used to detect or to measure the concentrations of halogenated VOCs, PAHs, TPH, BTEX, PCBs, organic pesticides, mercury, and bacteria in soil, sludge, sediment, surface water, groundwater, and composite residues.

Reported Advantages:

- Potentially cost-effective
- Near real-time data
- Reproducible results
- Reasonable correlation with laboratory results
- Low rate of false negative results, except when fuel compounds were highly degraded
- Portability
- Detection limits capable of meeting action levels
- Capable of defining boundaries of contamination

Reported Limitations:

- High rate of false positives found in results from PCB and organic pesticide kits
- Incapable of identifying individual PAHs
- Poor extraction efficiency in peat or bog samples

Mercury Vapor Analyzer (Number of Sites: 2)

This technology monitors mercury vapors emitted from soil. These analyzers have been used for health and safety monitoring and to determine soil sampling locations.

Reported Advantages:

- Allowed for real-time understanding of exposure
- Quick turn-around time for data

Reported Limitations:

- Learning curve associated with equipment

X-ray Fluorescence (Number of Sites: 39)

X-ray fluorescence (XRF) analyzers operate on the principle of energy dispersive XRF spectrometry. Energy dispersive XRF spectrometry is a nondestructive analytical technique used to determine the metals composition of environmental samples. Field-portable and transportable XRF units were used to detect or measure concentrations of heavy metals (mercury, chromium, lead, cadmium, copper, nickel, and arsenic) in both *in situ* and *ex situ* soils, sludge, sediment, and groundwater.

Reported Advantages:

- Potentially cost-effective
- No investigation-derived waste (IDW)
- Good correlation with analytical laboratory results
- Real-time data
- Quick turn-around time
- Capability to determine multiple analytes simultaneously
- Nondestructive method
- Little sample preparation
- Consistent quality of data

Reported Limitations:

- Limit on penetration depth
- Some field-portable units require liquid nitrogen
- One field-portable unit weighs 50 pounds
- Preparation of quality control sample required
- Difficulty in obtaining sufficiently low detection limits because of matrix interference
- Detection limits sometimes not low enough to respond to ecological concerns

Geophysical Technologies

Bore-hole Geophysical (Number of Sites: 4)

Bore-hole geophysical technologies include ground penetrating radar (GPR), electromagnetic induction, and acoustic methods. These technologies have been used to map fractures in bedrock, and to determine groundwater flow and depth of the water table, to generate data for use both in site characterization and in placement of monitoring wells.

Reported Advantages:

- Accurate results
- Sensitivity
- Facilitation of better understanding of groundwater flow

Reported Limitations:

- Well diameter must be greater than 2 inches
- Well casing must be nonmetallic

Direct-push Electrical Conductivity (Number of Sites: 1)

The direct-push sensing of electrical conductivity is a geophysical technique based on the physical principles of inducing and detecting the flow of electrical current within geologic strata. Measurements of soil conductivity and logs of soil conductivity combine to supply information about the lithologic features of a site. This technology has been used for site characterization and mapping to support placement of monitoring wells, and also to define subsurface geologic and hydrogeologic conditions.

Reported Advantages:

- Potentially cost-effective
- Easy to use
- Portable turn-around time
- Capability to identify thin stratigraphic layers that conventional methods miss
- No soil cuttings

Reported Limitations:

- Large metal objects can cause interference
- Susceptible to operator error
- Experienced operator needed to calibrate and interpret logs

Electromagnetic Induction (Number of Sites: 3)

Electromagnetic induction units use a transmitter coil to establish an alternating magnetic field that induces electrical current flow in the earth. The induced currents generate a secondary magnetic field that is sensed by a receiver coil. This technology has been used during site characterization to locate disposal trenches at a landfill.

Reported Advantages:

- Easy to use
- Portable
- Quick results

Reported Limitations:

- Large metal objects such as fences can cause interference

Ground Penetrating Radar (Number of Sites: 4)

Ground penetrating radar (GPR) provides a rapid, real-time display of information about the subsurface, ranging from geological features to hydrologic features. The GPR method uses a transmitter that emits pulses of high-frequency electromagnetic waves into the subsurface. The electromagnetic energy that is scattered back to the receiving antenna on the surface is recorded as a function of time. This technology has been used during site characterization to identify abandoned waste pits and other subsurface disturbances, bedrock stratigraphy, and the depth to water table, as well as to develop profiles of a river bottom.

Reported Advantages:

- Data useful in identifying subsurface disturbances without soil borings
- Data allowed the selection of optimal soil boring locations
- Focused mapping of sample location
- Information compared favorably with that obtained from other methods

Reported Limitations:

- Surface vegetation can inhibit transmission of signals
- Soils with high electrical conductivity can inhibit transmission of signals
- Interpretation of data is complex; experienced data analyst required

Magnetometry (Number of Sites: 2)

Magnetometers detect the presence of ferrous objects in the subsurface by measuring the earth's magnetic field or how the field changes spatially. Hand-held and vehicle-towed magnetometry units have been used during characterization and mapping to identify buried ferrous metals.

Reported Advantages:

- Ability to detect large ferrous metal objects 12 to 20 feet below ground surface
- Ability to discriminate among subsurface anomalies

Reported Limitations:

- Vehicle-based magnetometers limited by terrain and field conditions
- Vehicle-based magnetometers tend to underestimate the number of targets, as compared with hand-held devices
- Signals from extraneous metals must be filtered out

Seismic Profiling (Number of Sites: 8)

Seismic profiling technology is based on the principle that if an acoustic signal is introduced into the ground, a wave will echo to the surface whenever a change in the medium is encountered. Sensors at the surface receive the signal, which is recorded by a seismograph and processed by software developed by the oil industry. Two- and three-dimensional seismic profiling technologies have been used during site screening and characterization to determine bedrock stratigraphy, soil type, and depth to water table.

Reported Advantages:

- Potentially cost-effective
- Very detailed image of soil stratigraphy
- Bedrock fractures defined to within 1 foot
- Easy to use
- Drilling costs minimized

Reported Limitations:

- Large surface objects cause interference
- Data return is very specific
- Trained technician required to interpret data
- Vegetation must be removed
- Equipment requires direct contact with the ground, presenting a problem for use in buildings

Radionuclide Technologies

Gamma-Radiation Detector (Number of Sites: 3)

Gamma-radiation detectors are portable instruments that often use sodium iodide or cesium iodide scintillation counter detectors to detect gamma emissions. The technology has been used to detect radionuclides in soil, sediment, and liquid waste.

Reported Advantages:

- Easy to use
- Portable
- Lower cost than conventional methods
- Data compared favorably with laboratory data
- Real-time data

Reported Limitations:

- Sensitive to power fluctuations
- Liquid nitrogen required
- Protection from weather required

Passive Alpha Detector (Number of Sites: 1)

Two types of commercially available passive radon detectors — electric ionization chambers and alpha track detectors — have been modified for use in screening of soil *in situ* for alpha contamination. The detectors have been used to measure alpha contamination in soil.

Reported Advantages:

- Potentially cost-effective
- Easy to use
- Fast

Reported Limitations:

- None identified

Sampling and Sampler Emplacement Technologies

Closed-Piston Soil Sampling (Number of Sites: 1)

This technology is a discrete-depth sampling technology that uses a locking piston. The locking piston enables the user to collect samples from a previously sampled boring without allowing unwanted material from the overlying borehole to be included in the sample. This sampling technology has been used in conjunction with direct-push technology during site characterization to obtain continuous soil cores from below the water table.

Reported Advantages:

- No soil cuttings
- Less expensive than conventional drill rigs
- Faster than conventional methods

Reported Limitations:

- Sampler is designed for use only in soils and unconsolidated sediments
- Generally used at depths of less than 50 feet
- If used for sampling discrete subsurface intervals, the hole must be preprobed

Direct-push Prepacked Well Screen (Number of Sites: 1)

This technology uses a direct-push method to install prepacked stainless steel screens. The technology has been used during site characterization and compliance monitoring to install small-diameter monitoring wells.

Reported Advantages:

- Less expensive and faster than installing a conventional well
- No soil cuttings

Reported Limitations:

- Cannot be used in bedrock
- Limit on depth
- Small diameter of well may limit sampling options

Low-flow Groundwater Pumping (Number of Sites: 9)

Low-flow groundwater sampling involves the use of any number of groundwater sampling pumps that purge a slowly monitoring well so as not to cause turbulent flow into the well. The method decreases the turbidity of the water sample and allows collection of a more representative groundwater sample than is possible with conventional technologies. The technology has been used to obtain groundwater samples for analysis of VOCs and heavy metals.

Reported Advantages:

- Production of low-turbidity samples possible
- Less purge water generated
- More effective in low recharge wells

Reported Limitations:

- None identified

Soil Gas Sampling (Number of Sites: 5)

A number of passive and active sampling devices can be used to obtain soil gas samples. Passive soil gas absorption devices, in-well monitoring equipment, and canister devices have been used to obtain soil gas samples for on- and off-site analysis of VOCs.

Reported Advantages:

- Potentially cost-effective
- Quick turn-around time
- Easy to use
- Large amounts of data generated
- Passive soil gas sampling technology can absorb low-volatility compounds
- Good correlation with monitoring well data

Reported Limitations:

- Active soil gas sampling is not effective in impermeable soils
- Passive soil gas sampling results may not correlate well with results of active soil gas sampling

Vertical Groundwater Profiling (Number of Sites: 4)

Vertical groundwater profiling technology collects point samples rather than samples over a screened interval, as is the case with conventional monitoring wells. The technology uses a probe that is advanced by a pneumatic piercing tool (air hammer) driven by a gasoline-powered air compressor. Groundwater is extracted from the profiler by means of a peristaltic pump. This technology has been used to vertically delineate contaminants in groundwater.

Reported Advantages:

- Potentially cost-effective
- Enables vertical profiling
- Enables tracking the boundaries of the contaminant plume

Reported Limitations:

- Problem with data comparability
- Difficulty in modeling the migration of TCE

Vibrating Well Installation (Number of Sites: 6)

This technology uses a specially designed all-terrain vehicle employing a vibrating push mechanism to install small-diameter wells. This vibrating well installation technology has been used to install groundwater wells and monitoring wells to depths up to 200 feet.

Reported Advantages:

- No soil cuttings
- Can be installed to 100 ft without pilot hole
- Equipment fits into tight spaces

Reported Limitations:

- Well screens easily clog
- Equipment frequently overheats
- Casing requires welding

Process Waste

Process waste is often easier to sample and characterize than environmental media, unless high radiation levels render physical handling of samples hazardous. In these few cases, special sampling and handling must be executed — including, but not limited to, the use of specialty hot cells for chemical analysis. While such samples can be diluted or smaller portions used, these practices often lead to reduced analytical sensitivities, and higher method detection limits. In addition, very few facilities, government or private, are equipped with the requisite hot cells/laboratories. One exception is the Idaho Nuclear Technology and Engineering Center at the Idaho National Engineering and Environmental Laboratory, owned by the Department of Energy and located near Idaho Falls, Idaho. See http://www.inel.gov for additional information.

Where radiation levels exceed safe working limits, it is often difficult to obtain any kind of sample. Issues of sample representativeness of the waste stream and variability over time often seem of secondary importance. However, in these cases, analytical data must then be regarded as simply a rough estimate of the actual composition of the waste being considered. Absent adequate quality and confidence in the data, its usefulness for many tasks is questionable.

Assuming radiation levels are sufficiently low to allow routine handling and analysis of samples, several issues must be determined prior to characterization of process waste; these include variability over time, the phase(s) present, and end-use of the data.

Ideally, process waste should vary little over time. In this ideal case, once a waste has been adequately characterized, then it need not be repeated unless and until the process changes. In most cases, issues of process control and waste management require ongoing and periodic waste analysis. Adequate characterization can often be obtained through the same inline equipment used on non-radioactive systems. In all cases, issues pertinent to radioactive waste must be considered. These include radioactive dose during routine operations, maintenance, and ultimate waste disposal. The radioactive dose will depend on the volume of material/waste in the equipment, plate-out, and accumulation of radioactive material in low-flow areas. Damage or interference to the sensors from the alpha, beta, gamma, or neutron emissions from the material/waste must also be considered when using inline analytical equipment.

Where inline analytical techniques are inadequate, other routine sampling methods and analytical techniques must be employed. Other than in the care given to prevent or reduce radioactive dose to sampling and analytical personnel and preventing spread of radioactive contamination, these methods are identical to those used on non-radioactive wastes. Excellent guidance on sampling and analysis of various types of industrial wastes are published by the EPA and ASTM. These include the EPA's manual Test Methods for Evaluating Solid Waste, SW-846, 3rd edition.

Legacy Waste

Due to the nature of many operations that generated mixed waste, waste residues were often left in place when systems were abandoned or replaced. These residues now require characterization during closure or decommissioning activities. These residues are neither environmental media nor ongoing process waste. Instead, they are often found in tanks and pipes. They may be liquid, semi-solid, or solid. Their source may be known or unknown. In all cases, safety is of paramount importance. Long-unused residues may have undergone unexpected chemical reactions and produced unexpected compounds. These residues should be sampled only after proper review and planning by competent professionals in the areas of safety, radiological controls, chemists, samplers, and operations personnel.

Initial characterization likely includes simple in situ methods such as radiation and contamination surveys, and vapor space testing for explosive, organic, or acidic compounds. Once it has been determined that additional samples can be taken, then both standard *in situ* and *ex situ* characterization techniques can be employed.

Identify the Purpose for Characterization

Environmental Media

Characterization of environmental media contaminated with mixed waste can serve a number of functions, often sequentially. These functions include (1) determining the nature and extent of contamination, if any; (2) conducting a risk assessment to human health and/or the environment of any contaminants found; and (3) investigating methods to reduce the mobility, toxicity, or volume of the waste, either *in situ* or *ex situ*.

Determining the nature and extent of environmental contamination is, by nature, a broad topic addressed in several guidance documents already mentioned. Characterization may be as simple as collecting soil samples over a broad surficial area; or it may require drilling many wells into an aquifer several hundred feet below ground surface. Chemical and radiological analyses tend to be very broad and non-specific so that all possible and likely contaminants are detected.

Part of the process of identifying the nature and extent of environmental contamination includes determining the “background” concentrations of those constituents. For many contaminants, such as organic solvents, one expects the background concentrations to be at or below the lower limits of detection. But other chemicals, such as arsenic or thorium decay products, may exist naturally in the media being sampled. Thus, these naturally occurring chemicals and radionuclides must be identified and their “background” concentrations determined so that statistically significant deviations from “background” can be identified.

This process typically uses a “totals analysis” of contaminants in soil or water rather than an extraction method such as the EPA Toxicity Characteristic Leach Procedure (TCLP). The “totals” method typically extracts metals from soil through an acid extraction; washes organic material from soil using an appropriate solvent; and strips organic compounds from water by purging with a gas followed by gas chromatography and mass spectrometry. Metals in water are analyzed directly.

Once the mixed waste contaminants and their footprints have been identified, an assessment of the risk to human health or the environment is generally conducted by comparing the concentrations of contaminants to standardized tables available from the EPA. The process of assessing routes of exposure and risk-related calculations is beyond the scope of this section. Suffice to say that if the risk from contaminants is deemed excessive, then site remediation will be required and additional characterization is often a prerequisite to remediation.

Remediation can either be *in situ* or *ex situ*. Methods include stabilization, destruction, and removal followed by other treatment. In all cases, suitability of the mixed waste to the proposed remediation must be ascertained. Appropriate types of characterization might include leachability of waste constituents, usually determined through a TCLP extraction; presence and concentration of underlying hazardous constituents to determine RCRA Land Disposal Restriction (LDR) compliance; pH or Eh; speciation of metals, such as determining if chromium is present in the +3 or +6 oxidation state; alkalinity or water hardness; constituents that might interfere with the proposed remediation technology; BTU content if thermal treatment is being considered; moisture content of soil; and many others, depending on the remediation technology. If the waste will simply be exhumed for treatment and disposal, then characterization needs will be dictated by the waste acceptance criteria of the facility receiving the waste.

For characterization requirements for environmental media contaminated with a hazardous/mixed waste and destined for *ex situ* storage, treatment, or disposal, see the following discussion and Figure 2.4.1.

Process and Legacy Waste

The primary purpose for characterization of process and legacy waste is that of management (e.g., storage, treatment, and disposal). Only federal RCRA requirements are discussed here. Because many states impose additional requirements, the reader is encouraged to refer to applicable federal, state, or local hazardous/mixed waste regulations.

The first determination is: Is this waste a hazardous waste under RCRA regulations? Part of this determination is whether the waste is exempt from all or some RCRA regulations as imposed by the EPA or an authorized state. These exemptions are generally found in 40 CFR 261, or state equivalent, with most found in 40 CFR 261.4(a) and (b). If an exemption does not apply, then the generator must determine if the waste is an RCRA hazardous waste listed in 40 CFR 261.31–261.33.

When reviewing these lists, the generator must also consider the “derived-from” and “mixture” rules. In short, if a waste is derived from the storage or treatment of a listed waste, it is also a listed waste. If a waste was mixed with a listed waste, the entire mixture must generally be managed as a listed waste (see 40 CFR 261. 3 for the full requirements). If the waste is an RCRA listed waste as generated or as a result of either the derived-from or mixture rules, then it must be managed as a hazardous/mixed waste.

It is important to note that determining if a waste is an RCRA listed waste is not based on chemical analysis, but on knowledge of the waste and comparison of the waste to the specific listings found in the regulations 40 CFR 261.31–261.33, or state equivalent.

If the waste is not a listed waste, it must be tested to determine if it exhibits a characteristic of a hazardous waste, ignitability, corrosivity, reactivity, toxicity (see 40 CFR 261.21–261.24 for the testing requirements). If the waste exhibits a characteristic of a hazardous waste, then it must be managed as a hazardous/mixed waste. If the waste is neither listed nor a characteristic waste, then it is not a hazardous/mixed waste and can be managed as a non-hazardous or radioactive waste.

If the waste is either a listed or characteristic hazardous/mixed waste (and no exemptions apply), then it must be managed in accordance with federal or state hazardous/mixed waste regulations, including requirements applicable to accumulation and storage in containers and tanks and for ultimate treatment and disposal of the waste. This hazardous/mixed waste determination process is depicted in Figure 2.4.1. The process of conducting a hazardous/mixed waste determination can be documented on the form provided in Appendix A. This form provides additional information that may be required by facilities providing additional storage, treatment, or disposal of hazardous/mixed waste.

One of the hazardous/mixed waste management requirements is additional characterization for compliance with LDRs (see 40 CFR 268.40). Depending on the RCRA hazardous waste codes applicable to the waste, characterization must be performed for those underlying hazardous constituents (UHC) that the generator believes may be present. The list of UHCs and their required maximum concentrations (or required technologies) is found in 40 CFR 268.48.

Mixed Waste Characterization

Required Analytical Methods

The EPA and Nuclear Regulatory Commission (NRC) have jointly published guidance in the *Federal Register* on the subject of characterizing mixed waste, 62 FR 62079, November 20, 1997. This guidance is noteworthy because it states that exposure to ionizing radiation is an important consideration when characterizing mixed waste. Some discretion is offered with respect to the use of smaller-size samples than otherwise required, the use of surrogates in lieu of actual mixed waste, and in explaining the concept of “acceptable knowledge” rather than relying solely on chemical analysis for mixed waste characterization.

Generators of hazardous and mixed waste are required to characterize waste for several purposes, including:

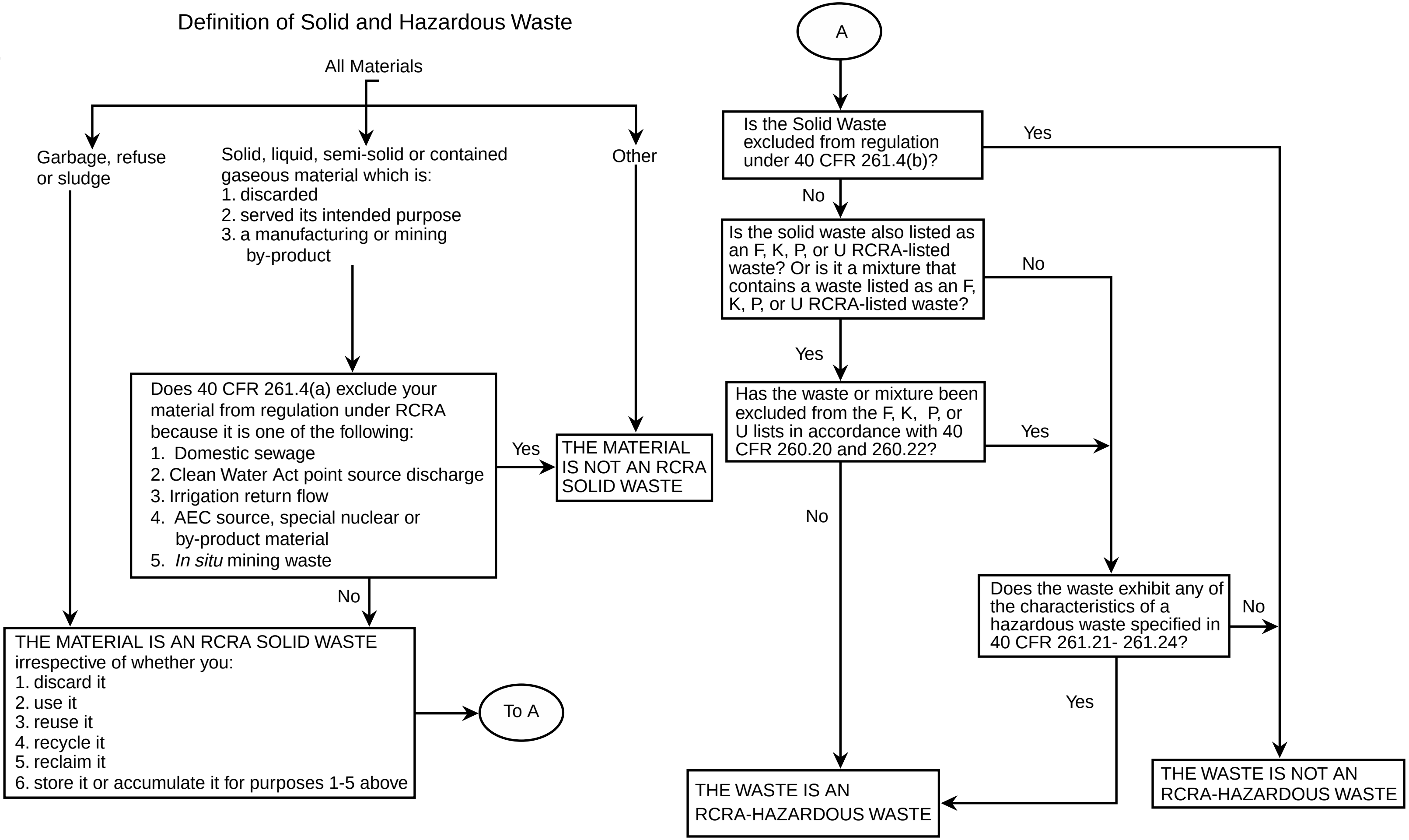

FIGURE 2.4.1 Definition of solid and hazardous waste.

1. To determine if the waste is hazardous waste
2. To comply with waste analysis requirements for hazardous and mixed waste Treatment, Storage and Disposal facilities that require:
    a. Chemical/physical analysis of a representative sample and/or, in some cases, use of knowledge of the waste
    b. Preparation of a waste analysis plan
3. To meet the waste analysis requirements that apply to the specific waste management methods under 40 CFR 264.17, 265.314, 264.341, 264.1034(d), and 268.7
4. To ensure, prior to land disposal, that the waste meets the required treatment standards

The EPA requires specific analytical methods, detailed in SW-846, in only a very few instances. These are:

1. 40 CFR 260.22(d)(1)(i): submission of data in support of a petition to delist a waste
2. 40 CFR 261(a)(1) and (2): evaluation of waste against the characteristic of corrosivity
3. 40 CFR 261.24(a): leaching procedure for evaluation of waste against the characteristic of toxicity
4. 40 CFR 261.35(b)(2)(iii)(A): evaluation of rinsates from wood-preserving cleaning processes
5. 40 CFR 264.190(a), 264.314(c), 265.190(a), and 265.314(d): evaluation of waste to determine if free liquid is a component of the waste
6. 40 CFR 264.1034(d)(1)(iii) and 265.1034(d)(1)(iii): evaluation of organic emissions from process vents
7. 40 CFR 264.1063(d)(2) and 265.1063(d)(2): evaluation of organic emissions from equipment leaks
8. 40 CFR 266.106(a): evaluation of metals from boilers and furnaces
9. 40 CFR 266.112(b)(1) and (2)(i): certain analyses in support of exclusion from the definition of a hazardous waste for a residue that was derived from burning a hazardous waste in boilers and industrial furnaces
10. 40 CFR 268.7(a), 268.40(a), (b), and (f), 268.41(a), 268.43(a) and 268.48(c)(1)(B): leaching procedures for evaluation of waste to determine compliance with LDR standards
11. 40 CFR 270.19(c)(1)(iii) and (iv), and 270.62(b)(2)(i)(C) and (D): analysis and approximate quantification of the hazardous constituents identified in the waste prior to conducting a trial burn in support of an application for a hazardous waste incineration permit
12. 40 CFR 270.22(a)(2)(ii)(B) and (270.66(c)(2)(i) and (ii): analysis conducted in support of a destruction and removal efficiency trial burn waiver for boilers and industrial furnaces burning low-risk wastes, and analysis and approximate quantification conducted for a trial burn in support of an application for a permit to burn hazardous waste in a boiler and industrial furnace

In some cases, the EPA specifies analytical methods described in ASTM procedures or any equivalent method approved by either the EPA or a state authorized by the EPA to enforce the RCRA program for mixed waste. Thus, one wishing to characterize mixed waste is largely free to use those sampling and analytical methods best suited to the situation and that also meet the necessary data quality objectives.

Use of "Waste Knowledge" for Characterization of Waste

EPA regulations allow for the use of "process knowledge" to fully or partially characterize waste. The term "process knowledge" refers to detailed information on processes that generate waste subject to characterization or to detailed information generated from processes that generate waste similar to that generated with original waste. Process knowledge includes waste analysis generated by others on the waste in question or on chemically identical waste. Process knowledge must be fully documented and retained for possible inspection by regulatory agencies.

In some cases, both the EPA and the NRC have endorsed the use of "waste knowledge" (sometimes called "acceptable knowledge") to characterize waste rather than actual chemical analysis. The term "waste knowledge" includes, where appropriate: (1) process knowledge, (2) records of analysis performed by the generator or others, or (3) a combination of (1) and (2) supplemented with current chemical analysis.

Waste knowledge can be used to determine if the waste is an RCRA characteristic hazardous waste; to meet waste analysis requirements under a formal waste analysis plan; and to determine compliance with LDRs.

The use of waste knowledge alone is appropriate for wastes that have physical properties that are not conducive to taking a laboratory sample or performing laboratory analysis. As such, the use of waste knowledge alone may be the most appropriate method to characterize mixed waste streams where increased radiation exposure is a concern. Mixed waste generators should contact the EPA regional office or authorized state to determine if they possess adequate waste knowledge to characterize their mixed waste.

Use of Surrogates

In determining whether a radioactive waste is also an RCRA hazardous waste (and thus a mixed waste), the generator may test a surrogate material (i.e., a chemically identical material with significantly less or no radioactivity) to determine the RCRA status of the radioactive waste. This substitution of a surrogate material may either partially or completely supplant the testing of the waste. A surrogate material, however, should be used only if the surrogate material faithfully represents the hazardous constituents of the mixed waste. As part of the hazardous waste determination, the generator must document test results or other data and methods used. (See 40 CFR 262.40(c) for additional information.)

Flexibility in Mixed Waste Testing

Flexibility exists in the hazardous waste regulations for generators and facilities managing mixed waste to tailor mixed waste sampling and analysis programs to address radiation hazards. As an example, the frequency for testing mixed waste prior to storage, treatment, or disposal might be reduced to address radiation hazards. EPA hazardous waste regulations also allow a mixed waste facility the latitude to change or replace EPA test methods (i.e., Test Methods for Evaluating Solid Waste, SW-846) for the same purpose. The instances where test methods from SW-846 are required are given at the beginning of the section. EPA approval of an equivalent analytical or testing method to replace the required EPA method can be requested.

Specific flexibility for mixed waste is allowed in the TCLP extraction to determine if a waste exhibits the characteristic of toxicity. The EPA Method 1311 found in SW-846 requires a sample size of 100 grams. For mixed waste testing, sample sizes of less than 100 grams can be used if the analyst can demonstrate that the test is still sufficiently sensitive to measure the constituents of interest at the regulatory levels specified in the TCLP and is representative of the waste stream being tested. Other variances to the published testing protocols are permissible but must be approved by the EPA or the authorized state prior to implementation.

Summary

Mixed waste may be encountered in environmental media, as waste from a defined process, or as a legacy waste from past operations. While characterization methods may differ depending on the situation, the ultimate goal remains constant: to identify the hazardous constituents and their concentration, and determine what methods might be used to treat or dispose of the waste. While regulatory requirements are very strict regarding hazardous/mixed waste characterization and management, some flexibility is available for mixed waste.

Appendix A

Waste Stream Identification ____

DIRECTIONS:
Section I should be filled out by the initial generator of the waste (e.g., lab personnel, operations personnel). They should include all information to the best of their abilities and experience. If the initial generators can't fill out much, but only provide basic information such as how the waste was generated and the process information (e.g., chemicals used, MSDS, cleanup of spill, solvent recovery system) that is fine.

Section II should be filled out by personnel trained in RCRA characterization. There may be a need to do some interaction with the initial generator (e.g., since they may not know what a solvent is per RCRA definition).

Section III should be filled out by personnel trained in RCRA after analytical data and the generator information is reviewed.

Section IV is information about LDR classification and should be completed by RCRA-trained personnel after reviewing analytical data or other information provided by the generator.

PURPOSE: To comply with the 40 CFR 262.11 and 268 requirements relating to characterization of solid waste/hazardous waste; PCB regulated waste (40 CFR Part 761) and to support CERCLA remedial activities. Upon completion, this form with required attachments will serve to meet the basic characterization assessments per the RCRA and TSCA-PCB programs. The use of this form will provide consistent waste evaluation for facility personnel.

SCOPE: Any characterization determinations provided below based upon Process Knowledge (PK) must accompany this form or be referenced. This includes the justification from omitting any RCRA regulated hazardous waste contaminant from an analytical request. PK information must be sufficient to provide a defendable position for excluding or partially excluding sampling and analytical request(s). PK can be in the form of a general statement provided by personnel knowledgeable in the basic characterization requirements for the applicable program. PK can include referencing the process and associated raw materials used in the process. If the waste is deemed hazardous due to a particular contaminant, a short statement will suffice for PK documentation (e.g., AF001-assigned due to known solvent use involving greater than 10 percent solvent constituents prior to use).

If facility personnel/generators use material safety data sheets (MSDSs) to satisfy all or part of the characterization assessment, the MSDSs must be provided for products used in the process generating the waste (caution: MSDS information may not reflect waste constituent concentrations or characteristics. MSDS information reflects the general characteristics and precautions for the unused product, but does not necessarily provide sufficient information for RCRA characterization).

Any previous analytical results associated with a waste stream must be attached or referenced.

SECTION I

4. NON-CERCLA GENERATED WASTE __________CERCLA-GENERATED WASTE __________

   1. Waste Generation Location: Building #____________________ Location __________________

5. Attach a detailed description of the process that generated the waste and the type of waste that will be generated.

6. Provide a physical description of the waste (wet, dry, damp, liquid, solid, soil).

   ☐ Aerosol ☐ Gas ☐ Liquid ☐ Solid ☐ Sludge ☐ Other ___________________________

   If solid, is the waste greater than 60mm in size? Yes ☐ No ☐ Unknown ☐

8. Can this waste be certified as a non-radioactive waste? Yes ☐ No ☐ Unknown ☐

   If no, attach Process Knowledge statement (e.g. list radiological area associated with waste) or radiological analytical results.
   See attachment # ________________

9. Does the waste contain friable asbestos or asbestos fibers? Yes ☐ No ☐ Unknown ☐

10. Does the process generating the waste involve metal fabrication, cleaning, grinding, dissolution or other means of potential metal or organic contamination? Yes ☐ No ☐ Unknown ☐

    If yes, attach a list known or suspected organic or metal contaminants. See attachment # ____________________

11. Have more than one type of waste or materials been mixed to generate this stream? Yes ☐ No ☐ Unknown ☐

    If yes, attach a description of the waste or materials that have been mixed together. See attachment # ___________________

12. Is the waste a treatment residual? Yes ☐ No ☐ Unknown ☐

EXCLUDED OR REDUCED REQUIREMENTS
(261.2, .3, .4, AND .6)

13. Is the waste to be recycled or treated? Yes ☐ No ☐ Unknown ☐

    If yes, describe the means of recycling or treatment
    (Note: scrap metal contaminated with listed waste cannot be recycled).

LISTED WASTE (40 CFR 261, SUBPART D)

14. Does the waste contain, or did the waste come into contact with, any RCRA listed waste (i.e., “F”, “P”, “U”, or “K”, as defined in 40 CFR 261, Subpart D)? Yes ☐ No ☐ Unknown ☐

    If yes, list or attach a list, of the EPA Codes and list constituents.

    If unknown, was the waste used as a solvent or extractant? Yes ☐ No ☐ Unknown ☐

    If yes, did the solvent or extractant before use exceed 10% of product composition for contaminants listed in EPA Codes F001, F002, F004, or F005? Yes ☐ No ☐ Unknown ☐

15. If the waste is an F003 listed solvent, did it retain the characteristic of ignitability upon generation as a waste? Yes ☐ No ☐ Unknown ☐
    (Note: F003 is very specific, it must be composed only of the constituent identified in 40 CFR 261, Subpart D or only composed of the constituent identified in 40 CFR 261, Subpart D and exceed 10% product composition of F001, F002, F004 or F005 prior to use).

16. Is the waste an unused chemical or an unused off-specification commercial chemical product meeting the listing for “U” or “P” waste; or from a non-specific source identified in 40 CRF 261, Subpart D (i.e., “K” waste)? Yes ☐ No ☐ Unknown ☐

    If yes, list or attach a list, of the applicable EPA hazardous waste code(s).

If yes, is the product a combination of unused commercial chemical products? Yes ☐ No ☐ Unknown ☐

If yes, is the unused commercial chemical product(s) the sole active ingredient(s) (meeting “P” or “U”)? Yes ☐ No ☐ Unknown ☐

If yes, is the waste: soil, water, or other media resulting from a spill or release of a unused commercial chemical product? Yes ☐ No ☐ Unknown ☐

CHARACTERISTIC WASTE (40 CFR 261, SUBPART C)

IGNITABLE WASTE (261.21)

17. Is the waste a known (or suspect) ignitable waste? Yes ☐ No ☐ Unknown ☐

If yes, is the ignitable waste an aqueous liquid and ignitable only due to alcohol concentration? Yes ☐ No ☐ Unknown ☐

If yes, give the percent of alcohol in waste ____________________

18. Is the waste a known or suspect oxidizer? Yes ☐ No ☐ Unknown ☐

19. Does the waste contain a high percentage of nitrates? Yes ☐ No ☐ Unknown ☐

If yes, give estimate of percent nitrate ________________________

CORROSIVE WASTE (261.22)

20. Is the waste a liquid? Yes ☐ No ☐

If known, what is the pH? Known______ Unknown ☐

21. Have acids or alkali liquids been used in the waste generating process? Yes ☐ No ☐ Unknown ☐

22. Does a representative sample corrode steel at a rate greater than 6.35 mm/yr (liquids only)? Yes ☐ No ☐ Unknown ☐

REACTIVE WASTE (261.23)

23. Is the waste a known or suspect reactive (e.g., sulfates, sulfur, cyanides, etc.)? Yes ☐ No ☐ Unknown ☐

If yes, attach a description of the possible list of reactive characteristics and precautions.

TCLP WASTE (261.24)

24. Is the waste TCLP for D004-D043? Yes ☐ No ☐ Unknown ☐

If yes, list or attach a list, of the EPA Codes assigned to the waste.

If known, list or attach a list, of the organic or metal constituents known or suspected in the waste.

PCB WASTE

25. Is the waste an oil filled electrical device, hydraulic equipment, or switch? Yes ☐ No ☐ Unknown ☐

If yes, provide volume of oil in the equipment. __________________

26. Is the waste known or suspected to contain PCBs? Yes ☐ No ☐ Unknown ☐

27. Is the waste a small capacitor (i.e., contains <100 cc or <3 lbs of dielectric fluid)? Yes ☐ No ☐ Unknown ☐

28. Is the waste a large capacitor (i.e., contains >100 cc or >3 lbs of dielectric fluid)? Yes ☐ No ☐ Unknown ☐

29. Is the waste an oil filled electrical transformer? Yes ☐ No ☐ Unknown ☐

If yes, provide the following: Oil Volume__________________
Equipment Serial # __________________

Manufacturer Name ___________________________________
Model # ___________________________

30. Is the waste PCB contaminated soil or debris? Yes ☐ No ☐ Unknown ☐

If yes, list the concentration of PCBs or any other information relating to the source of the contamination associated with the waste.

WASTE MANAGEMENT

31. If known, identify the receiving facility or location for the waste generated

APPROVALS

Waste Generator/Responsible Manager

Note: Your signature certifies that the information on this form and the attachments is true and accurate, that you have put forth a good faith effort to acquire and verify the information, that any willful or deliberate omissions have not been made, and all known and suspected hazards have, to the best of your knowledge, been made.

____
Generator's Name (typed or printed) Phone

____
Generator's Signature Title Date

____
Facility Manager's Name (typed or printed) Phone

____
Facility Manager's Signature Title Date

SECTION II

ANALYTICAL PARAMETERS

1. Based on the information in Section I, will the waste need to be analyzed? Yes ☐ No ☐

If yes, identify the analytical parameters:

Volatile Organic Analysis__
TCLP__
Paint Liquid Filter Test __
GC Screen __
BTU Content __
Density __
CN __
Iodine __

pH__
TCLP Metals __
TCLP Pesticides __
Mass Spectrometer __
Sulfur __
Flashpoint__
Ash Content __
TOC __

TCLP Semi-volatile__
Total Metals__
Total Organic Carbon__
Polychlorinated Biphenyl __
SO_4 __
NO_3 __
CL__
Total Halogens __

Total Suspended Solids__
Total Organic Halides (TOX)__
Pu Isotopes__
Gamma __
Specific Beta Emitters __
Total Alpha Spec. __
U Isotopes__
Other (list) __

Comments:

____

____

If individual parameters are to be selected that are a subset of any of the above analytical requests, please specify below (i.e., nickel, thallium, underlying hazardous constituents):

____

____

SECTION III

WASTE DETERMINATION SUMMARY

2. Is the waste excluded from RCRA per 261.2- 261.6? Yes ☐ No ☐ Unknown ☐

   If yes, list reasons for exclusion.

   ____

   ____

3. If applicable, provide results of the ignitability test (i.e., what is the flashpoint?)_______________
4. If applicable, list the TCLP EPA waste codes____
5. If applicable, list the Listed EPA waste codes____
6. If applicable, list the California waste constituents____________________________________
7. If applicable, list the PCB concentrations____
8. Does the waste contain friable asbestos or asbestos fibers?______________________________
9. Is the waste an oxidizer or reactive? Yes ☐ No ☐ N/A ☐

   If yes, identify the oxidizer and/or reactive characteristics ______________________________

10. Is the waste a Low TOC D001 (i.e., liquid and < 10% TOC that has been deactivated in lieu of incineration? Yes ☐ No ☐ N/A ☐

    If yes, list the Underlying Hazardous Constituents that exceeded Universal Treatment Standards upon generation (before treatment) or state that all Underlying Hazardous Constituents met LDR treatment standards upon generation.

    ____

    ____

    If yes, list the Underlying Hazardous Constituents that exceed Universal Treatment Standards after treatment or state that all Underlying Hazardous Constituents met LDR treatment standards.

    ____

    ____

11. Is the waste a Low TOC D001 (i.e., liquid and < 10 TOC) that is to be incinerated in lieu of deactivation (i.e., alternative treatments standards for Low TOC liquid ignitable? Yes ☐ No ☐ N/A ☐

    If yes, Underlying Hazardous Constituent identification is not required.

12. Is the waste a High TOC D001 (i.e., liquid and > 10% TOC)? Yes ☐ No ☐ N/A ☐
13. Is the waste a D002, D003, or D018 - D043? Yes ☐ No ☐ N/A ☐

If yes, list the Underlying Hazardous Constituents that exceeded Universal Treatment Standards upon generation or state that all Underlying Hazardous Constituents met LDR treatment standards upon generation.

____

____

14. Is the waste a D002-D043*? Yes ☐ No ☐ N/A ☐

*With the exception of D0012-D017 wastewaters (these have specified technologies).

If yes, list the Underlying Hazardous Constituents that exceeded Universal Treatment Standards upon generation or state that all Underlying Hazardous Constituents met LDR treatment standards upon generation.

____

____

15. Does the waste fail TCLP for mercury and exceed 260 ppm of mercury (the 260 ppm criteria is based upon total analysis not TCLP)? Yes ☐ No ☐ N/A ☐

16. Is the waste to be disposed into a Clean Water Act or CWA equivalent treatment system? Yes ☐ No ☐ N/A ☐

17. Can the waste be classified as debris? (i.e., greater than 60mm or 2.5 inches, non treatment residual, non lead acid battery, non cadmium battery or non radioactive lead). Yes ☐ No ☐ N/A ☐

SECTION IV

LAND DISPOSAL RESTRICTIONS (LDR) ASSESSMENT

Upon receipt of analytical results and review of all Process Knowledge statements, LDR treatability groups, categories/subcategories can be assessed (for hazardous waste subject to LDR requirements) by using the following information.

18. Identify the LDR treatability group applicable to the waste stream.

TREATABILITY GROUPS

	WASTE WATER	NON-WASTE WATER	Yes	No	N/A
P, K, U, F and Most D Wastes	<1% TOC and < 1% TSS	>1% TOC and/or >1% TSS			
Mercury (D009)	<260 mg/kg and <1% TOC and 1% TSS	>260 mg/kg or <260 mg/kg and >1% TOC and, or >1% TSS			
High TOC Ignitable Liquid	N/A	>10% TOC			
Low TOC Ignitable Liquid	N/A	>1% TOC but < 10% TOC			
Ignitable Liquid	<1% TOC and <1% TSS	N/A			

TOC - Total Organic Carbon
TSS - Total Suspended Solids

Identify the LDR category and subcategory applicable to the waste stream.

Note: Listed wastes do not have categories/subcategories unless a “characteristic,” as identified below, is present due to a contaminant other than the contaminant for which a waste is listed.

IGNITABILITY (D001)

19. Ignitable liquid: Liquids with a flashpoint less than 140 degrees Fahrenheit (includes high and low TOC). Yes ☐ No ☐

20. Ignitable Compressed Gases: Containerized ignitable gases with pressure above atmospheric pressure. Yes ☐ No ☐

21. Ignitable Reactive: Include materials such as alkali metals or metalloids, such as: sodium, magnesium (finely divided), aluminum (finely divided), potassium and calcium carbide slags. Generally includes wastes that react readily with air/water to produce ignitable gases. Yes ☐ No ☐

22. Ignitable Oxidizers: Include peroxides, perchlorates and permanganates, calcium hypochlorite or nitrates at concentrations at or near 50% and Ayields oxygen readily to stimulate the combustion of the organic matter. Yes ☐ No ☐

CORROSIVITY (D002)

23. Acid: Aqueous waste with pH less than 2.0 s.u. Yes ☐ No ☐

24. Alkaline: Aqueous waste with pH greater than 12.5 s.u. Yes ☐ No ☐

25. Other Corrosives: Nonaqueous wastes that are corrosive to steel per 40 CFR 261.22(a)(2) criteria (includes organic liquids and other nonaqueous streams such as ferric chloride, benzene sulfonyl chloride, acetyl chloride, formic acid, hydrofluoric acid etc.). Yes ☐ No ☐

REACTIVE (D003)

26. Reactive Cyanides: Cyanide bearing wastes that generate toxic gases between a pH of 2.0 s.u. and 12.5 s.u. in sufficient quantities to present a danger to human health and the environment (i.e., 250 ppm). See 40 CFR 261.23(a)(5). Yes ☐ No ☐

27. Reactive sulfides: Sulfide bearing wastes that generate toxic gases in sufficient quantities to present danger to human health and environment when exposed to pH concentrations between 2.0 s.u. and 12.5 s.u. in (currently based on 500 mg of hydrogen sulfide per kilogram of waste). See 40 CFR 261.23(a)(6). Yes ☐ No ☐

28. Explosive reactive: Those wastes that are capable of detonation or explosive reaction under various conditions are forbidden Class A or Class B explosives. See 40 CFR 261(a) (6) through (a)(8). Yes ☐ No ☐

29. Water reactive: Organic or inorganic wastes that are very reactive with water or can generate toxic or explosive gas with water (the reactions are usually very vigorous and difficult to control, not like ignitable gases identified in the ignitable reactive subcategory). See 40 CFR 261.23(a)(2), (a)(3) and (a)(4). Yes ☐ No ☐

30. Other reactive: Organic or inorganic wastes that are very reactive with water or can generate toxic or explosive gases with water (the reactions are usually very vigorous and difficult to control). See 40 CFR 261.23(a)(1) Yes ☐ No ☐

SUMMARY:

Provide a short synopsis of the waste stream in question. Include, at a minimum, (if applicable) a list of ALL EPA codes, RCRA treatability group designation and any and/or all Underlying hazardous constituents, as well as, PCB status and other hazards associated with the waste in question. If the waste is nonhazardous, not regulated by 40 CFR 761 (i.e., PCB program), NESHAPS, or any other regulatory program which requires special handling requirements, provide a statement confirming the classification.

APPROVALS

Note: Your signature certifies that the information on this form and the attachments is true and accurate, that you have put forth a good faith effort to acquire and verify the information, that any willful or deliberate omissions have not been made, and all known and suspected hazards have, to the best of your knowledge, been made.

(typed or printed) Phone

Signature Title Date

CONCURRANCE

☐ Concur ☐ Do not concur

Comments:

Signature Date

Chapter Three

Separation Techniques

3.1

In Situ Remediation of Contaminated Soils by Electrokinetic Processes

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Introduction

Soil systems are subject to contamination by a variety of hazardous chemicals, such as heavy metals and toxic organic compounds. The major sources of pollutants are attributed to landfills and industrial operations. For example, any hazardous substance present in a soil matrix represents a threat to public health and groundwater. The latter is one of the most valuable natural resources and a major source of drinking water in the United States. Many domestic, industrial, and agricultural activities depend on groundwater resources. Therefore, strategies for soil clean-up are increasing in demand.

Most of the host of soil remediation techniques available commercially are subject to a variety of restrictions during application. *Ex situ* treatments such as pump and treat and containment can be costly and therefore not totally attractive. Techniques including bioremediation, vitrification, freezing, and soil washing are some of the options available, but they are usually very site specific and do not offer a good prospect of *in situ* treatment. Vitrification and freezing do not extract contaminants from soils and therefore cannot be considered ultimate clean-up options. Bioremediation is limited by a number of technical difficulties such as nutrient transport and acclimation of microorganisms, among others. Few contaminants can be effectively removed by soil washing. Accounting for all of these obstacles, there is a necessity to develop new alternatives for *in situ* soil clean-up.

Electrokinetic processes treatment has emerged as a potential technique for *in situ* decontamination of contaminated soils. This is the same process used previously by geological engineers to consolidate foundations for construction. Electrokinetic treatment is an *in situ* treatment process that is capable of simultaneously transporting inorganic and organic compounds in porous media, including radionuclides. The electrokinetically aided transport is based on well-known electrokinetic processes primarily composed of electroosmosis, electrophoresis, and ion migration in wet soil. The two primary mechanisms that mobilize contaminants are (1) the movement of the charged species by electromigration or electrophoresis; and (2) the transport of contaminants by the advection of electroosmotic flow. The rate and efficacy of these processes are dependent on the type of soil and contamination.

The treatment involves applying a low direct current (on the order of milliamps per square centimeter of the cross-sectional area of the electrodes), or a low potential gradient (on the order of a few volts per centimeter) between electrodes inserted in the soil. As a result, the contaminants are transported toward the anode or cathode electrode sites by ionic or electrophoretic migration, and electroosmotic advection. The contaminants are then removed at the electrode sites by one of several different methods. These methods include electroplating, adsorption onto the electrode, precipitation or co-precipitation at the electrode, pumping near the electrode, complexing with ion exchange resins, or capturing in reactive permeable barriers.

While electroosmosis is analogous to soil washing, electromigration is the primary mechanism of electrokinetic transport when the contaminants are ionic or surface charged (Acar et al., 1989; 1990; Pamukcu and Wittle, 1992a; b; Probstein and Hicks, 1993; Reddy and Parupudi, 1997). Past experience with electrokinetic process in contaminated porous media has shown that the process is most effective when the transported substances are dissolved in the pore fluid, surfaces charged, or in the form of small micelles with little drag resistance (Electorowicz and Boeva, 1996; Hamed et al., 1991; Pamukcu and Wittle, 1992a; 1993a; b; Pamukcu et al., 1995b; 1997; Pamukcu, 1994; Pamukcu and Pervizpour, 1998).

Background

Overview

Research in electrochemical treatment for the purpose of restoring contaminated subsurfaces has accelerated in the past two decades. Some of the currently researched methods of electrochemical treatment are referred to as electrokinetic extraction, electrokinetic barriers, electrobioremediation, electrostabilization (injection), and electrocontainment. Earlier work in the mid-1970s and early 1980s focused on utilizing the technique for soil densification to improve performance of containment facilities. Later, studies focused on the effects of electrolysis soil chemistry and the use of electrokinetics for contaminant removal from soils. Most of this work was conducted on the laboratory scale and some on the pilot scale. The first field study was published in 1988 (Banerjee et al., 1988) as a feasibility study of potential application of electrokinetics for chromium removal from subsurfaces.

Research in 1989 first showed the importance of the process-generated pH gradients between anode and cathode. In the same year, field applications attempted to alleviate the effects of the pH gradients by controlling the chemical environment around the electrodes. In 1991, the effects of speciation and precipitation on the efficiency of electrokinetic transport of metal ions through soil were presented. Since the early 1990s, numerous laboratory studies have substantiated the applicability of the technique to a wide range of contaminants in soils. Among the contaminants shown to react to electrochemical treatment in the laboratory and some in the field are non-aqueous phase liquids such as chlorinated hydrocarbons, mononuclear aromatic hydrocarbons (MAHs), polynuclear aromatic hydrocarbons (PAHs), phenols, sulfurous, and nitrogenous compounds, and heavy metals. More recently, integrated methods of soil restoration that rely on electrochemical technology as well as other technologies (e.g., bioremediation, funnel-and-gate, and reactive membranes) have been introduced; and some have been demonstrated in the field, such as the Lasagna™ Soil Remediation project (Ho et al., 1995). Furthermore, powerful analytical models and their numerical solutions have been developed; this has helped to better understand the underlying mechanisms of transport of single and multiple ionic species under constant or transient electric fields.

These laboratory studies have clearly shown that electrochemical treatment is a powerful *in-situ* process that can be used to simultaneously treat inorganic and organic compounds in porous media. However, the technology must be used judiciously in the field because each contaminated site is unique. The application must be engineered to site specifics and the treatment steps must be sequenced properly for an optimum solution. Soils are heterogeneous, silty, and contain fine metallic oxide and colloidal organic and inorganic substances. In field situations, the contaminants are often found adsorbed onto soil surfaces, iron oxide coatings, soil colloids, and natural organic matter, or retained in clay interstices as hydroxycarbonate complexes, or in the form of immobile precipitates in soil pore throats and pore pockets. It is now well recognized that the contaminated soil becomes dynamically complex under an applied electrical potential. The solid and liquid components of the soil are reactive, which allows complex electrochemical reactions to take place. Given such conditions, it may be preferable to base the treatment on a phenomenological approach using site-specific information rather than on analytical models of well-controlled systems.

Historical Development

In 1808, Reuss observed electrokinetic phenomena when a dc current was applied to a clay-water mixture. Water moved through the capillary toward the cathode under the electric field. When the electric potential was removed, the flow of water immediately stopped. Napier (1846) distinguished electroosmosis from electrolysis; and in 1861, Quincke found that the electric potential difference through a membrane resulted from streaming potential. Helmholtz was the first to treat electroosmotic phenomena analytically in 1879. A mathematical basis was provided by his work. Pellat (1904) and Smoluchowski (1921) later modified it to apply to electroosmotic velocity. Out of this treatment of the subject, the well-known Helmholtz-Smoluchowski (H-S) theory was developed. The H-S theory deals with the electroosmotic velocity of a fluid of certain viscosity and dielectric constant through a surface-charged porous medium of electrokinetic potential (zeta, ζ), under an electric gradient. The H-S equation is:

$$u_{eo} = \frac{\varepsilon\varsigma}{\mu}\frac{\partial\phi}{\partial x} \tag{3.1.1}$$

where,

u_{eo} = Electroosmotic velocity
ε = Dielectric constant of pore fluid
ζ = Zeta potential of soil particles
μ = Viscosity of fluid
$\partial\phi/\partial x$ = Electric gradient (field strength)

It must be noted that Eq. (3.1.1) is valid only for large pores in which the electrical double layer is small compared with the pore radius, and all the mobile charge is assumed to be concentrated near the pore wall. In 1939, Casagrande demonstrated that applying electro-osmosis to soils with high water content caused such an increase in the effective stress that the gain in shear strength kept steep slope cuts remain stable. Casagrande indicated that small reductions in water content by electroosmosis could produce significant increases in soil strength. Since then, electrochemical treatment of soils has been investigated and used in many field projects, including improvement of excavation stability, electrochemical hardening, stabilization of fine-grained soils, consolidation, and densification. In the late 1960s and early 1970s, direct current was successfully applied to recover residual oil from deep-seated geological formations (Enhanced Oil Recovery) (Waxman and Smits, 1967; Amba et al., 1964). Utilization of direct current to drive contaminants out of the soil pores started in the late 1970s and early 1980s. Segall and co-workers reported detection of high concentrations of metals and organic compounds in electroosmotically drained water of a dredged sludge in the field in 1980. Since then, successful applications of the electrochemical decontamination technique have been demonstrated on pure soil-contaminant mixtures in the laboratory by numerous researchers (Pamukcu et al., 1990; 1995; 1997; Hamed et al., 1991; Bruell et al., 1992; Acar et al., 1992; 1994; 1995; Probstein and Hicks, 1993; Runnels and Wahli, 1993; Ugaz et al., 1994; Hicks and Tondorf, 1994; Eykholt and Daniel, 1994; Pamukcu, 1994; Yeung et al., 1996; Alshawabkeh and Acar, 1996a; b; Dzenitis, 1997).

Theoretical Aspects

Electrokinetic phenomena in a porous medium are based on the relative motion between a charged surface and the bulk solution at its interface (Adamson, 1986; Hunter, 1981). The formation of an *electric* *double layer* at the charged surface of clay particles explains these electrokinetic phenomena of interest: electroosmosis, electrophoresis, and electromigration.

The Electric Double Layer

Consider a negatively charged clay particle surface in contact with a water solution of ions. The attraction of counter ions and repulsion of co-ions, when combined with the diffusion along concentration gradients and the mixing by random thermal motion of the ions, leads to the formation of an electric double layer (Gouy, 1910; Chapman, 1913).

According to Stern (1924), the electric double layer is composed of a fixed layer (Stern layer) and a diffuse layer (Gouy layer). In the Stern layer, the ions are assumed to oscillate about fixed adsorption sites, whereas in the diffuse layer, ions are assumed to undergo Brownian motion. In a porous plug of clay, the surface becomes negatively charged when wetted with water. This charge is balanced by the adjoining Stern and Gouy layers, which carry the positively charged ions. The thickness of the Stern layer is approximately the radius of a hydrated cation adsorbed on the clay particle surface. The Stern and Gouy layers are divided by three planes: one is the plane of the clay–water interface; the second is the outer Helmholtz plane (OHP); and the third is the plane of shear. The OHP is the plane that defines the outer limit of the Stern layer, the layer of positively charged ions condensed onto the clay particle surface. The drop in potential in the Stern layer is linear from the surface potential of ψ_o to ψ_d at the OHP. The plane of shear is the plane at which the mobile portion of the diffuse layer can "slip" or flow past the charged surface. The potential at this shear plane is referred to as the electrokinetic potential, or zeta (ζ) potential. The potential distribution in the diffuse layer is given by the Poisson-Boltzmann equation, which describes an exponential fall of the potential.

$$\psi_x = \psi_o \, e^{-\kappa x} \tag{3.1.2}$$

where

κ = Reciprocal thickness of the diffuse double layer
Ψ_x = Potential at distance x from the OHP or surface
Ψ_o = Potential at the OHP or surface

Integrating the Poisson-Boltzmann equation with appropriate boundary conditions will provide the thickness of the diffuse layer, which is indirectly related to the ionic concentration in the bulk solution and the valence of the counter-ions.

$$\kappa = \left[\left(\frac{Qe^2}{\varepsilon k T}\right)\sum_i z_i^2 n_{i\infty}\right]^{1/2} \tag{3.1.3}$$

where:

e = Electron charge
k = Boltzmann constant
z_i = Ionic charge or valence
$n_{i\times}$ = Ionic concentration in the bulk solution

Electrophoresis

Electrophoresis is defined as the migration of charged colloids in a solid-liquid mixture under an electric potential gradient. This migration is the movement of colloidal particles, not small ions. For clay-water systems, if we place a direct current (dc) field across its suspension, negatively charged clay particles migrate toward the anode. The unrestrained particle transport through water in a poorly consolidated system will likely compact the soil to the anode and disintegrate it on the cathode side. In a compact system of a porous plug, electrophoresis is of less importance due to the restrained solid phase. But in the process of soil decontamination under direct current, electrophoresis of clay colloids could still play an important role if the migrating colloids have the toxic chemicals adsorbed onto them. This was demonstrated by Grolimund et al. (1996), who showed strongly sorbing lead was transported by mobile colloids.

An important contribution of electrophoretic movement to contaminant transport may be when the contaminants are in the form of colloidal electrolytes or ionic micelles. Micelle formation is promoted as the concentration of the aggregating groups increases. Ionic micelles often carry a high charge and exhibit high conductance in dilution. The conductance increases with increasing concentration owing to buildup of charge with further aggregation. However, at a critical concentration, a sudden and sharp decrease in conductance occurs that is attributed to (1) increasing association of the ionic colloids, which results in increased fraction of neutral colloids; and (2) retarding inter-ionic forces. Evidence of micellar transport was observed in a study by Pamukcu (1994), in which highly mobile anionic-surfactant micelles facilitated the transport of nonpolar organic compounds toward the anode in the opposing direction of electroosmotic flow.

Electroosmosis

Electroosmosis is the complement of electrophoresis. The latter involves discrete particle transport through water, while electroosmosis is the transport of water through a continuous soil particle network. The diffuse layer of water close to the solid surface contains an abundance of counter charges (cations) to balance the surface charge deficiency. These counter charges are strongly held on the surface and diffuse away toward the free water in the middle of the pore. The section referred to as *free* constitutes the pore water that is free to flow under a hydraulic gradient. When an electric field is applied, the surface or particle stays fixed, while the mobile diffuse layer moves, carrying the adjacent water with it. The fluid on the surface is set into motion due to the electromigration of the cations contained in it. As the cations start shearing toward the negative electrode, the thick fluid of the surface layer is dragged along. The velocity of this motion is zero at the solid surface and maximum at the plane of shear, which can “slip” or flow past the charged surface. This interface velocity sets the central or free pore fluid in motion. It is not clear how the central portion moves, but it is usually assumed to be viscous drag. The water molecules, being slightly positive because of dipolar fluctuations, may also contribute to the movement of the central layer. The liquid transport in porous media by a combination of these processes is known as *electroosmosis*.

In negatively charged clay particles, an abundance of cations in the diffuse layer generate a net water flow toward the negative electrode (cathode). The ability of electroosmosis to produce a rapid flow of water in a compact, low-permeability soil makes it a significant contributor to soil decontamination processes by advection. Inside the “soup” of dissolved, suspended, and particulate matter residing in the pore space, the charged species are expected to move independently through the fluid as long as there is connectivity of the fluid phase. The others are carried or advanced to the next locale by the electroosmotic flow of the fluid. During electroosmosis, diffuse layer charges are displaced and polarized in the direction of flow, thus producing a potential difference between the electrode locations. This effect is called the *streaming potential*, which may decrease the effect of electroosmosis by reversing the polarity in the soil. Electroosmotic flow was shown to be independent of pore size distribution or the presence of macropores (Acar and Alshawabkeh, 1993). Therefore, electroosmosis may be an efficient method to generate a uniform fluid and mass transport in clayey soils. The relative contributions of electroosmosis and ion migration to the total mass transport vary according to soil type, water content, types of ion species, pore fluid concentration of ions, and processing conditions. Electroosmotic advection is most useful for transporting contaminants in clays and low permeability soils because the electroosmotic conductivities of clays are often several orders of magnitude higher than their hydraulic conductivities. Electroosmotic advection is able to transport nonionic and nonpolar as well as ionic species through soil pores toward the cathode. This is best achieved when the state of the material (dissolved, suspended, emulsified, etc.) is suitable for the flowing water to carry it through the tight pores of soil without causing an immovable plug of concentrated material to accumulate at some distance from the electrode.

In 1952, Schmid presented the following equation to explain the electrokinetic phenomenon in special cases of very small pores, where it is postulated that the cations are uniformly distributed across the pore cross-sectional area (Mitchell, 1970):

$$u_{eo} = \frac{r^2 qF}{8\mu}\frac{V}{L} \tag{3.1.4}$$

In this equation, r is the pore radius, q is the volume charge density, and F the Faraday constant. It is noticed that the flow is independent of the system pore size in the Helmholtz-Smoluchowski equation, while, according to Schmid, the flow depends on the square of the mean pore radius. Meanwhile, neither theory allows for an excess of electrolyte in the pores beyond the number of cations needed to balance the negative surface charge of clay particles. In other words, the influence of the bulk electrolyte concentration is neglected.

Esrig and Majtenyi, based on the attempt made by Oel in 1955 to unify the two previous theories, have presented a simple equation that appears to include both the Helmholtz-Smoluchowski and Schmid theories (Esrig and Majtenyi, 1966):

$$u_{eo} = \frac{1}{2}\ln\left(1 + \frac{d}{r}\right)\frac{r^2}{\mu}\rho\frac{V}{L} \tag{3.1.5}$$

where ρ is the average mobile excess electric charge density and d is a parameter characterizing the double layer. According to the authors, this equation can be used with any of the existing double layer theories; it also permits the estimation of fluid velocities for a wide range of capillary sizes. A simplification of Eq. (3.1.5) results in (Casagrande, 1949):

$$u_{eo} = \frac{Q_e}{A} = \left(\frac{1}{2}\ln\left(1 + \frac{d}{r}\right)\frac{r^2}{\mu}\rho\right)\frac{V}{L} \tag{3.1.6a}$$

$$Q_{eo} = \left(\frac{1}{2}\ln\left(1 + \frac{d}{r}\right)\frac{r^2}{\mu}\rho\right)\frac{V}{L}A \tag{3.1.6b}$$

$$Q_{eo} = k_e i_e A \tag{3.1.6c}$$

in which Q_{eo} represents the electroosmotic flow rate, k_e the coefficient of electroosmotic permeability, $i_e = V/L$ the electrical potential gradient, and A the cross-sectional area of flow. The above equation is very similar to Darcy's equation for hydraulic flow through a soil column:

$$Q_h = k\ i_h\ A \tag{3.1.7}$$

where i_h is the hydraulic gradient, A the cross-sectional area, and k the permeability of the soil. However, the hydraulic and electroosmotic permeability (k and k_e, respectively) have different properties. The electroosmotic permeability k_e depends primarily on the pore area and is independent of the size of the individual pores; k is very strongly influenced by the actual pore size (Casagrande, 1949). Casagrande (1952) established that k_e for almost all soils in which electroosmotic treatment is feasible varies within only about one order of magnitude, with an average value of about 5×10^{-5} cm^{2}V^{-1}s^{-1}. Thus, estimates of flow rates can be made directly without using any of the kinetic models leading to Eqs. (3.1.6a), (3.1.6b), or (3.1.6c), provided the value of k_e, the electroosmotic water flow rate, can be predicted by knowing A and i_e.

Although Eq. (3.1.6c) describes the theoretical rate of fluid flow in a soil core under potential gradient, there is some uncertainty associated with the effect of interfering factors such as the possible compression of the double layer because of high salinity, loss of electrical energy through the electrolysis of water, changing soil structure, and the reactions of electrode material with the chemicals in water (Ray and

Ramsey, 1987). Significant implications of the electrochemistry associated with the electroosmosis process may influence the efficiency of the remediation technique.

Spiegler's friction model (1958) showed that electroosmotic water transport per unit electrical charge increases with increasing cation: water ratio in the system. Experimental evidence of this theory has been given by a number of researchers (Gray and Mitchell, 1967). An extension of the H-S theory considers a portion of the electric current transported near the surface of or through the solid phase (Wiedemann, 1856). The resulting equation is often referred to as the current efficiency, (time rate of volume of water flow per quantity of electricity), of the system:

$$Q_{eo} = -\frac{\varepsilon \varsigma I}{u\left(\lambda_o + 2\frac{\lambda_s}{r}\right)} \tag{3.1.8}$$

where

Q_{eo} = Electroosmotic flow rate
I = Current
r = Radius of the capillary
λ_0 = Specific conductance of the bulk liquid
λ_s = Surface conductance of the capillary wall

Surface current is due to the ionic motion in the diffuse layer. In narrow capillaries with low ionic concentrations, thus thick diffuse layers, a disproportionate fraction of the current flows in this layer due to the low conductivity of the bulk fluid. Experimental evidence shows that the current efficiency, Q/I, decreases with increasing ionic concentration in the bulk fluid (Wittle and Pamukcu, 1993). This can be readily explained from Eq. (3.1.2) because ζ and ε/μ are expected to decrease, and λ_0 to increase with increasing ionic concentration of the bulk fluid. The surface conductance also changes with ionic concentration. As the ionic concentration in the bulk liquid increases, the diffuse double layer shrinks toward the particle surface and the shear plane shifts away from the particle surface so that the majority of the charge is now compensated by the immobile Helmholtz layer. Therefore, the charge density in the diffuse layer decreases, giving rise to a lower surface conductivity, λ_s. As a result of this lowered conductivity, a smaller portion of the current flows on the capillary surface. In contrast, in the presence of low ionic concentrations, the diffuse double layer is swollen and much of the charge is compensated by the ions in the diffuse layer. Therefore, the capillary surface conductivity is high and so is the fraction of the current that is transported on the surface.

The significance of surface conductance on the prediction of electroosmotic flow as it relates to contaminant migration was investigated by Khan (1991). He proposed a modified theory of electroosmotic velocity of water through soil. In this theory, the "true electroosmotic" flow is directly proportional to the current carried by the charged solid surfaces in soil. The soil is modeled as parallel resistances of the soil surface and pore fluid, and the zeta potential used in H-S theory is replaced by the surface potential, ψ_d, at the Outer Helmholtz Plane (OHP):

$$u_{eo} = \frac{\varepsilon \psi_d}{\mu}\frac{I_s R_s}{L} \tag{3.1.9}$$

where

R_s = Surface resistance of soil
I_s = Surface current of soil
L = Length

With u_{eo}/I_s shown to remain fairly constant for clays of different surface conductivity and also pore fluid electrolyte concentrations below 10^{-2} M, experimentally, Eq. (3.1.3) was further reduced to:

$$u_{eo} = K\, I_s \tag{3.1.10}$$

where

K = $\{\varepsilon\, \psi_d / \mu\}\, R_s / L$ = Constant

The modified theory basically emphasized that the surface conductivity of the porous compact medium is the most essential precondition for electroosmotic water flow, thus uncoupling it from the water drag component of the migrating ions in pore fluid of high ionic concentration. This theory is in agreement with Spiegler's theory of water: cation ratio, as well as Gray and Mitchell's (1967) approach of a co-ion exclusion principle based on Donnan theory of membrane equilibrium (1924). Additional evidence to support this finding was presented by Pamukcu and Wittle (1992) for a variety of ion species, where the ionic concentration effect on the measured current efficiency appeared to be most pronounced in clays with high anion retention capacity. At the same concentrations of dilute solutions of electrolytes, kaolinite clay with higher anion retention capacity (poor co-ion exclusion) showed consistently higher electroosmotic flow than montmorillonite clay with lower anion retention capacity (good co-ion exclusion). This observation suggested that the anionic dragging of water toward the anode diminished the net flow toward the cathode compartment in the montmorillonite clay.

The zeta potential in Khan's (1991) model is defined at the outer limit of the Stern layer and to be a constant surface potential that is invariant with respect to electrolyte concentration. Therefore, the true electroosmotic flow becomes independent of electrolyte concentration in the pore fluid. Results reported by Yin and co-workers (1995) support Khan's theory. They found that there is no apparent relationship between electroosmotic mobility and the applied electric field. The term "electroosmotic mobility" refers to the average velocity achieved by the pore water relative to the solid skeleton, due to an externally applied electrical field of unit strength. The mobility appeared to be proportional to the specific conductance of the soil specimen. The mobile ions in the pore solution primarily come from the surface of the clay particles; thus, a higher ionic concentration and hence a higher conductance for clay with a lower initial water content are expected. For kaolinite, Yin et al. (1995) concluded that a mobility value of 0.6×10^{-4} cm^2/s. volt and a specific conductance of 0.4 m.mho/cm are representative values, and they showed these values do not vary appreciably under low electric field and constant water content. Based on the above discussion, the electroosmotic flow velocity can be expressed as:

$$u_{eo} = K' E \tag{3.1.11}$$

where

K' = Constant (electroosmotic mobility)
E = Electric gradient $(\partial\phi/\partial x)$

It should be noted that the electroosmotic mobility should not be treated as a phenomenological constant. Electroosmosis velocity can be approximated by the Helmholtz-Smoluchowski equation (Eq. 3.1.1). According to Shapiro and Probstein (1993), for a typical water-saturated clay, with ζ potential of 10 mV, and an electric field strength of 100 V/m, the electroosmotic velocity has a value of 10^{-6} m/s or ~10 cm/day. Notably, this is at least 10 times lower than the electromigration velocity (Acar and Alshwabkeh, 1993). Therefore, in ion-rich pore fluids, the electroosmotic transport of ions becomes negligible compared with electromigration (Baraud et al., 1997).

It must be noted that the above derivations are mostly applicable for saturated porous media. Water flow behavior of an unsaturated soil is totally different from that of a saturated system. In the presence of an electrical field, a friction force is created when water molecules begin to move in the soil pores. The frictional stress decreases as the thickness of the water layer increases. For an unsaturated soil-water system, the water layer is extremely thin, usually ranging from 10^{-10} cm to 10^{-8} cm. Under such circumstances, all water molecules exhibit strong frictional interaction with the soil surface. In the case of a saturated water-capillary system, the radii of capillaries are relatively large, ranging from 10^{-1} cm to 10^{-3} cm. As a result, most capillary water molecules do not interact physically or chemically with the capillary wall (Yukawa et al., 1991). Recently, Chang et al. (2000) have proposed a semi-empirical equation for the prediction of electroosmosis flow under unsaturated soil-water system based on the finite plate model. They reported the following expression:

$$Q_{eo} = k'\sigma_e\left(\frac{V}{L}\right)\left(\frac{\varpi m}{\rho}\right)^2 = K\sigma_e\left(\frac{V}{L}\right)\varpi^2 \qquad (3.1.12)$$

where K is a characterized coefficient (i.e., $K = kfw/\mu\rho^2\Sigma^2$). This characterized coefficient, K, collects several physical properties of the soil-water system such as the fluid density (ρ), the specific surface area (Σ), the width of the water layer (w), and the fluid viscosity (μ).

Electromigration

Electromigration, or ionmigration, is the primary mechanism of electroremediation when the contaminants are ionic or surface charged. Speciation and precipitation are major factors in mobilization and transport of heavy metal constituents by the ionmigration component of electrokinetics. The speciation is dependent on a number of fairly well-understood parameters, including pH, redox potential, and ion concentration. These same factors influence the equilibrium conditions relating to both the soil and the contaminants.

Charged ions moving toward the oppositely charged electrode relative to solution is called electromigration. In a dilute system or a porous medium with moderately concentrated aqueous solution of electrolytes, electromigration of ions is the major cause of current conduction. Electromigration velocity measures ion movement in the pore water caused by the electric field at infinitely dilute solutions:

$$u_m = -\frac{zF}{RT}D^*\frac{\partial\phi}{\partial x} \qquad (3.1.13)$$

where

u_m = Electromigration velocity
z = Valence or charge of ion
F = Faraday constant
R = Universal gas constant
T = Absolute temperature (K)
D^* = Effective diffusion coefficient of ion

The convective-diffusion equation used to describe the transport of a contaminant through porous media is given by (Shapiro et al., 1989):

$$\frac{\partial C_i}{\partial t} = \frac{D_i\partial^2 C_i}{\tau^2\,\partial x^2} - \frac{\partial}{\partial x}[C_i(u_{e,i} + u_c)] + R_i \qquad (3.1.14)$$

where for each species i, c_i is the concentration in moles per unit of volume, D_i the diffusion coefficient, τ the experimental tortuosity factor, $u_{e,i}$ the electromigration velocity in the x direction, U_c, the convection velocity in the x direction, and R_i the molar rate of production due to chemical reactions.

The electromigration velocity $u_{e,i}$ is represented by:

$$U_{e,i} = U_m/\tau^2 \qquad (3.1.15)$$

where R, T, z_i, F, and ϕ are the gas constant, temperature in units of Kelvin, charge number, Faraday constant and electrical potential, respectively.

The convection velocity, or electroosmotic velocity, can be written as:

$$u_c = \frac{\varepsilon\zeta}{\tau^2\mu}\frac{\partial\phi}{\partial x} \tag{3.1.16}$$

where ε, ζ, and μ are the dielectric constant of the liquid, zeta potential of the solid surface, and viscosity of the liquid, respectively. The applied electrical field $^1\phi/^1x$ necessary for the calculation of the electromigration and convection velocities is assumed constant in this model development. The zeta potential is strongly influenced by the chemical conditions of the system, such as pH and ionic concentration; therefore it cannot be taken as a single average value.

To incorporate the retardation factor (adsorption) to the governing equation, the linear isotherm is used in this model. Among the various equilibrium adsorption isotherms, the linear isotherm is the simplest and can be applied to systems in which the adsorbate concentration is much below the saturation limit of the surface sites available. The governing equation then becomes:

$$\frac{\partial C_i^t}{\partial t} = \frac{1}{1+K_{d,i}}\left\{\frac{D_i}{\tau^2}\frac{\partial^2 C_i^t}{\partial x^2} - \frac{\partial}{\partial x}[C_i^t(u_{e,i}+u_c)]\right\} \tag{3.1.17}$$

where $K_{d,i}$ is the distribution coefficient and C_i^t is the sum of the amount of species i adsorbed and in solution. It is observed from the above equation that the rate of transport of species i is decreased by a factor of $\frac{1}{1+K_{d,i}}$ by adsorption.

In the case of weak acids, it is also necessary to consider the chemical equilibrium reaction:

$$HA \Leftrightarrow H^+ + A^- \tag{3.1.18}$$

where HA and A are the protonated and deprotonated acids, with equilibrium constant, K_a, respectively. The governing equation for the transport of a weak acid is then written as:

$$\frac{\partial[HA]^t}{\partial t} = \frac{1}{1+K_a}\left\{\frac{D_{HA}}{\tau^2}\frac{\partial^2[HA]^t}{\partial x} - \frac{\partial}{\partial x}[[HA]^t(u_{e,HA}+u_c)]\right\} \tag{3.1.19}$$

where $[HA]^t$ is the sum of $[HA]$, $[A^-]$, and $[HA]^{ads}$; and $u_{e,HA}$ is defined as:

$$u_{e,HA} = (1+K_a)\frac{[A^-]u_{e,A^-}}{[HA]^t} \tag{3.1.20}$$

Moreover, it is assumed that the diffusion coefficient for the undissociated acid molecule, D_{HA}, is approximately equal to that for the dissociated ion, D_{A^-}:

$$D_{HA}\,\text{Ý}D_{A-} \tag{3.1.21}$$

Laboratory Studies

Electrokinetic Extraction

Electrokinetic extraction is analogous to soil washing, whereby the contaminant is *extracted* from the soil and subsequently collected in aqueous phase in a collection well or deposited at the electrode site. The alkali metals (e.g., Na(I), K(I), and Cs(I)), and alkali earth metals (e.g., Sr(II) and Ca(II)) tend to remain ionic under a wide range of pH and redox potential values; therefore, they are expected to electromigrate and be extracted from soils readily unless they become preferentially sorbed onto solid surfaces and clay interstices. Under ideal conditions, the predominant cation and its accompanying anion may be caused to separate efficiently by electromigration only, for which little or no electrosmotic water advection may be necessary. Small anions such as chloride and thiosulfate are so mobile that they can migrate toward the anode despite a strong electroosmotic flow toward the cathode.

Most of the work reported in the literature to date has concentrated on the mobilization and extraction of the heavy metal contaminants by applying an electric field to a contaminated soil. As discussed above, extraction of contaminants by electrokinetic methods is based on the underlying assumption that the contaminant is in the liquid phase of the soil pores. A majority of the past research on electroremediation of contaminated soils has focused on the feasibility of transport and removal of mixed contaminants from pure clay, or synthetic reference soil matrices.

As an example, results of electrokinetic treatment of 11 selected metals in five different combinations of synthetic soil and pore fluids were reported by Wittle and Pamukcu (1993). These tests were performed using the Lehigh Electrokinetic (EK) test cells described below. The classes of metals included cations (Cd(II), Hg(II), Pb(II), Ni(II), Zn(II)), surrogate radionuclides (Co(II), Ce(III, IV), Sr(II), U(V)), and anions ($HAsO4^-$, $Cr_2O_7^{2-}$). Five soil types were studied: kaolinite clay (KS), Na-montmorillonite clay (MS), sand with 10% Na-montmorillonite (SS), kaolinite clay with simulated groundwater (KG), and kaolinite clay with humic solution (KH). Table 3.1.1 summarizes results of all heavy metals removal from soil samples (3 in. long) tested (from the anodic chamber for the cationic species, and from the cathodic chamber for the anionic species) under a constant voltage of 30 V in 24 hr. As observed, the removal (percentages) of a number of metals tested in these synthetic soil samples were fair to good. This was mostly due to the low soil pH attained (on the order of 2 to 3) during the electrokinetic processing of these synthetic matrices, which helped to keep the metals away from the soil surface, in solution, and thus migratory or readily transportable (Acar, et al., 1989; 1991; Shapiro et al., 1989).

TABLE 3.1.1 Percent Removal of Heavy Metals from Clays and Clay Mixtures by Electrokinetic Treatment

	Soil Type[a]				
Metal	KS	KG	KH	MS	SS
As(V)	54.7	56.8	27.2	64.3	54.7
Cd(II)	94.6	98.2	92.7	86.6	98.0
Co(II)	92.2	93.9	95.9	89.4	97.5
Cr(VI)	93.1	94.8	97.6	93.5	96.8
Cs(I)	71.9	80.1	74.7	54.7	90.5
Hg(II)	26.5	13.1	42.5	—	78.3
Ni(II)	88.4	95.4	93.9	93.6	95.9
Pb(II)	69.0	75.2	66.9	—	83.0
Sr(II)	97.8	99.5	96.0	92.3	99.0
U(V)	79.3	84.3	67.4	39.8	33.0
Zn(II)	54.6	43.3	36.3	64.4	54.5

[a] KS: kaolinite; KG: kaolinite and simulated groundwater; KH: kaolinite and humic substances; MS: montmorillonite; SS: clayey sand.

From Wittle and Pamukcu, 1993.

In natural soils with high buffering capacity and carbonate content, or those that are under the groundwater table, pH often remains neutral or basic, which inhibits the solubilization and thus transport of most metals to a collection well. Complete removal of those metals that possess complex aqueous and electrochemistry, and the tendency for speciation and forming hydroxide complexes, is particularly difficult under variable pH and redox conditions. In field applications, the electrokinetic treatment may need to be augmented by washing the soil with an appropriate conditioning fluid to ensure a high degree of solubility.

The organic compounds are transported by electroosmotic advection if the compound remains poorly sorbed and non-ionized during the process. If the concentration of such an organic compound (i.e., *o*-nitrophenol) in pore space is known, then the rate of electroosmotic flow can be used to predict the rate of transport of the compound (Khan, 1991). Ionizable organic compounds, or those treated with ionic surfactants, may form micelles that would tend to electromigrate. The size of the micelles may limit their advective transport due to large viscous drag; however, the large electric charge they often carry promotes their electromigration despite the opposing direction of electroosmotic flow (Pamukcu, 1994).

EK Test Cells

Several laboratory EK test cells have been reported in the literature. The Lehigh EK test cell consists of a soil container and two water reservoirs that house the electrodes on each side of the container. The reservoirs are connected to the measuring burettes to monitor the inflow and the outflow at the reservoirs. Figure 3.1.1 presents a schematic of the Lehigh EK test cell. The soil container, or sample tube, has an ID of 2.7 cm and a length of 10.2 cm and is made of clear glass tube with threaded ends. The tube accommodates three auxiliary graphite electrodes (1 mm in diameter), separated at equal distance along one side, through which voltage can be measured during experiments. The tube is attached to the electrode chambers with O-rings placed inside the housings cut on the inner walls (facing the sample tube) of the chambers. Porous dividers made of glass frit are placed at each end of the sample tube to hold the soil sample in place during the experiments. The electrode chambers are approximately 175 cm^3 in volume. They house the electrodes at each end of the soil sample tube. These chambers are removable for filling and emptying of fluid and also to facilitate cleaning after each test run. Teflon couplers are used to attach the soil sample tube to the electrode chambers at each end. Electrode assemblies with a surface area of 22.6 cm^2 facing the soil specimen are constructed of graphite rods with a 0.635-cm diameter held together with conductive adhesive. Dedicated electrical units for each electrokinetic cell consist of a variable dc power supply capable of applying either constant voltage (0 to 120 V) or constant current (0 to 1500 mA). These units also contain analog meters for measuring voltage and current. Teflon or stainless steel quick-connections are provided on the back wall of the electrode chambers. These outlets or inlets are then connected to volume measuring tubes via Teflon tubing. Gas expulsion or liquid extraction/injection ports are provided on the top of each electrode chamber. These valves have metal surfaces that are coated to control any deterioration by electrochemical reactions or metal ion deposition on them. Sample extractions or fluid injections are accomplished using a volumetric syringe that allows for accurate control of quantities of fluids. Glass burettes with a capacity of 25 cm^3 are used to measure inflow, normally at the anode (positive electrode) chamber, and outflow, normally at the cathode (negative electrode) chamber to an accuracy of 0.1 cm^3. The specific techniques used to operate this equipment have been adequately discussed elsewhere (Wittle and Pamukcu, 1993; Pamukcu, 1994).

Electrokinetic Extraction

Sodium chloride (NaCl)

Figures 3.1.2 and 3.1.3 show extraction of sodium (Na) and chloride (Cl) from drilling mud soil samples of different water saturations. The final pH profiles attained at the end of the tests are superimposed. As observed in Figure 3.1.2, close to 100% recovery of the Na is accomplished in the 81% saturated specimen (S1) at the termination of the test, while about 70% of Na is recovered for the 53% saturated specimen (S2). The specimen designated S1 shows a substantial recovery of Cl in the anode chamber (Figure 3.1.3), although not as high a recovery as Na. The analysis showed little or no presence of Cl in the soil, which suggested the inability to account for all the Cl transported to the anode chamber. This result was attributed to formation of gaseous chlorine, which would have been ventilated from the anode chamber periodically. In sufficiently acidic solutions having high Cl^- concentrations (pH below approximately 4), oxidation of chloride ion will lead to the formation of gaseous chlorine (Pourbaix, 1974). This oxidation can be brought about chemically or electrolytically, as would be the case in the anode chamber of the EK cell where oxygen is generated.

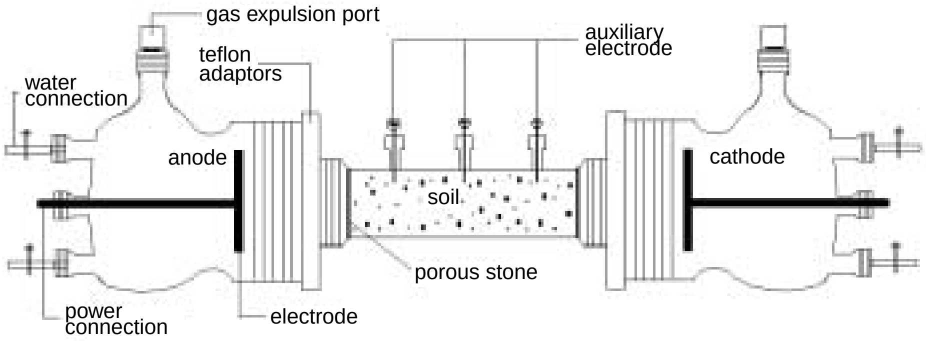


FIGURE 3.1.1 Schematic of the Lehigh electrokinetic (EK) test cell. (Reprinted from *J. Haz. Mat.*, 55, Pamukcu, S., Weeks, A., and Wittle, J.K., Electrochemical separation and stabilization of selected inorganic species porous media, 305–318, copyright 1997, with permission from Elsevier Science.)

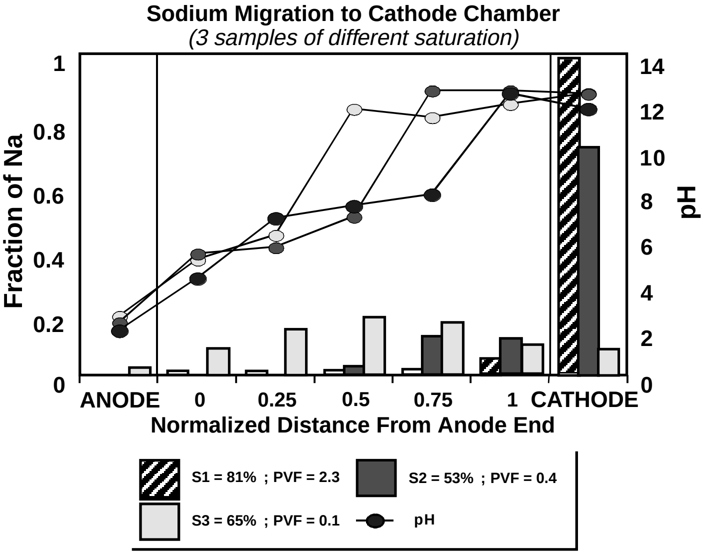


FIGURE 3.1.2 Post electrokinetic treatment distribution of Na in drilling mud soil of various initial water saturation degrees (S1, S2, S3). (Reprinted from *J. Haz. Mat*, 55, Pamukcu, S., Weeks, A., and Wittle, J.K., Electrochemical separation and stabilization of selected inorganic species porous media, 305–318, copyright 1997, with permission from Elsevier Science.)

Perchlorate

The soil and local water samples received from an industrial facility site in California were tested in Lehigh EK cells to evaluate the feasibility of removing perchlorate from the soil by electrokinetic treatment. The laboratory test specimens were prepared by mixing the samples of soil and water to a 25.7% water content by dry weight, which was then packed into the soil chambers of the EK cells at a bulk density of 2.8 g/cm^3, and void ratio of 0.6.

Two tests were conducted in parallel, one of which served as a control test (i.e., with no electrical current). In the treatment cell, the soil was subjected to a constant 30 V across the electrodes. The current

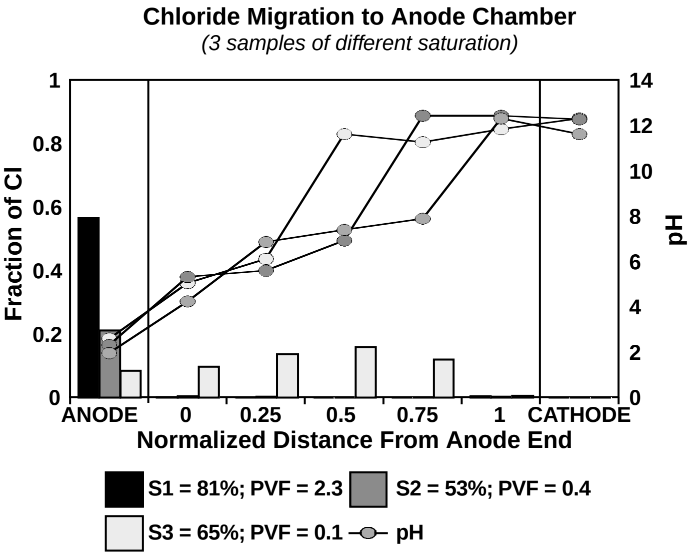


FIGURE 3.1.3 Post electrokinetic treatment distribution of Na in drilling mud soil of various initial water saturation degrees (S1, S2, S3). (Reprinted from *J. Haz. Mat.*, 55, Pamukcu, S., Weeks, A., and Wittle, J.K., Electrochemical separation and stabilization of selected inorganic species porous media, 305–318, copyright 1997, with permission from Elsevier Science.)

density varied from a maximum of 1 mA/cm^2 to a minimum of 0.006 mA/cm^2. Current peaked to 1 mA/cm^2 at 24 hr of treatment, and dropped down to less than 0.01 mA/cm^2 by the end of the fourth day of treatment. This signaled depletion of most current carriers (i.e., ions in solution) in the soil. The electrolytic gases generated in the electrode chambers were minimal due to the low current density achieved. The soil electrical potential gradient also showed a systematic decrease, from about 8 V across the two ends of the soil sample to 1 V by the end of the treatment.

Close to 100% of the initial mass of the perchlorate (the initial perchlorate concentration of the wet soil was 840 mg/kg) was removed from the soil by the end of 7 days of electrokinetic treatment. The control specimen showed less than 30% removal by diffusion for the same duration. The rate of electrokinetic removal was significantly faster for the first 3 days of treatment, by the end of which 80% of the initial mass of perchlorate was removed. The soil remained conductive, even after the current carriers in the pore fluid were depleted. The ratio of moles of perchlorate removed to moles of electrons transferred reached a maximum of 11% and ceased to increase once the current carriers were depleted. The lower ratio was attributed to the presence of co-ions in the pore solution with higher transference numbers.

Electroosmotic flow of water continued in the positive direction (from anode to cathode) for the first 8 days of treatment, but reversed direction afterward. The quantity of flow in the reverse direction was only a fraction of the initially observed flow. The average electroosmotic equivalent hydraulic conductivity, k_{eh}, was computed as 1×10^{-5} cm/s, and the electroosmotic permeability k_{eoh} as 1.7×10^{-5} cm^2/s/V. Electroosmotic flow had no significant effect on the perchlorate removal rate, because most of the flow occurred in the opposite direction of perchlorate migration (i.e., toward the anode).

The perchlorate mass accumulations in the anode and cathode chambers of the test and control samples are shown in Figure 3.1.4. Figure 3.1.5 shows the mass fraction distribution of perchlorate in the test and control soils and their adjacent liquid chambers at the end of the treatment. In the test sample, approximately 92% of the perchlorate was removed to the anode chamber, while the remaining 8% was diffused into the cathode chamber. The residual amount of perchlorate measured in the post-treatment soil was less than 0.2%, and therefore not evident on the graph. In the control sample, less than 30% of the perchlorate diffused into the adjacent liquid chambers for the same duration of time. It is noted that

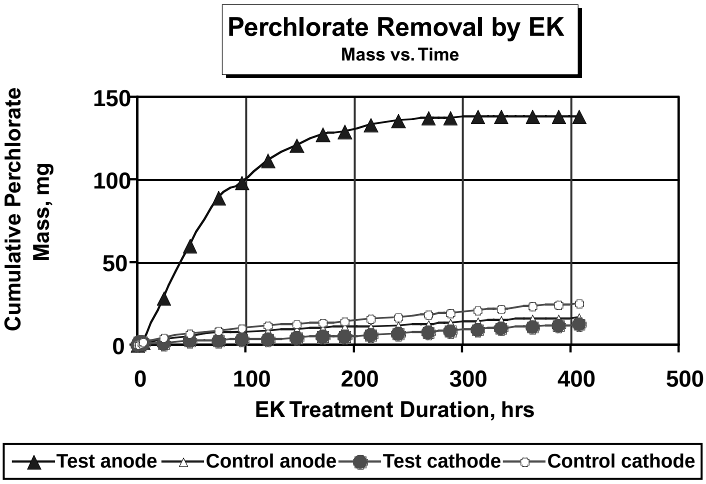
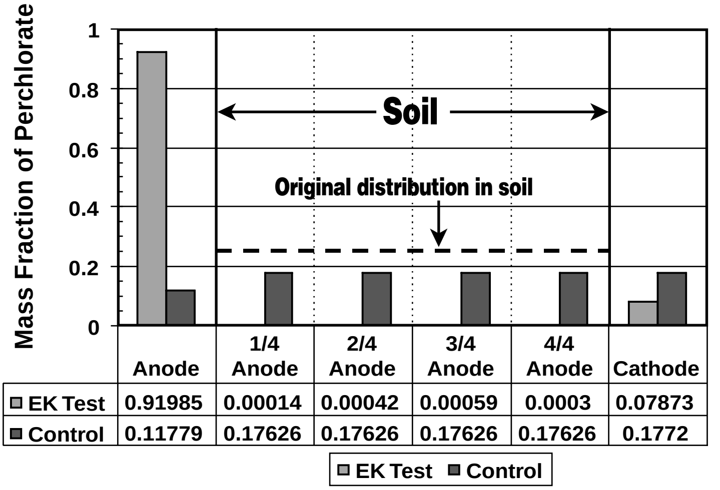


FIGURE 3.1.4 Cumulative perchlorate mass removed.



	Anode	1/4 Anode	2/4 Anode	3/4 Anode	4/4 Anode	Cathode
▨ EK Test	0.91985	0.00014	0.00042	0.00059	0.0003	0.07873
■ Control	0.11779	0.17626	0.17626	0.17626	0.17626	0.1772

FIGURE 3.1.5 Post-treatment distribution of mass fraction of perchlorate.

perchlorate accumulation in the test cathode is lower than in the control cathode. This result confirmed that electromigration of the anion inhibited its accumulation in the chamber containing the negative electrode (cathode).

Ammonia

The processed municipal sludge by N-Viro Soil technique produces a Ca-rich material, a potentially inexpensive source of calcium for cement production. The fresh N-Viro soil gives out ammonia ($NH_3(g)$) as a by-product of the process, which is to be mitigated prior to possible handling by the cement industry. Electrokinetic extraction was proposed to reduce the excess ammonia in N-Viro soil.

The N-Viro soil and leachate liquid samples were retrieved from a utilities authority plant in New Jersey. The visual and textural observation of the N-Viro soil indicated a material of fine sand to silt size with little plasticity. The leachate was a brown-colored liquid. Upon arrival, the leachate was acidified to arrest NH_4^+ in the liquid, and thereby preserve the original concentration of the substance. The soil material, however, was not treated. The test soils were prepared by mixing the N-Viro soil with the leachate at the reported water content of approximately 40% by total weight, or 65% by dry weight.

The laboratory experiments consisted of packing the N-Viro soil in the Lehigh EK cells and applying a constant 30 Vdc across the electrodes for the duration of treatment. The voltage gradient measured in the soil was approximately 0.3 V/cm. This voltage gradient was consistent with measurements in previous tests of similar materials (i.e., saturated loose clayey sand soils).

The inflow and outflow reservoirs were filled with tap water. The rate of effluent discharge was monitored (at cathode and anode) and the tests continued until a substantial decrease in either the current or rate of discharge was observed. At the termination of each test, the soil was sampled at four points along its length and analyzed for moisture content, pH, and NH_4^+ concentration distribution. Figure 3.1.6 shows the post-EK distribution of mass fraction and the measured concentration of NH_4^+ along the soil sample and the anode and cathode liquid chambers. The mass fraction determination showed that more than 50% of the substance was unaccounted for and therefore a mass balance could not be completed properly.

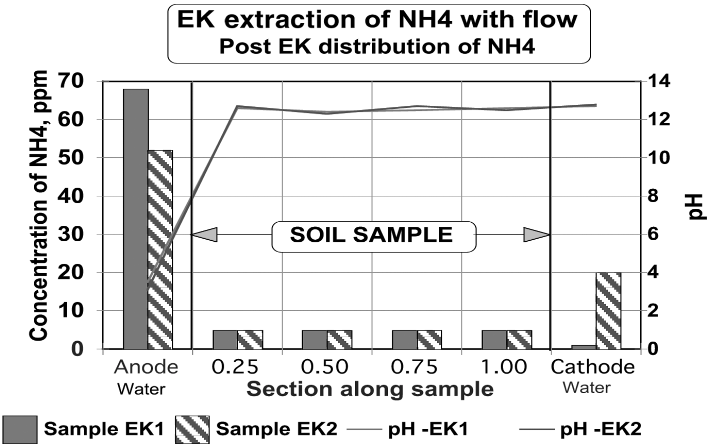


FIGURE 3.1.6 Post electrokinetic distribution of NH_4 in processed municipal sludge soil.

In the two tests conducted, a larger fraction of ammonia was found in the anode chamber. Judging from the distribution of pH in the soil and in the electrode chamber liquids, at the low pH of about 4, the ammonia in the anode chamber should be in the form of ammonium ion. In the cathode chamber, where the pH is well above 9.3, the ammonium is converted to uncharged ammonia (NH_3). The solubility of ammonia is fairly low in water (Henry's constant, K_H = 57.6 mol/L.atm). Therefore, the ammonia removed to the cathode would have converted to gaseous ammonia and readily escaped into the head space of the chamber. A strong ammonia smell was detected when the trapped gases were released periodically at the cathode reservoir. The inability of the equipment set-up to collect and provide mass measurement of the released gases was the main reason for the unaccounted ammonia in the form of gas. The portion of ammonia that was collected in the anode chamber is probably due to colloidally enhanced transport, whereby the positive NH_4^+ ion is transported toward the positive electrode by electromigrating colloids. Charged colloids are known to strongly adsorb ions of opposite charge and enhance transport of these substances in porous media (Grolimund et al., 1996).

Overall, the concentration of ammonia in the soil samples was reduced from about 150–160 mg/kg to less than 6 mg/kg in all samples tested. The tests were conducted for approximately 200 hr. (8 days). The results of the experiments presented above indicate that the transport occured primarily by electromigration of the ammonium ion and partly by colloidal transport, and it was relatively independent of the quantity or rate of liquid flow through the sample.

The rate of migration of charged particles or ions is dependent on the applied electrical field strength, localized concentration of the substance, the size of the particle, and the tortuosity of the porous medium. The rate of transport by electromigration is significantly higher than that of water advection by electroosmosis. Prior experience with electromigration of soluble metal ions in tight porous clay media showed close to 100% extraction of the metal in a few hours of treatment under 30 Vdc field strength (Pamukcu and Wittle, 1992; 1993; Pamukcu et al., 1997). These observations warrant the conclusion that NH_4^+ migration would have occurred at those similar rates per volt of field strength.

Electrokinetic Stabilization

When extraction becomes ineffective or infeasible, electrochemistry can still be useful to stabilize and/or contain certain groups of metals and some organic compounds in the ground. In terms of environmental restoration, *stabilization* is defined as fixing the toxic substance in place, thereby rendering it less likely to move elsewhere under ambient hydrogeological conditions. Electrochemical stabilization can be accomplished by delivering an appropriate oxidizing or reducing agent to the contaminant in the soil that subsequently will (1) degrade the contaminant, (2) change it to a nontoxic or immobile species, or (3) enhance stable sorption and incorporation of the contaminant into the clay minerals. Zero-valent iron enhanced degradation of TCE (Ho et al., 1995), and Fe(II) degradation of toxic Cr(VI) to less toxic and less mobile Cr(III) are examples of such processes (Haran et al., 1995; Pamukcu et al., 1997).

The category of metals that could be altered in such a manner are those that are least likely to be extracted by electrochemical treatment. Metals such as Cr, As, and Hg, owing to their complex electrochemistry or perhaps strong interaction with the soil constituents, are possible candidates for electrochemical containment. Depending on their initial state of speciation and age of interaction with the host soil, Pb, Cu, Mn, and Zn may also be contained in the soil to a certain degree of permanence and/or reduced toxicity. A good example of electrochemical stabilization may be the relatively well-studied reduction of Cr(VI) to Cr(III), by delivering iron (Fe(0), Fe(II), or Fe(III) with co-reagents) in aqueous environments (Powell et al., 1995; Eary and Rai, 1991). In soils, chromium exists in two possible oxidation states: trivalent Cr(III) and the hexavalent Cr(VI). At low pH conditions (2 to 6.5) the predominant form of the hexavalent chromium is chromate or dichromate ion. Due to their negative charge, these anions remain in soil pore water and are readily transported. This was observed in an earlier study by successful removal of the chromate ion with electrokinetic migration in the opposite direction of water flow (Pamukcu and Wittle, 1992). However, at sufficiently low pH, the soil surface sites may become positively charged and tend to retain and accumulate anions such as chromate. Therefore, complete removal may not be achieved unless precise control of pH is maintained during an electrokinetic process. Figure 3.1.7 shows a good example of such an experiment where only a small mass of Cr is removed with increasing duration of treatment and applied current.

Cr(VI) can be reduced to Cr(III) under normal soil and pH conditions, for which soil organic matter acts as the electron donor (Rai et al., 1987; Bartlett, 1991) reported that in natural soils, this reduction may be extremely slow, requiring years. In subsurface soils where there is less organic matter, the Fe(II)

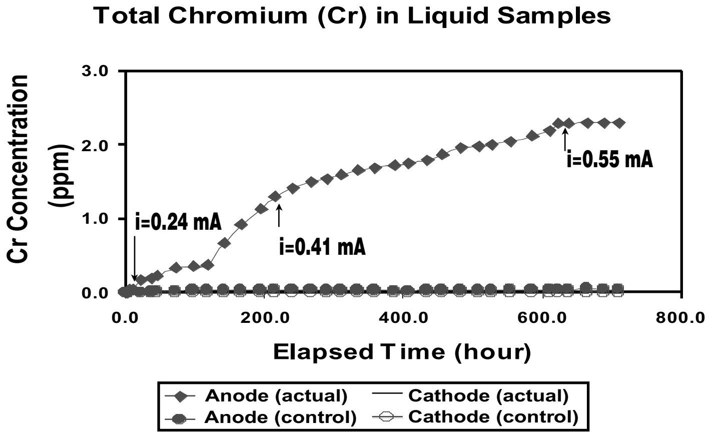


FIGURE 3.1.7 Accumulation of Cr in anode and cathode chamber of the EK cell with time and increased current.

containing minerals reduce Cr(VI) at pH less than 5 (Eary and Rai, 1991). Electrochemically injected Fe(II) into a matrix of soil containing Cr(VI) should facilitate the reduction of Cr(VI) because the electrochemical process produces low pH conditions. The delivery of Fe(II) has also been shown to enhance formation of a chromium-iron hydroxide solid solution $[(Cr_xFe_{1-x})(OH)_3(ss)]$, which has a lower equilibrium solution activity than pure solid phases (Powell et al., 1995).

Electrokinetic Containment

Containment can be defined as causing controlled accumulation of the toxic substance by sorption in a small volume of substrate. Electrochemical containment can be accomplished by causing the electromigration or electroosmotic transport of the contaminants to reactive permeable barriers strategically situated between the electrodes, where they are attenuated and the filtered water is allowed to pass through (Hansen, 1995; Weeks and Pamukcu, 1999). In actual field applications, such permeable structures could be installed at various positions throughout a contaminated site, serving as primary and secondary treatment locations. Such structures are referred to as "reactive permeable barriers" (Rael et al., 1995; Blowes et al., 1995). The basic idea behind these reactive barriers is to allow the flow to advance the contaminant plume through an *in situ* structure containing a substance that will react with the contaminant. When a directed flow of contaminants by electroosmosis or electromigration enters a permeable bed of sorbent material situated in the path of the flow, the water may be filtered sufficiently, depending on the rate of flow through the bed as well as the attenuation characteristics of the bed.

It should be noted that these two processes — stabilization and containment — should be regarded as interim or pretreatment processes to permanent treatment technologies, since these too would require *ex situ* treatment of the contaminant at a later time. For example, Cr may still be required to be taken out of the ground if it is transported from the stabilized site due to changing hydrogeological conditions. Likewise, a saturated bed of sorbent material would either be regenerated or taken out of the ground for disposal.

Kaolinite samples precontaminated with Pb(II) were tested to determine the effectiveness of using permeable reactive caps to contain heavy metals. The reactive permeable caps were composed of approximately 50% glauconite (green sand), 30% zeolite, and 20% bentonite clay. The average particle size of green sand and zeolite was on the order of medium to fine sand. Bentonite was added to enhance the bonding or cohesive potential of the green sand caps. The caps were prepared by first hydrating overnight the predetermined mass of bentonite, and then mixing in the other two ingredients dry. The final water content of the mixture was 37.5%. These caps are referred to as GS caps throughout this chapter section.

The metal salt used to prepare the mixing solutions was a readily soluble salt of $Pb(NO_3)_2$. Initially, kaolinite clay was mixed with the metal solution (5000 ppm) to form a slurry. These slurry mixtures were allowed to sit in an airtight container overnight, re-mixed, and then poured into one-dimensional consolidometers to be normally consolidated. At the completion of consolidation, the soil cylinder was extruded and placed into the sample holder of the EK test set-up. Pre-electrokinetic soil samples were taken for chemical and water content analyses. The Pb(II)-contaminated samples were run with parallel sets of control samples, that is, those without GS caps.

Each test sample was prepared by mixing approximately 300 g kaolinite clay with approximately 220 mL of distilled water and normally consolidated at 290 kPa. The average water content of the Pb(II)-containing samples was 60%. The caps were constructed by packing the green sand, zeolite, and hydrated bentonite mixture in lifts at either end of the soil sample holder once the soil was in place. Distilled water was added to the anode and cathode chambers of the EK cell prior to testing. The Pb(II) samples were tested for approximately 300 hr.

At a constant voltage of 15 Vdc. Voltage, flow (inflow and outflow), current, and pH readings were taken at regular time intervals during each test. The EK tests were terminated when the current readings appeared to be constant or dropped significantly below the initial value observed at the start of each test. Upon completion of all experiments, post-EK soil and liquid samples were obtained for analysis. The soil samples without GS caps were divided into four equal sections of approximately 1 in. length. The average weight of each section was approximately 27.5 g. The post-EK soil specimens with GS caps were also divided into four equal portions, each weighing approximately 20 g. The average length of these samples was 0.88 in. The designations of A-Cap and C-Cap were used to describe the caps located near the anode and cathode chambers in the EK cell, respectively. The caps had approximate lengths and weights of 0.25 in. and 13 g, respectively. Anode and cathode liquid samples were collected for all tests and analyzed along with the appropriate soil samples.

The current distributions for both Pb(II) samples tested with and without the GS caps were comparable during testing. The current distributions were reasonably uniform throughout the test samples, with an average peak current of nearly 2.0 mA. The maximum anodic and cathodic pH were 2.50 and 11.51, and 2.45 and 11.34, respectively, for samples tested with and without the GS caps.

Typically during an EK test, three electrodes designated P1, P2, and P3 are installed in the soil sample starting at the positive electrode toward the negative electrode, located in the anode and cathode chambers, respectively. Figure 3.1.8 shows the resistance variations between P3 and the negative electrode in tests conducted with and without GS caps. The resistance variations across electrodes P1 and P2 appeared to be very low throughout the Pb(II) experiments. In general, these resistances tended to peak initially and then drop off to very low values during testing. The relative increase in soil electrical resistance across P3 (nearest electrode in the soil to the cathodic electrode) and the cathodic electrode were attributed to the accumulation or precipitation of the migrating ions in soil at that location. The caps sorbed the lead without causing an increase in resistivity.

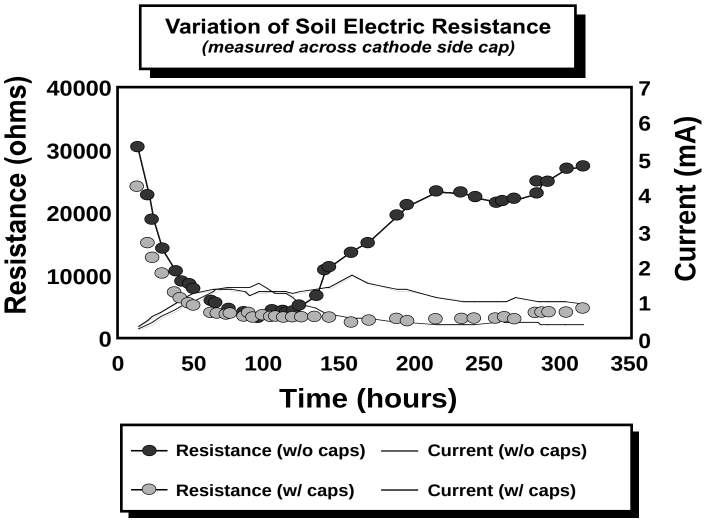


FIGURE 3.1.8 Resistance variation across electrodes for Pb in samples tested with and without GS caps.

Figures 3.1.9 and 3.1.10 show the average pre- and post-EK mass fraction distributions (with respect to the original total mass) of Pb(II) in each section of soil and electrode chambers tested with and without the GS caps, respectively. The sample containing the GS caps showed larger concentrations of Pb(II) accumulated in the caps. Table 3.1.2 shows a comparison of the average post-EK concentrations of Pb(II) remaining in each section of soil tested with and without the GS caps after the EK experiment. Overall, the results showed that, in samples tested without the GS caps, more of the Pb(II) remained in the soil; while the samples containing the caps showed lesser concentrations of Pb(II) in the soil with larger concentrations in the areas of the GS caps.

Removal of Chlorophenols

Four electroosmosis experiments were conducted using various phenolic compounds (Huang et al., 1991). Soils contaminated with phenol, 2-chlorophenol, 3-chlorophenol, and 4-chlorophenol were

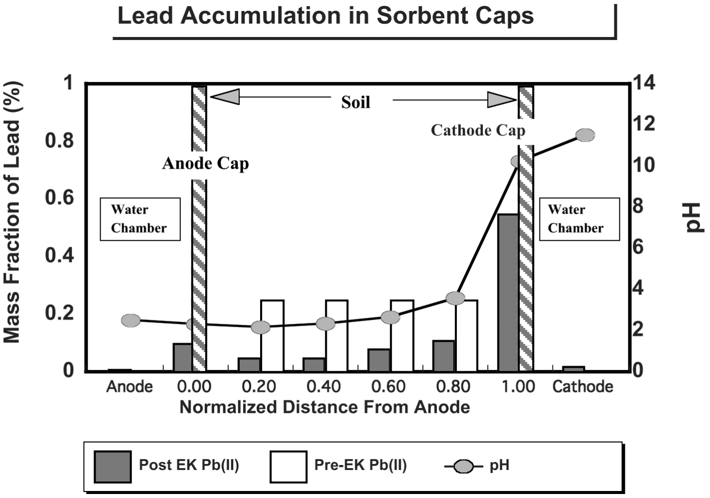


FIGURE 3.1.9 Mass fraction (%) of Pb remaining in soil and liquid samples tested with the GS caps; pH superimposed.

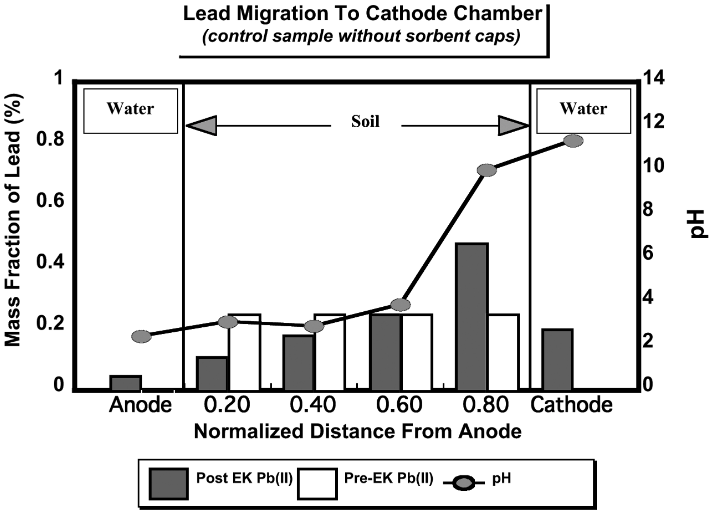


FIGURE 3.1.10 Mass fraction (%) of Pb remaining in soil and liquid samples tested without the GS caps; pH superimposed.

utilized and the same experimental procedures were applied in all of the tests. Table 3.1.3 below shows some of the experimental conditions of the electroosmosis tests performed with phenolic compounds.

Figure 3.1.11 shows the electroosmosis apparatus employed to perform the experiments. The electroosmosis cell consists of an acrylic unit with a central cylinder 11.5 cm in length and 8.9 cm in internal diameter into the soil samples are placed. The volume of both cathode and anode compartments is 700 mL. To separate the soil from the water solution, a set of two nylon meshes (Spectrum; Model PP, mesh opening 149 μm) with a filter paper (Whatman; qualitative) in between were used as a membrane in each of the electrode reservoirs. Graphite rods (Ultra Carbon Co.; type ultra “F” grade 014144-08 U7/SPK; 0.615 cm in diameter) are utilized as electrodes and a series of eight rods are held at each compartment near the central cylinder, right behind the membranes.

TABLE 3.1.2 Average Post EK Concentrations for Lead (Pb) Removal in Soil Samples Tested With and Without Green Sand (GS) Caps

Sample ID	Normalized Distance from anode (%)	Pb Conc. (mg/L)	Pb Mass per Section (mg)	Mass Fraction (%)
Pre-EK (soil)		1606.67	1992.27	1.00
Anode	1	576.67	96.82	0.05
	20	516.67	211.83	0.11
Control Sample	40	953.33	358.45	0.18
	60	1233.33	503.20	0.25
	80	2376.67	955.42	0.48
Cathode	1	2190.00	389.82	0.20
Error (%)				**27**
Pre-EK (soil)		1606.67	1670.93	1.00
Anode	1	83.33	13.70	0.01
A-Cap	0	393.33	163.65	0.10
	20	180.00	78.12	0.05
GS-cap Sample	40	203.33	86.21	0.05
	60	266.67	132.80	0.08
	80	396.67	179.20	0.11
C-Cap	100	2183.33	912.57	0.55
Cathode		233.33	40.09	0.02
Error (%)				**3**

TABLE 3.13 Some Experimental Conditions of the Electroosmosis Tests with Phenolic Compounds

Test No.	Contaminant	Concentration (ppm)	Potential Gradient Applied (V/cm)
Blank	None	0	1.2
PhI	Phenol	166	1.2
PhII	2-Chlorophenol	143	1.2
PhIII	3-Chlorophenol	143	1.2
PhIV	4-Chlorophenol	143	1.2

The soil was a combination of Ottawa sand (U.S. Silica Company) and Georgia kaolinite (Georgia Kaolin Company) at ratio 1:1 (w:w). A solution of the phenolic compound (in NaCl 10^{-3} M) was mixed well with the dry soil and allowed to stand for about 24 hr to reach an equilibrium and consequently provide uniform distribution of the contaminant in the soil system. The mixture was then carefully packed in the acrylic cylinder to avoid formation of large air spaces.

To begin the tests, the electrodes were connected to a 12-Vdc power supply (Power/Mate Corporation; Model E-12/158). The anode container was kept filled with 10^{-3} M NaCl electrolyte solution and the cathode compartment was initially empty. Daily water samples were taken at the cathode side and, during the experiments, parameters such as amount of water flow, current, effluent contaminant concentration, pH of catholyte and anolyte were monitored as a function of time.

After the conclusion of the test, the soil samples were removed from the cell and sliced into ten sections. Each one was then analyzed for water content, pH, and contaminant concentration.

Electroosmotic Flow Rate

Figure 3.1.12 shows the amount of electroosmotic flow produced as a function of time. In general, the flow reached a maximum value and then decreased gradually, possibly due to changes in the electrical properties of the packed soil cores originating from the electrochemistry associated with the electroosmosis process. By applying a potential to the system, water decomposed to H^+ and O_2 at the anode and these hydrogen

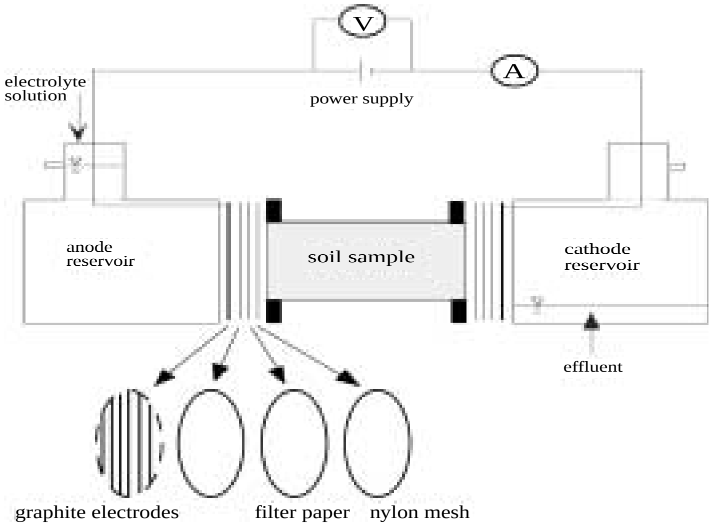


FIGURE 3.1.11 Schematic presentation of the electrokinetic cell used in the study. (From Huang et al., 1991.)

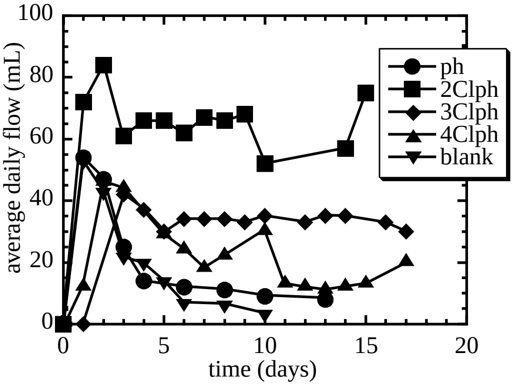


FIGURE 3.1.12 Daily electroosmotic flow in the presence of phenol and chlorophenols. (From Huang et al., 1991.)

ions flushed across the cell, modifying the original conditions of the pore fluid. Simultaneously, vigorous production of OH^- took place at the cathode because of the reduction of water. Accounting for these occurrences, the hydraulic properties of the soil could be altered by dissolution of salts and clay minerals, adsorption/desorption interactions, precipitation of metal hydroxides, and cation exchange (Hamed et al., 1991). Owing to the complexity of the soil system, it became very difficult to interpret the specific causes of the changes of the electrical properties soil core. Khan and Pamukcu (1989) suggested that reversing the current of the electrical system and replacing the electrolyte solutions with fresh solutions would indicate any structural changes in the packed soil. If there are any variations in water flow after these changes, the hydraulic properties of the soil system could be altered with respect to those of the initial condition. Based on this, the authors demonstrated that no changes in the soil structure were observed during the electroosmosis process — at least for kaolinite — and that the changes in electrical properties of the pore fluid significantly affected the electroosmotic water flow. To better illustrate these changes, a plot of current density (current per cross-sectional area of flow) vs. time is presented in Figure 3.1.13. It was observed that the current also reached a maximum value during the first days of experiments and then gradually decreased.

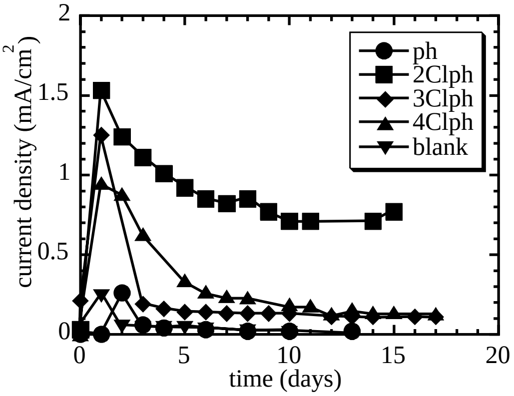


FIGURE 3.1.13 Current density as a function of time in the presence of phenol and chlorophenols. (From Huang et al., 1991.)

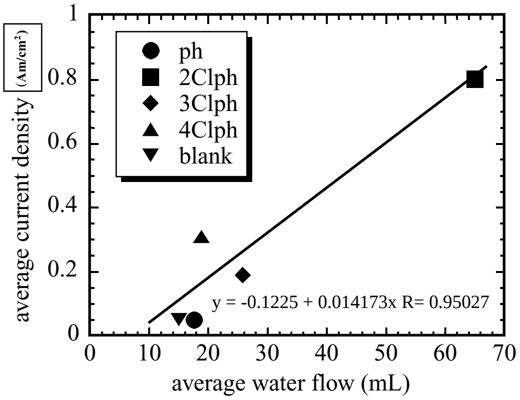


FIGURE 3.1.14 Correlation between electroosmotic flow rate and current density. (From Huang et al, 1991.)

A linear correlation was found between the average water flow and the average current density (Figure 3.1.14): the higher the current density, the greater the water flow. The current passing through the soil core was mainly credited to the ions in the liquid phase. Some of these ions (cations) were responsible for the water flow and a high current should evidently yield high electroosmotic water flow. Therefore, the monitoring of current density could be used as a good assessment of the efficiency during the application of the electroosmotic process.

Noticeable differences among the experiments were related to the water flow. Figure 3.1.15 presents the diagram of cumulative flow vs. time. The test with 2-chlorophenol produced the highest flow, while the blank test showed the lowest water flow. It was noticed that the water flow was also related to the pore volume of the soil core: the larger the pore volume, the larger the electroosmotic water flow (because more water was available to be transported). Obviously, there is a limitation to this occurrence; if the pore volume is too large (see blank test), the system behaves as a free electrolyte solution and less electroosmotic flow is recorded. Figure 3.1.16 exhibits the total average flow of each experiment vs. pore volume; with increasing pore volume, there was an increase in the average flow until a point at which an abrupt decrease was observed.

Changes in pH

The influent and effluent pH variation during the electroosmosis experiments are presented in Figures 3.1.17 and 3.1.18, respectively. As mentioned previously, hydrogen ions (H^+) were produced from the

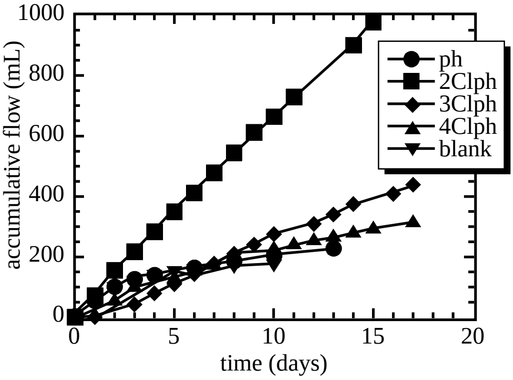


FIGURE 3.1.15 Cumulative electroosmotic flow as a function of time in the presence of phenol and chlorophenols. (From Huang et al., 1991.)

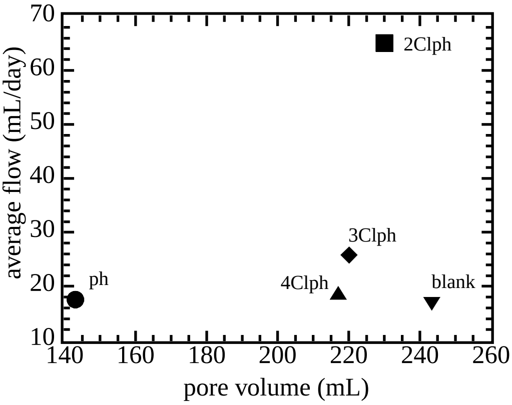


FIGURE 3.1.16 Average electroosmotic flow as a function of pore volume in the presence of phenol and chlorophenols. (From Huang et al., 1991.)

oxidation of water, causing the drop in pH at the anode, and hydroxyl ions (OH^-) from the reduction of H_2O were responsible for the pH increase at the effluent. For all experiments, the pH at the anode (influent) decreased from values around 5 to approximately 2.5 to 3.0, while the effluent pH (cathode) rose to values between 12 to 13 and then decreased gradually due to the acid front generated at the anode. It is well known that hydrogen ions have higher mobility than hydroxyl ions (Acar et al., 1990). Thus, hydrogen ions move toward the cathode faster (due to their higher electrochemical mobility and convection) than the hydroxyl ions to the anode, and a decrease in pH would be expected at the cathode solution.

Removal Efficiency

Figures 3.1.19 and 3.1.20 present the percent removal as a function of time and the removal related to the total water volume flushed through the soil cores (in units of pore volumes of flow), respectively. The results demonstrated that good contaminant removal was achieved from the cathode side. For these experiments, no samples of the anode were analyzed for contaminant concentration. The 2-chlorophenol was almost completely removed from the soil (94%) while only 58% of the phenol was carried out by the electroosmosis process. The removal efficiencies of 3-chlorophenol and 4-chlorophenol were 85% and 79%, respectively. In Figure 3.1.20, one can observe that the removal efficiency was proportional to the amount of water passed through the soil samples: the greater the amount of liquid flushed through the soil, the greater the contaminant removal. Acar et al. (1992) demonstrated that a high removal

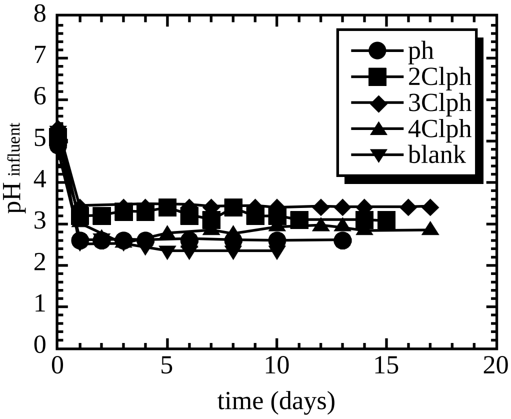


FIGURE 3.1.17 Influent pH as a function of time for phenol and chlorophenol experiments. (From Huang et al., 1991.)

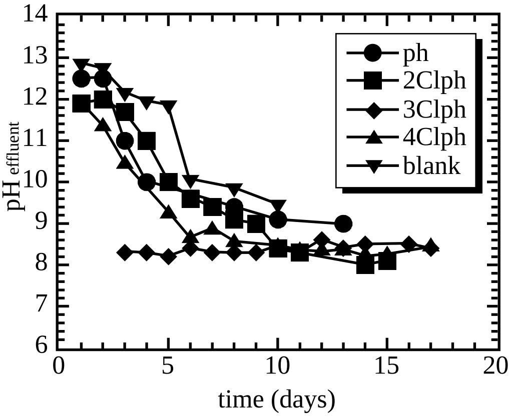


FIGURE 3.1.18 Effluent pH as a function of time in the presence of phenol and chlorophenols. (From Huang et al., 1991.)

efficiency of phenols from kaolinite was achieved by passing at least 2 pore water volumes through the soil. High removal efficiencies were observed in the tests with 3-chlorophenol and 2 chlorophenol and Figure 3.1.20 shows that more than 2 pore water volumes were flushed through the simulated contaminated soil. All the tests were run for 13 to 17 days, and the differences in contaminant removal efficiency were significantly affected by the fluid velocity through the soil. The test with 2-chlorophenol presented the highest removal efficiency and average fluid velocity. With regard to the effictiveness of the electroosmotic process, it is therefore crucial to understand factors influencing the fluid velocity (or water flow rate). From this study there is an indication that the physical properties of the soil core can be of great importance. Assuming that all the contaminants are chemically similar, the only differences encountered among the tests were the physical properties of the packed soil.

The Distribution of pH, Water Content, and Contaminants

After the completion of the tests, the samples were sliced into ten sections and analyzed for pH, water content, and contaminant concentration. The resultant pH profiles for the five tests performed (shown in Figure 3.1.21) originated exclusively from the redox reactions of water at the electrodes and were demonstrated to have the same pattern as the profiles determined by Hamed et al., (1991). The acidic electrolyte solution generated at the anode reservoir flowed across the soil sample, lowering the pH to

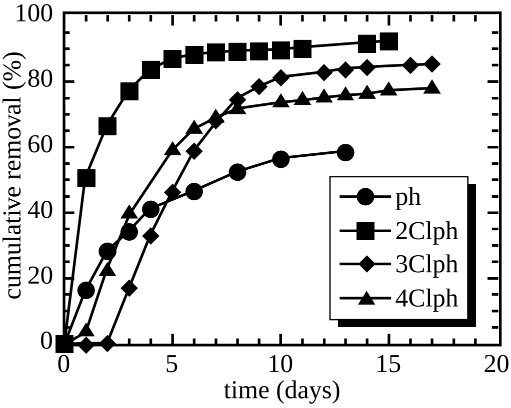


FIGURE 3.1.19 Cumulative removal (%) of phenol and chlorophenols as a function of time. (From Huang et al., 1991).

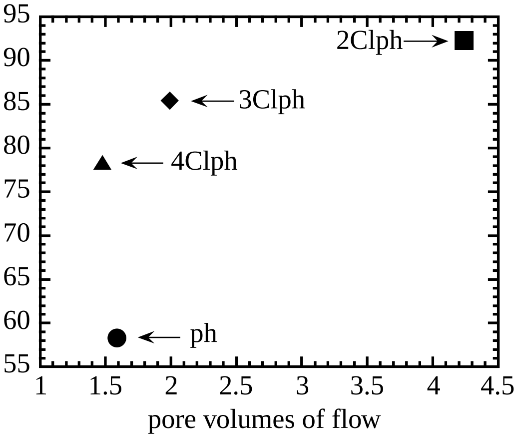


FIGURE 3.1.20 Percentage contaminant removal as a function of pore volumes of flow. (From Huang et al., 1991.)

values around 3 to 4 until near the cathode when the pH rose to values of about 8 to 9 because of the basic conditions produced by the reduction of water.

Water content was measured to determine the concentrations of the phenolic contaminants per gram of dry soil, and it was found to have an almost uniform distribution across the cell, with an average value of 14 to 15% as presented in the Figure 3.1.22. The section closest to the anode presented higher water content than the other sections. This result was expected because the liquid flow was directed toward the cathode and water was continually supplied at the anode side.

Figure 3.1.23 shows the distribution in relative concentration of the phenolic compounds remaining in the soil where C denotes the actual determined concentration and Co denotes the initial concentration of the contaminant in the soil. Small amounts of 4-chlorophenol and high concentration of phenol were retained while no 2-chlorophenol and 3-chlorophenol were found in the soil. An accumulation of phenol above the initial concentration (represented by the solid straight line at C/Co value of 1) was detected near the cathode, indicating that the contaminant does not move uniformly across the soil core. At high pH conditions (such as in the vicinity of the cathode), the phenol molecules (pKa = 9.9) were in the unprotonated form, or as anions, and therefore suitable for electromigration toward the anode. Because the water flow rate of the experiment with phenol was low, the electromigration overcame the convective velocity in the region close to the cathode. As a result, a high concentration of phenol was detected in

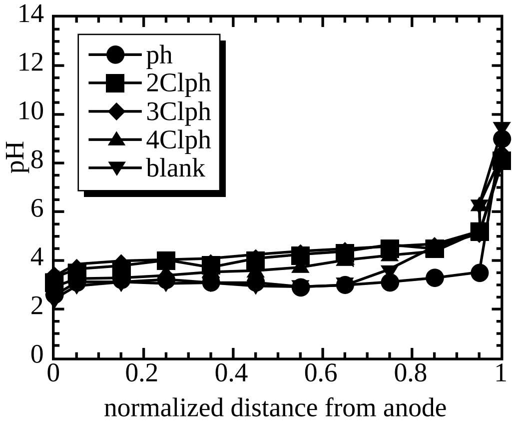


FIGURE 3.1.21 The pH profile as a function of normalized distance from anode for phenol and chlorophenol experiments. (From Huang et al., 1991.)

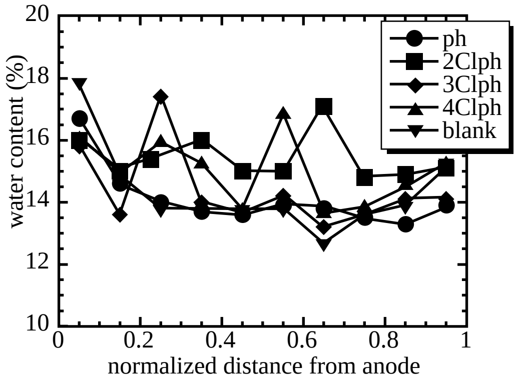


FIGURE 3.1.22 Water content distribution as a function of normalized distance from anode for phenol and chlorophenol experiments. (From Huang et al., 1991.)

that zone. For the other tests, similar accumulation was not observed because the convective velocity was large enough to "push" the contaminants out of the soil.

Mass Balance

The mass balances for the phenol and mono-chlorophenols are summarized in Table 3.1.4. The differences can be attributed to the transport (diffusion and/or migration) of the compounds to the anode reservoir and to the efficiency of the extraction method used to determine the contaminant concentrations in the soil.

Field Applications

Research in electrochemical treatment for the purpose of restoring contaminated subsurfaces has accelerated in the past two decades. Some of the currently researched methods of electrochemical treatment (Marks et al., 1994; 1995; Ho et al., 1995; Yeung, 1990; Mitchell and Yeung, 1991; Hansen, 1995; Pamukcu et al., 1997; Haran et al., 1995) include:

- Electrokinetic extraction
- Electrokinetic barriers
- Electrobioremediation

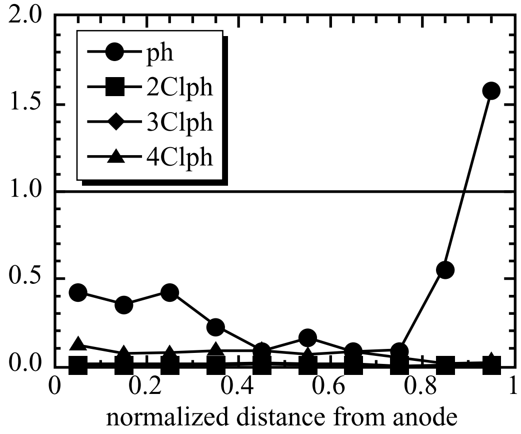


FIGURE 3.1.23 Contaminant distribution through the soil as a function of normalized distance from anode for phenol and chlorophenol experiments. Figures represent the concentration with respect to the initial chemicals. (From Huang et al., 1991.)

TABLE 3.1.4 Mass Balance for Phenol and Chlorophenol Experiments

Test Mass	ph1 (phenol)	ph2 (2-Clph)	ph3 (3-Clph)	ph4 (4-Clph)
Removed from the soil (mg)	120.6	165.5	157.1	144.2
Remained in the soil (mg)	81.3	N.D.[a]	N.D.[a]	10.4
Total (mg)	201.9	165.5	157.1	154.6
Initial mass (mg)	207.0	179.2	183.9	185.0
Difference (mg)	5.1	13.7	26.8	30.4

[a] Not detected

- Electrostabilization (injection)
- Electrocontainment

The earlier work focused on utilizing the technique for soil densification as an aid in containment facilities (Krizek et al., 1976; Sprute and Kelsh, 1982). Others have studied the effects of electrolysis on soil chemistry and the use of electrokinetics for contaminant removal from soil (Hamnet, 1980; Segall et al., 1980; Runnells and Larson, 1986; Renaud and Probstein, 1987; Acar et al., 1989; Khan et al., 1989; Shapiro et al., 1989; Trombley, 1984). The feasibility and cost-effectiveness of the contaminant extraction technique have been demonstrated through numerous laboratory studies and some pilot-scale studies (Hamed et al., 1991; Bruell et al., 1992; Pamukcu and Wittle, 1992; Acar et al., 1992; Wittle and Pamukcu, 1993; Shapiro and Probstein, 1993; Runnels and Wahli, 1993; Ugaz et al., 1994; Acar et al., 1994; 1995; Hicks and Tondorf, 1994; Pamukcu, 1994; Pamukcu et al., 1995; Shapiro et al., 1995; Acar and Alshawabkeh, 1996; Yeung et al., 1996).

Banarjee and co-workers (1988) published a field feasibility study for the potential application of electrokinetics for chromium removal; Acar and co-workers (1989) realized the importance of pH gradients generated from anode through cathode by the process; and in the same year, Lageman (Lageman, 1989) attempted to utilize pH gradients by controlling the chemical environment around the electrodes. Pamukcu et al. (1990) presented the effects of speciation and precipitation on the efficiency of electrokinetic transport of zinc through soil. Other lab studies further substantiated the applicability of the technique to a wide range of contaminants in soils. Among the contaminants that have been shown to react to electrochemical treatment in the laboratory, and a few in the field, are nonaqueous-phase liquids such as chlorinated hydrocarbons, mononuclear aromatic hydrocarbons (MAHs), polynuclear aromatic hydrocarbons (PAHs), phenols, sulfurous, and nitrogenous compounds, and, of course, metals. Ho and co-workers (1995) presented an integrated method of soil restoration that relies on electrochemical technology. Current field demonstration results of this technology, also known as Lasagna™ Soil Remediation.

Furthermore, powerful analytical models and their numerical solutions have been developed; these have contributed significantly toward a better understanding of the underlying mechanisms in transport of single and multiple ionic species under constant and also transient electric fields (Alshawabkeh and Acar, 1996; Denisov et al., 1996; Jacobs and Probstein, 1996; Cao, 1997).

Advantages

The main advantage of electrokinetically aided transport in soils is its ability to move water, dissolved contaminants, and colloidal and micellar particles through low-permeability soils that are not amenable to hydraulic treatments (Acar et al., 1989; 1990; 1991; Acar and Alashawabkeh, 1993; Alshawabkeh and Acar, 1996a; Bruell et al., 1992; Dzenitis, 1997; Pamukcu and Wittle, 1992; 1993; Pamukcu et al., 1990; 1991; 1995; Pamukcu, 1994; 1997; Pamukcu and Pervizpour, 1998; Shapiro and Probstein, 1993; Wittle and Pamukcu, 1993).

Electrokinetic treatment has shown promise as a powerful soil restoration and environmental risk reduction technique under difficult site conditions that include those where the contaminants are found adsorbed onto soil surfaces, iron oxide coatings, soil colloids, and natural organic matter. Difficult site conditions also present contaminants as hydroxycarbonate complexes retained in clay interstices, or in the form of immobile precipitates in soil pore throats and pore pockets that "lace" the vadose zone (Basta and Tabatabai, 1992; Kuo and Baker, 1980). This exasperates the situation because the available technologies, such as *in situ* bioremediation, chemical treatment, or the traditional pump-and-treat, may not be able to treat an entire site effectively. As a remedy, properly selected solubilizing fluids, complexing agents, or ligands can be used. Selection of these substances is critical because they may require secondary treatment once injected into the soil. It may also be difficult to separate the contaminants from these arresting agents, which often form a colloidal sludge at the collection wells. Nevertheless, all these technologies face the similar problem of moving the selected agents, chemicals, nutrients, or inoculated bacteria to within proximity of the contaminants using only hydraulic pressure in low-permeability soils.

The field applications of electrokinetic treatment have demonstrated the following advantages (Lageman, 1993; Runnells and Wahli, 1993; Ho et al., 1995):

1. It is a technology shown to treat low permeability soils effectively, both in the vadose and the groundwater zones.
2. The process controls the direction of the contaminant transport by which the contaminant can be captured in strategically located collection wells or other installations, such as reactive permeable barriers.
3. It is a versatile technique that can be used either alone or to enhance other treatment methods (e.g., bioremediation, chemical oxidation and reduction, or soil vapor extraction).
4. The treatment process does not require the use of heavy equipment, excavation, or installation of large plants, thereby rendering cost-effective treatment of large open spaces as well as populated urban areas or tight spaces such as under buildings, paved areas, and other difficult-to-reach places.
5. In field applications of the process, soil need not be disturbed to cause the release of contaminants. The only disturbance is due to the installation of electrode wells and collection wells. A properly engineered field system can be operated remotely and continuously with minimal need for operator control.
6. An operating cost estimate of \$43 to \$130 per metric ton dry soil has been projected for electrokinetic decontamination. This estimated cost compares favorably with costs that might run up to \$350/t for other *in situ* and *ex situ* methods.

Artifacts and Limitations

Some of the common phenomena experienced with electrokinetic treatment of soils that may interfere with the steady transport of fluid or charged particles to an electrode site include the spatial and transient variation of soil pH and electric gradients; reversed polarity of the diffuse layer; resistance heating; and negative pore pressures generated throughout the soil pore space. These phenomena, unless accounted for in an electrokinetic transport model, affect the accurate prediction of the mass transport (Eykholt and Daniel, 1994; Dzenitis, 1997; Pamukcu and Pervizpour, 1998).

The resistance heating of the soil, which is a controllable by-product of the electrokinetic process, can enhance desorption by volatilization and reduce the viscous drag of immiscible organic fluids in higher permeability soils. An artifact of electroosmosis is streaming potential, which is caused by the electrical potential difference due to water flow through soil under a hydraulic gradient. During electroosmosis, double-layer charges are displaced in the direction of flow. Sometimes, this streaming potential can decrease the effect of electroosmosis by reversing the polarity.

When an electric field is applied to wet soil, the soil pH undergoes transient and spatial variation due to decomposition of water, which, in turn, can affect soil surface properties such as the cation exchange capacity, the ion (cation and anion) adsorption capacity, and the magnitude and sign of the zeta potential. Similarly, the electric gradient does not remain constant in time and space, due to the changing electrical resistance and redistribution of the charges in the soil, and the oxidation/reduction state of the soil, contaminants, and the aqueous solutions near the electrodes. These make it difficult to assess a constant advection velocity term for the duration of electroosmotic transport.

It is well known that electrokinetic treatment in soil-water systems causes migration of an acid front from the anode to the cathode, due to decomposition of water at the electrode sites (Hamed et al., 1991; Pamukcu and Wittle, 1992). The reduced pH is beneficial in desorption of metals from soil, as well as dissolution of most metal precipitates. Natural soils with high buffering capacity and carbonate content, or those under the groundwater table, tend to neutralize the acid front and maintain a higher pH environment (Pamukcu, 1994). The base front generated at the cathode electrode penetrates the soil a narrow distance, creating a zone of high pH, and promoting retention of inorganic species on the clay surfaces and precipitation of hydroxide salts (Alshawabkeh and Acar, 1992; Cao, 1997; Pamukcu, 1997). These process artifacts may be overcome by adjusting the pH of the analyte and catholyte, and/or by adjusting the current density in the soil.

Theoretically, for a homogeneous medium of low ionic strength, uniform pH, and high water content, the electric potential gradient is expected to remain constant throughout the soil matrix, rendering uniform flux, q_{eh} (Mitchell, 1993). Electroosmotically achieved steady-state flow has been demonstrated numerous times in saturated homogeneous kaolinite clay soil for which electrical gradients had remained fairly constant throughout the soil samples (Wittle and Pamukcu, 1993).

If the electrical potential in the soil is nonlinear, large hydraulic potential differences may generate between sections of the soil sample. Nonlinearity of the electrical potential may be due to a number of factors, including the stratification and inclusions and other variables in the physical and chemical properties of the soil. The dynamic change in the chemistry and pH of the soil during the electroosmotic process also induces a transient effect on the electrical potential distribution. As a result of these factors, mass balance of water may not be assessed by seeking equilibrium of $q_{eh,in}$ and $q_{eh,out}$ at any given time during electroosmosis. As the electrical potential gradient, $\Delta V/L$, fluctuates, it creates variable hydraulic potentials within the soil matrix. Soils with low hydraulic conductivity develop negative pore pressures (or suction), where needed to compensate for the pore fluid mass required in each region.

The inflow reservoir of an electrokinetic treatment cell, which normally contains the anode electrode, simulates the inflow reservoir of constant or falling-head hydraulic conductivity test equipment. In these cells, the electrodes can be removed from the soil interface by a conductive liquid and a porous element to alleviate accumulation of charged species on the electrodes. Such a configuration is an open anode system in which an analyte is in contact with soil, but not the anode. Alternatively, in a closed anode system, only a solid anode is in contact with the soil. In either case, when an electric potential is applied, sudden egress of the pore water from soil at the anode/soil or analyte/soil interface causes negative pore pressures (or suction) in the soil behind the migrating electroosmotic front. In classical applications of electroosmosis, when no water source is provided at the boundary of a closed electrode configuration, the suction force, combined with the electroosmotic seepage force, causes the soil pores to collapse and the soil matrix to consolidate Casagrande, 1952; Esrig, 1968; Gray, 1970; Mitchell, 1993; Bjerrum et al., 1967.

The soil suction triggered by non-linear electrical potential distribution has also been measured and documented by others (Hamed et al., 1991; Acar and Alshawabkeh, 1996). Those sections of soil where suction is highest tend to densify, creating regions of higher electrical resistance and larger electrical potential drop. If densification is accompanied by the formation of vertical cracks between the zones of potential difference (orthogonal to potential direction), they may further disrupt the electric potential distribution by creating zones of high or low conductivity. Longitudinal cracks, on the other hand, may create preferential pathways for water flow when hydraulic potentials prevail.

For overconsolidated soils or soils containing swelling clays, soil suction and exposure to free water at the inflow interface may cause swelling of the clay, resulting in decreased pore throats and hydraulic conductivity. In a controlled volume of soil, such as in laboratory experiments, internal swelling of clay should not necessarily impose volume expansion of the soil matrix, but rather decrease in available pore size as the clay particles swell into the macropore space and disperse. In electroosmosis predictions, the important effect of clay swelling may be the dispersion and subsequent increase in the electrokinetic potential (zeta potential) of the charged surfaces (Hunter, 1981). Dispersion would also occur as soil electrolytes are depleted by ion migration and the ionic strength of the pore water decreases. Ionic strength decreases locally at the cathode interface where the high pH removes the charged species, while it increases in the remainder of the soil as the acid front migrates from the anode toward the cathode. An increase in electrokinetic potential would translate to an increase in electroosmotic flux according to the classical treatise of electroosmosis in clay soils (Hunter, 1981; Hiemenz, 1986). The low ionic strength promotes a region of low electrical conductivity and high electric potential gradient, which provides the primary pumping power for electroosmotic flux. Lowering of soil pH as the acid front migrates from the anode to the cathode causes a decrease in electrokinetic potential and a decrease in electroosmotic flux. In addition, high ionic strength renders low electric potential gradient, thus reducing the electroosmotic flux further. However, at low pH, clays tend to flocculate with decreased Debye length (thickness of the sorbed liquid layer adjacent to the charged clay surface: diffused double layer), causing the enlargement of pore sizes.

An alternate cause for the decrease in pore throat size may be colloidal and salt plugging, where the migrating colloids of negative surface charge tend to accumulate in the pores toward the anode, and inorganic salts tend to precipitate at higher pH environment toward the cathode. Even when there is no significant consolidation or volume change of pore space, colloidal and salt plugging may still cause a measurable decrease in the rate of water infiltration, a decrease in total water volume in pore spaces, and an increase in soil electrical resistance.

In summary, in field-retrieved soils, physical and chemical variations and anomalies within the soil matrix substantially affect the distribution of the electrical potential, and also the migration of ions and water. In such soils, zones of variable electrical resistance with different q_{eh} regimes form quickly across the electrodes as a result of precipitation, ion exchange, clay flocculation, and dispersion or swelling with changing pH and moisture content. These effects have been shown to take place in electrokinetic processing of field soils as well as in pure clays by current and other investigators in the past (Pamukcu et al., 1990; 1997; Pamukcu and Wittle, 1992; Wittle and Pamukcu, 1993; Eykholt and Daniel, 1994; Alshawabkeh and Acar, 1996; Dzenitis, 1997). At low soil pH, the packing of hydrogen ions on the clay surfaces creates a positively charged surface and a positive electrokinetic potential that cause reversal of fluid flow from cathode to anode (Hunter, 1981; Yong and Mohamed, 1992; Yong et al., 1993). Therefore, there may be too many soil variables to correctly assess steady-state flow by the indirect measurement of the electroosmotic discharge at one of the electrode sites.

Enhancement of Electrokinetic Treatment

Past experience with electrochemical treatment of contaminated porous media has shown that the process is most effective when the transported substances are ionic, surface charged, or in the form of small micelles with little drag resistance. Among the contaminants that have been shown to react to electrochemical treatment in the laboratory, and a few in the field, are nonaqueous phase liquids such as chlorinated hydrocarbons, mononuclear aromatic hydrocarbons (MAHs), polynuclear aromatic hydrocarbons (PAHs), phenols, sulfurous and nitrogenous compounds, and heavy metals (Acar et al., 1986; 1990; 1992; 1995; Bruell et al., 1992; Hamed et al., 1991; Hicks and Tondorf, 1994; Pamukcu et al., 1990; Pamukcu and Wittle, 1992; 1993; 1993a; b; Pamukcu, 1994; Runnels and Wahli, 1993; Shapiro and Probstein, 1993; Ugaz et al., 1994; Wittle and Pamukcu, 1993). However, unlike a treatment barrier, electrokinetically aided transport cannot degrade or capture contaminants in soil. The use of reactant materials may augment electrokinetic treatment by either transporting the reactant to the immobile contaminants, or transporting the mobile contaminants to reactants placed in a treatment barrier (Ho et al., 1995; Lingren and Brady, 1995). In all situations, the necessary transport through the low-permeability soil can be feasibly accomplished by electrokinetics.

Some of the processes, such as net electroosmotic water flow and transient acid–base distributions, have been studied in more detail than others. For constituents of ionic nature, transport takes place by ion migration. For nonionic species, such as nonpolar organic compounds, the mobilization is by electroosmotic advection. Electroosmotic flow can be induced and sustained in most soil types. In ion migration, the aqueous chemistry and electrochemistry of the ionic species forced to migrate play an important role. Electroosmotic advection — that is "electrically enhanced soil washing" — is primarily dependent on soil mineralogy and the physical state of the contaminant in the pore fluid, that is dissolved, suspended, emulsified, or trapped in pore throats.

There are metal and alkaline earth species that tend to remain ionic under a large range of pH and redox potential values. Such substances are expected to separate and electromigrate readily unless they become adsorbed onto soil surfaces and clay interstices. For those species that tend to precipitate at high pH, shorter distances of electromigration may be provided whereby the contaminant can be captured in preconstructed reactive zones before they precipitate in the soil. Electrochemical treatment in this manner is an alternative process when sufficient ionic migration is not achieved for extraction in the liquid phase. When extraction becomes ineffective or infeasible, electrochemistry may still be useful to stabilize or contain certain types of contaminants in the ground. Other approaches that use electrochemistry aim to degrade the target compounds and metals to their benign components, or less toxic species such as degradation of TCE by oxidation or reduction of Cr(VI) to Cr(III).

In most field situations, the contaminants are often found adsorbed onto soil surfaces, iron-oxide coatings, soil colloids and natural organic matter (humic substances), or retained in clay interstices as hydroxycarbonate complexes, or in the form of immobile precipitates in soil pore throats and pore pockets (Kuo and Baker, 1980; Stahl and James, 1991; Stevenson and Chen, 1991; Basta and Tabatabai, 1992; Godfretsen and Stone, 1994; Siantar and Fripiat, 1995). Application of electrochemical treatment under severe field situations may not be feasible, unless the process is augmented by flushing solubilizing fluids that help to mobilize the contaminants. A number of solubilizing or complexing agents, such as inorganic acids or organic ligands, are available to enhance electrochemical treatment. Utilization of these products in the quantities required for extraction warrants that they also be taken out of the ground or be neutralized because they may be harmful to the ecological makeup of the subsurface. However, the use of natural agents such as humic, fulvic, lactic, or citric acids can be effective and feasible because most of them would be prone to biodegradation in the subsurface.

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3.2

Mercury Separation

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Introduction

Mercury is one of two elements that occur as a liquid at normal room temperature and pressure. It is a silvery-white metal that is naturally present in the environment at low concentration. It can exist in various forms in air, water, sediments, soil, and rocks. The metal is produced from primary sources via the thermal extraction of mercury from ore containing cinnabar (mercuric sulfide, HgS). Approximately 4100 metric tons were produced worldwide in 1990. Seven years later, the production had dropped to 3200 metric tons. The last dedicated mercury mine in the United States closed in 1990; since then, mercury has been produced only from primary sources as a by-product of gold mining (Plachy, 1996). In 1997, only five mines were producing mercury as a by-product of gold recovery (Reese, 1997). Because of its toxicity, discarded products containing significant amounts of mercury are usually reprocessed and the mercury is recovered.

Elemental mercury is the most common form found in environmental samples (Munthe et al., 1990; Fitzgerald and Clarkson, 1991), and the vapor pressure (p, in atm) over this form can be estimated from Eq. (3.2.1) (Barin and Knacke, 1973):

$$\log[p] = -\frac{3305}{T} - 0.795\log[T] + 33.0 \tag{3.2.1}$$

where T is the absolute temperature (K). Other chemical properties are listed in Table 3.2.1. Most inorganic compounds have low solubility in deionized water, but the presence of halide ions or other inorganic ligands increases the solubility dramatically (Dean, 1985).

TABLE 3.2.1 Properties of Some Common Mercury Compounds

Compound	Water Solubility (μg/L)	Boiling Point (°C)
$Hg(0)$	60–80	357
$HgCl_2$	70×10^6	303
Hg_2Cl_2	2000	Sublimes at 385
HgO	53,000	Decomposes at 450
Hg_2O	Very low	
HgS	10	Sublimes at 583

The toxicity of mercury has been well documented (Henke et al., 1993). The chronic lifetime inhalation reference concentration (RfC) limit listed by the U.S. Environmental Protection Agency's (EPA's) IRIS system is 300 ng/m^3 for elemental mercury; a reference dose for chronic lifetime daily oral exposure (RfD) does not exist. The RfD for mercuric chloride is 300 ng/kg/day, and RfD values for phenylmercuric acetate and methyl mercury are 80 and 100 ng/kg/day, respectively (EPA, 1999). The safe drinking water standard has been set by the EPA at 200 μg/L to protect against the risk of adverse health effects (CFR, 1998). Consumption of fish contaminated with methyl mercury creates the most serious threat to human health. Methyl mercury is produced via biotic and abiotic routes in water and sediments and is easily absorbed by fish and other aquatic life. Because of the short biological half-life of elemental and inorganic mercury compounds, human ingestion of small amounts does not cause much damage. However, in large quantities, they may cause liver and kidney damage (Hammond, 1971; Henke et al., 1993). Methyl mercury remains in the human body for a longer period and can attack the nervous system, causing symptoms that are generally untreatable (Hammond, 1971; Bogle, 1972). The average mercury and methyl mercury concentrations in pristine samples can be found in Table 3.2.2.

TABLE 3.2.2 Ranges for Mercury Concentrations in Various Environmental Media

	Mercury Concentration	
	Total Mercury	Methyl Mercury
Open ocean (ng/L)	0.1–1	0.01–0.05
Pristine lake (ng/L)	0.5–5	0.01-1
Pristine rain (ng/L)	1–10	0.01–2
Urban atmosphere (ng/m^3)	2–20	<0.005–0.01
Ocean atmosphere (ng/m^3)	1–2	<0.005
Rocks (mg/kg)	0.01–0.1	
Sediments (mg/kg)	0.01–0.2	0.0001–0.002

From Bloom, 1994.

The approach to the separation of mercury from hazardous or hazardous-radioactive waste is complicated by the fact that the mercury may be present in many forms in the waste, each having different chemical and physical properties. Of course, it is desirable to consider a treatment technology that is robust enough to handle all forms of mercury. To review the various technologies available or under development for separation of mercury from mixed wastes, we consider three broad categories of mercury-contaminated waste. A fourth category, gaseous waste, is considered elsewhere in this book.

1. **Solid waste** such as soils, sludges, and debris. In this waste type, the mercury is likely to be in the form of insoluble metal or salts.
2. In **aqueous waste**, the mercury is soluble and most is in the soluble ionic form or associated with particulates or in a soluble organomercury state.
3. The **liquid organic waste** is a very special waste type that may contain mercury in an elemental form, an organomercury form, or as a soluble salt.

The source of most mercury-contaminated mixed waste can be traced to Cold War activities of the U.S. Department of Energy (DOE). Between 1950 and 1963, elemental mercury was used at the DOE Oak Ridge Y-12 Plant in Oak Ridge, Tennessee, as part of the separation of ^{6}Li from ^{7}Li for use in thermonuclear weapons. Two large production processes were constructed at the site, and operation began after approximately 5 years of research and pilot-scale activities. The production of lithium continued at the site until 1963. The release of mercury to the environment during this period and the subsequent 20 years is estimated to be 332 metric tons. In addition, an estimated 590 tons of mercury cannot be accounted for; a substantial fraction of this still remains in equipment, pumps, tanks, piping, etc. in the production facilities (Gunter, 1991). Oak Ridge National Laboratory (Oak Ridge, Tennessee) supported the pilot-scale work at the Y-12 Plant, and, as a result, large amounts of elemental mercury were handled at this site as well. Mercury was also used at DOE sites for nuclear fuel reprocessing, resulting in large volumes of aqueous waste. The Mixed Waste Integrated Program was established by the DOE to provide complex-wide solutions for handling and treating mixed waste. The DOE mixed waste inventory was 590,000 m^3 in 1993 (DOE, 1993), and an attempt to assess the types of mercury-contaminated mixed waste present at DOE sites and the type of available treatment technologies was also performed that year. A summary of the identified technologies is listed in Table 3.2.3. DOE's mixed waste inventory was updated in 1995, and 410,000 m^3 of mercury-contaminated waste was included (DOE, 1995). In 1996, the DOE Mixed Waste Focus Area (which replaced the Mixed Waste Integrated Program) established the Mercury Work Group to address and resolve the issues related to the mercury-contaminated waste stored at DOE sites (Morris et al., 1997). Among the technology deficiencies identified, mercury amalgamation, stabilization, and removal ranked high.

TABLE 3.2.3 Mercury Separation Technologies as Identified by the Mixed Waste Integrated Program

Waste Stream Type	Mercury Separation Technology
Noncombustible solids and aqueous sludges	• Acid leach with sulfuric acid–sodium hypochlorite and recovery of mercury from leach solution • Thermal treatment with mercury recovery from gases • Chemical oxidation via chlorination, followed by separation of mercury chloride complexes from solution by methods for aqueous liquids • Chemical oxidation with hypochlorite, followed by complex binding with sulfide • Contact with potassium iodide–iodine solution to form stable complexes, followed by recovery from the leach solution
Combustible solids	• Combustion/incineration, with mercury recovery from gases
Organic liquids	• Incineration, with mercury recovered from gases
Aqueous liquids	• Adsorption/reaction of mercury with sulfur-impregnated activated carbon • Chemical reduction with borohydrate, followed by filtration or adsorption • Precipitation of mercury sulfide by sulfide addition • Ion exchange for removal of oxidized mercury by iminodiacetic acid- or thiol-based resins • Extraction with liquid organic amines • Adsorption of mercury by crown ethers attached to silica particles embedded in membranes • Sorption of mercury onto chelating resins • Adsorption of mercury on biomedia • Cementation/reduction of mercury by elemental metal
Gases	• Adsorption and reaction of mercury in beds of sulfur-impregnated activated carbon • Sorption of mercury onto polysulfide resins • Boliden-Norzine process. Gas scrubbing with mercuric chloride to form insoluble mercurous chloride

From Perona and Brown, 1993.

As the regulations for waste clean-up criteria change, so does the approach to the clean-up. For example, in 1997, the Mixed Waste Focus Area discussed criteria for treatment technologies for mixed waste (DOE, 1997). For the treatment of high-level mercury (>260 mg/kg) non-wastewaters that do not pass the limit of 0.2 mg/L established by the Resource Conservation and Recovery Act (RCRA) Toxicity Characteristic Leaching Procedure (TCLP) via SW 846 Method 1310, the primary functional requirements were as follows:

- The mercury-removal/separation technology to be developed must reduce the mercury content in the primary waste to at least the TCLP limit of 0.2 mg/L.
- The desired mercury-removal technology must be capable of treating DOE mixed wastes with mercury levels between 0.2 mg/kg and >50,000 mg/kg. Although regulations require separations only for wastes containing 260 mg/kg or more of mercury, the developed separation technology or technologies must address lower values to accommodate those waste streams that cannot be stabilized.

- The mercury-removal/separation technology must be able to remove mercury in various forms, including mercuric salts, organic mercury complexes, mercuric oxides, and elemental mercury.

In the analysis by the Mixed Waste Focus Area, it was also concluded that an effective separation process should be as mercury specific as possible and address many types of wastes, operate at low temperature (<350°C), keep the secondary waste volume low, and produce secondary waste streams that might possibly be stabilized or amalgamated (DOE, 1997). The treatment goal mentioned above was established before the final ruling of the Land Disposal Restrictions, which establish a new treatment goal for non-wastewaters of 0.025 mg mercury/L in the TCLP leachate. For the specialty case of soils, the new treatment goals become even more complicated (LDR, 1998).

Mercury Separation from Noncombustible Solids and Aqueous Sludges

Thermal desorption of mercury (retorting) is the Best Demonstrated Available Technology (BDAT) for inorganic and some organic solids. The applicability of this process to treat some specific DOE mixed waste streams was investigated by researchers at the Oak Ridge Y-12 Plant (Baker et al., 1993). As part of this study, a literature review was conducted that revealed that full-scale thermal desorption had been used only for organics — no full-scale demonstration on mercury-contaminated environmental media was identified. The bench-scale study focused on operating parameters (such as the desorption temperature and off-gas system) for soils and sludges. The raw waste streams passed TCLP testing, although the total mercury concentration was as high as 83,000 mg/kg. The tests highlighted the difficulty of closing a mercury mass balance, even in the case of pure mercury desorption and recovery. The Oak Ridge Y-12 Plant continued its treatability studies on other mixed waste streams with a refined bench-scale apparatus (Krabill and Shippy, 1996). In these tests, the mercury concentration was substantially reduced. The results are given in Table 3.2.4. The operating desorption temperature was approximately 500°C, and the holding time was 1 to 5 hr. The co-contaminants were uranium, technetium, and, in some cases, polychlorinated biphenyls.

TABLE 3.2.4 Thermal Desorption Result from Several Studies with Different Waste Matrices

		Mercury Concentration		
Waste Stream Description	Test	Initial (mg/kg)	Final (mg/kg)	TCLP (mg/L)
Soil and debris	Test 1	560	5.2	<0.02
	Test 2	380	4.5	<0.02
	Test 3	400	8.5	<0.02
Tank sediments	Test 1	2,200	4.9	<0.02
	Test 2	2,200	11.0	<0.02
Storm sewer sediments	Test 1	24,600	34	<0.02
	Test 2	24,600	53	<0.02

Pilot-scale testing of thermal desorption on soils from locations around the Oak Ridge Y-12 Plant site have also been performed (Lea et al., 1995). Although these soils contained mercury at levels up to 1000 mg/kg and passed the TCLP criterion of 0.2 mg/L, they were tested anyway. Low levels of radionuclides (mainly uranium) were also present. Several companies performed various tests using different temperatures (203 to 600°C), residence times (10 to 188 min), feed rates (13 to 49 kg/hr), and carrier gases (steam or air). An indirect rotary kiln or paddle dryer was used as a desorber, and a 91 to 97% removal efficiency was obtained. All treated material passed the TCLP limit of 0.2 mg/L. Mixed waste storm sewer sediment was also treated with a laboratory-scale pilot unit using a rotary dryer with carrier gas recycle Palmer (1996). The starting material contained 34,000 mg/kg and was treated at 724°C to achieve a final concentration of 228 mg/kg (0.0095 mg/L TCLP).

Mercury-contaminated mixed waste soils have also been vitrified in laboratory experiments (Cicero, 1995). Soil containing 1316 mg/kg mercury was combined with calcium and sodium carbonate (60%/16%/24%) and heated to approximately 700°C; the volatized mercury was collected in a condenser and in a potassium hydroxide wash. The solid matrix was then heated to 1350°C for the glass formation. The glass passed TCLP testing for mercury, but only 8.4 to 34% of the mercury was recovered in the off-gas system. A very small amount of the cesium was volatilized and captured.

The leaching of mercury-contaminated mixed waste sediments using sodium hypochlorite and sodium chloride was conducted on the bench scale by Bostick and Fellows (1998) using 0.12 mol/L hypochlorite and 0.4 mol/L sodium chloride. Only 28% of the mercury (initially present at 5900 mg/kg) was removed in a single leaching step followed by a wash. In a two-stage leaching procedure followed by a solids rinse, 43% was removed. When a five-stage leaching was completed, a total of 79% of the mercury was removed from the solids. Using a single-stage leaching with a solution of potassium iodide (0.4 mol/L) and iodine (0.2 mol/L), followed by a rinse, 87% of the mercury was removed. It was speculated that the stronger mercury-chelating capability of iodide over that of chloride contributed to the difference and could dissolve mercury salts.

Sodium hypochlorite has also been used for leaching of mercury from fluorescent lamps, sometimes handled as mixed waste (Gates et al., 1995; Bostick et al., 1996). Although the hypochlorite solution was effective in removing mercury, a simple rinse solution consisting of 0.08 mol/L sodium bisulfite was sufficient to reduce the mercury concentration to below 0.025 mg/L in the TCLP leachate (Bostick et al., 1996). Gates et al. investigated several other leach solutions—such as sodium chloride, acidified sodium chloride, sodium bromide, acidified sodium bromide, and nitric acid—without success (Gates et al., 1995).

The use of potassium iodide and iodine as leach solutions for mercury compounds was developed by the General Electric Company (Foust, 1993). This technology was first investigated on a bench scale for use with mixed waste by Oak Ridge National Laboratory (Gates et al., 1995; Klasson et al., 1997). The process is based on oxidation of mercury compounds by iodine and complexing of dissolved mercury by iodide. The oxidized mercury is cemented by iron metal, and the iodine/iodide is recovered for subsequent leachings. A simplified schematic of the process is shown in Figure 3.2.1 (Klasson et al., 1997).

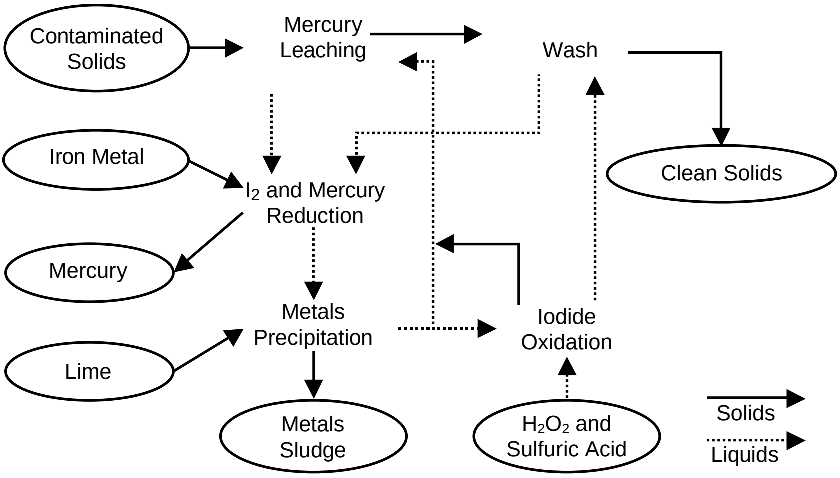

FIGURE 3.2.1 Simplified schematic of the KI/I2 leaching process.

The entire process was tested on mercury- and radionuclide-contaminated sediments, with mercury-removal efficiencies of over 97%. When soluble, the uranium present in the soil will dissolve in the leachate. However, as much as 96% may be removed in the reduction and precipitation step (Bostick et al., 1997). These results correspond well with experiments conducted by the licensees of the technology, Metcalf & Eddy (Wakefield, Massachusetts), when conducting experiments on two different DOE soils contaminated with mercury and uranium (Weir et al., 1999; DOE, 1999). In that study, mercury removal was 62 to >99%; and only about 0.1% if the uranium was solubilized. The TCLP values for the treated soil were between 0.04 and 0.18 mg/L. In the current configuration, iron is used to remove the mercury from the leachate, but other sorbents have also been investigated (Mattigod et al., 1997).

Mercury Separation for Combustible Solids

The removal of mercury from combustible solids has been considered primarily as an incineration activity. The DOE is operating three mixed waste incinerators: the Consolidated Incinerator Facility in Aiken, South Carolina; the Toxic Substances Control Act Incinerator in Kingston, Tennessee; and the Waste Experimental Reduction Facility Incinerator in Idaho Falls, Idaho. None of these facilities have specifically designed mercury-removal systems. Instead, the waste acceptance criteria must be strictly followed. For example, the Kingston incinerator is limited to processing 0.22 kg of mercury per day and continuous emissions monitoring of mercury is being considered (Gibson et al., 1999). These incinerators routinely operate using low-mercury feed but are limited by the daily allowance.

Polyelectrolytes have also been examined for leaching of mercury from contaminated waste or decontamination of surfaces (Smith et al., 1999). These electrolytes consist of water-soluble chelating polymers and have been demonstrated on a laboratory scale with surrogate waste. The method is based on the binding of ionic mercury to the polymers, ultrafiltration of the leachate, and recovery of the polymer. When mercury is not in the appropriate oxidized state, the leaching process must be combined with an oxidizing agent such as nitric acid or hydrogen peroxide. This method can also be used for treatment of aqueous waste, noncombustible solids, and aqueous sludges.

Removal of Mercury from Organic Liquids

The EPA has proclaimed incineration to be the BDAT for oil contaminated with mercury and tritium (Perona and Brown, 1993), with mercury capture from the off-gas. As in the case with contaminated combustibles, the current mixed waste incinerators process mercury-contaminated waste within allowable limits. The treatment of mercury- and tritium-contaminated oil has also been investigated by Klasson et al. (1999). In these studies, a variety of sorbents were investigated for sorption of mercury from the oils. A recently developed sorbent (Self-Assembled Mercaptan on Mesoporous Silica) was found to be the best for removal of mercury in large-scale testing, achieving treatment levels down to <0.025 mg/kg. The removal method consisted of mixing the sorbent with the oil for a period of 24 hr, followed by filtration to remove the sorbent particles laden with mercury.

Mercury has been removed from an organic solvent used for extraction of actinides in acidic wastes (Brewer et al., 1995). In the TRUEX process, a mixture of octyl(phenyl)-N,N-diisobutyl-carbamoylmethyl phosphine oxide, 0.2 *M*, and tributyl phosphate, 1.4 *M*, in dodecane was used to extract mercury (as mercuric chloride) and neodymium (a surrogate for americium) in small-scale contactors in eight stages. Greater than 99.9% of the neodymium and 98% of the mercury were extracted by the TRUEX solvent. The solvent was then stripped from the neodymium in eight stages; subsequently, greater than 99% of the mercury was extracted from the solvent using 0.25 *M* sodium carbonate. Nitric acid (5 *M*) also successfully removed the mercury from the solvent.

Removal of Mercury from Aqueous Liquids

Sulfide precipitation is a common method for removal of mercury from aqueous waste. This procedure has also been used when treating mixed waste contaminated with uranium, thorium, radium, and heavy metals. Schmidt and Hempill (1997) treated 3500 L in several batch stages.

1. Lowering of pH to 2.0 with sulfuric acid
2. Addition of sodium metabisulfite (95 mg/L) to reduce oxidized chromium
3. Lime-slurry addition to raise pH to 7.5

4. Sodium sulfide addition (0.5 mg/L) to precipitate mercury
5. Addition of ferric sulfate (70 mg/L) as a coagulant
6. Lime-slurry addition to pH 11.5 for precipitation of other metals and radionuclides
7. Anionic polymer addition for flocculation
8. Settling and filtration

The untreated waste contained 1.3 mg/L mercury, the treated water had a mercury concentration of 1 µg/L, and the precipitated solid passed the TCLP test at 0.046 mg/L.

The removal of mercury from various types of aqueous wastes using different sorbents was investigated by Taylor et al. (1995). These studies focused on the removal of mercury from very saline solutions stored at DOE sites. Both low- and high-pH solutions were investigated. A summary of results for batch experiments is given in Table 3.2.5. Some of the removal efficiencies are low due to the rather small amount of sorbent used (0.2 to 0.4%, w/v). In further isotherm and column studies, removal efficiency improved as expected. The studies were performed on surrogate waste streams.

TABLE 3.2.5 Removal of Mercury from Liquid Waste as Recorded in Batch Experiments

Waste Type	Best Sorbent Types	Removal Efficiency (%)
LiOH (23 mg/L mercury)	Proprietary carbon based	74.2
	Isothiouronium based	69.1
	Iminodiacetate based	67.8
$NaNO_3/HNO_3$ (278 mg/L mercury)	Thiol based	25.6
	Proprietary molecular recognition	25.2
$NaNO_3/NaOH$ (108 mg/L mercury)	Sulfur-impregnated carbon	99.3
	Proprietary carbon based	79.2
	Isothiouronium based	79.2

A thiol-based resin, pretreated with sodium hydroxide, has also been used to treat large volumes of alkaline wastewater (pH 12) at a flow rate of 3 bed volumes per hour (Ritter and Bibler, 1992). The process routinely removed mercury from 0.2 to 70 mg/L to below 10 µg/L. It was noted that performance of the system was substantially improved when pre filtration was added. A schematic of the system is shown in Figure 3.2.2. Elemental iron has been used to demonstrate the removal of mercury (41 mg/L) from acidic (pH <1) laboratory mixed waste but only after neutralization to pH 5.3 [Bostick and Fellows, 1998]. The mercury and uranium were effectively removed in small-scale batch and

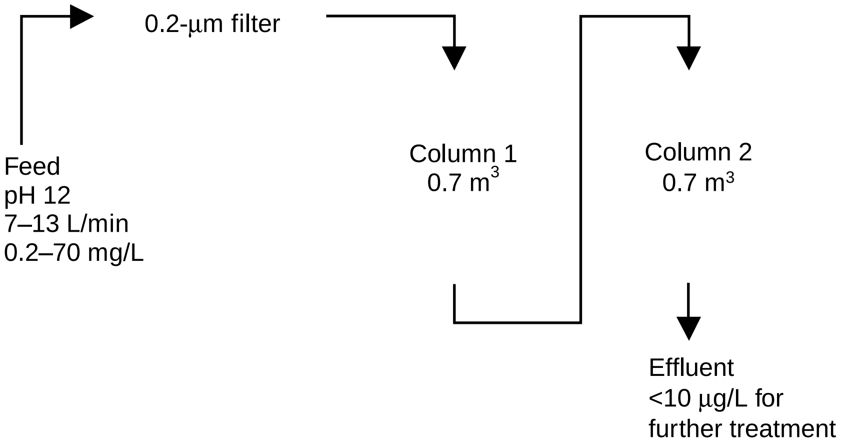

FIGURE 3.2.2 Full-scale mercury treatment system.

column studies. This same method is used by the Kodak Chemical Company to remove silver from photographic solutions.

A thiouronium-based ion-exchange resin has also been used for low-level mercury removal from a mixed waste at the Idaho National Engineering and Environmental Laboratory (Haefer, 1995). Approximately 129,000 L of waste (approximately pH 2.5) contaminated with mercury (0.24 mg/L), lead (15 mg/L), other metals ^{60}Co, and ^{137}Ce were treated via filtration (0.3 µm-pore size) and ion exchange. The size of the mercury-removal column was 0.445 m^3, and the operational flow rate was 87 L/min. Approximately 90% of the mercury was removed by the ion-exchange column. The other metals and radionuclides were removed using three additional columns (0.445 m^3 each) in series with strong-acid cationic resin.

Thiacrown organic polymers have also been studied in the laboratory for use in the treatment of acidic (pH range: 1.5 to 6.2) mixed waste containing mercury (Baumann et al., 1999). After the addition of the polymer to the aqueous solution, the polymer was removed via filtration and the mercury stripped from the polymer after drying with dithizone in chloroform. In these small-scale experiments, 91 to 99% of the mercury was removed from 4- to 170-mg/L solutions, even in the presence of high levels of competing metal ions (lead, cadmium, iron, and aluminum).

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3.3

Separation of Radionuclides from Aqueous Mixed Waste Solutions Using Liquid–Liquid Extraction Processes

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Introduction

The presence of long-lived radionuclides in aqueous mixed wastes can significantly increase the complexity and cost of treating the waste for disposal. Incidental wastes resulting from processes utilizing nuclear fission may contain radionuclides (e.g., ^{137}Cs and ^{90}Sr) that require remote handling of the waste and process equipment. Other wastes that contain actinide elements (U, Np, Pu, Am, or Cm) or radionuclides of lanthanide elements (Ce, Sm, and Eu, for example) require, at a minimum, extensive containment controls, if not limited shielding to handle the waste. Separation of the major radioactive elements from the waste allows downstream processing to be performed in less expensive equipment and facilities with hands-on operation and maintenance. This lowers capital and operating costs of treatment facilities.

Radionuclide separation technologies can be grouped into categories that describe the general unit operation of the separation process. These include liquid–liquid extraction, ion exchange, and precipitation. This section focuses primarily on liquid–liquid extraction methods, because ion exchange methods are described elsewhere in this handbook. A brief description of precipitation processes is also included in this section.

Liquid–liquid extraction was initially utilized in the petroleum industry beginning in the 1930s. It has since been utilized in numerous applications, including the petroleum, hydrometallurgical, pharmaceutical, and nuclear industries. Liquid–liquid extraction describes a method for separating components of a solution by utilizing an unequal distribution of the components between two immiscible liquid phases. In most cases, this process is carried out by intimately mixing the two immiscible phases, allowing for the transfer of components from one phase to the other, and then allowing the two phases to separate. Typically, one phase is an aqueous solution, usually containing the components to be separated; and the other phase is an organic solvent that has a high affinity for some specific components of the solution. The process is reversible by contacting the solvent loaded with solute(s) with another immiscible phase that has a higher affinity for the solute than the organic phase. The transfer of solute from one phase into the solvent phase is referred to as extraction, and the transfer of the solute back from the solvent to the second phase is referred to as back-extraction or stripping. Liquid–liquid extraction can be performed on a continuous basis by assembling a number of contactors (equipment to mix and separate the phases) with the phases flowing countercurrently between contactors. Excellent separation efficiencies (>99.99%) are possible with liquid–liquid extraction processes because the extractant concentration, diluent, number of stages, and solution flowrates can be varied.

There are three basic types of liquid–liquid contacting equipment: mixer-settlers, centrifugal contactors, and columns. The mixer-settler is simply a tank with two chambers: one with a mixing impeller to mix the phases, the other to let the phases separate by gravity. Centrifugal contactors are similar to mixer-settlers, except that they use a spinning rotor to mix the solutions and the centrifugal force on the inside of the rotor to separate the phases. Extraction columns utilize countercurrent flow through a column containing either packing or plates to disperse the phases. Phase separation is accomplished in a disengaging section, usually of larger diameter than the column, located at either end (or both ends) of the column. Each type of contactor has inherent advantages and disadvantages, and all have been used in processes with radioactive elements (Todd et al., 1998). Recent developments in centrifugal contactors have resulted in increased acceptability in the nuclear industry because of small facility size requirements, high throughput, low solvent inventory, and the ability to rapidly reach steady-state conditions.

Four liquid–liquid extraction technologies are described that are effective for the removal of (1) actinides and lanthanides (TRUEX process); (2) strontium (SREX process); (3) cesium, with or without the simultaneous removal of strontium (cobalt dicarbollide process); and (4) cesium, strontium, and the actinides simultaneously (UNEX process). In some cases, hazardous metals can also be partitioned from the waste and the radioactive products. These processes represent the state-of-the-art for liquid–liquid extraction for the removal of radionuclides from mixed wastes; however, other processes have also been developed and are briefly mentioned.

Transuranium Extraction Process (TRUEX)

The TRUEX process was originally developed by E.P. Horwitz and W.W. Schulz for the separation of transuranium elements from acidic waste solutions (Horwitz, et al., 1985). The process is based on a powerful extractant, octyl(phenyl)-N,N-diisobutylcarbamoylmethyl phosphine oxide (CMPO), which is effective in extracting +3, +4, and +6 valance lanthanides and actinides over a wide range of nitric acid concentrations. The TRUEX process solvent is typically composed of 0.2 M CMPO in 1.2–1.4 *M* tri-*n*-butyl phosphate (TBP) and a paraffinic hydrocarbon. Addition of TBP to the solvent increases the solubility of metal complexes in the organic phase and prevents third phase formation. The development of the TRUEX solvent was based on the extensive knowledge of the plutonium and uranium extraction (PUREX) process, which utilizes TBP in a hydrocarbon diluent as the process solvent. This allowed for the extensive development of process equipment and safety parameters that existed for the PUREX process to be utilized for the TRUEX process.

Extraction is carried out in the TRUEX process in acidic solutions, typically 0.5 to 6 M nitric acid, while stripping of trivalent elements is performed with dilute nitric acid and stripping of tetra- and hexavalent elements is accomplished with some type of complexant (such as HF, oxalates, or diphosphonic acids). Reduction of Pu to the trivalent state, followed by stripping with dilute nitric acid, can also be used to strip Pu from the TRUEX solvent.

The initial development of the TRUEX process was performed at Argonne National Laboratory (ANL) for the treatment of dissolved Hanford sludge waste streams. Later, the TRUEX process was utilized to treat over 100 L of TRU analytical waste at ANL and the New Brunswick Laboratory using 20 stages of 4-cm centrifugal contactors (Chamberlain et al., 1997).

The Oak Ridge National Laboratory (ORNL) tested the TRUEX process for separation and recovery of macroquantities of Am and Cm from irradiated Mark-42 PuO_2 targets (Felker and Benker, 1995). The test runs were performed in a shielded hot cell using three banks of 16-stage mixer-settlers. The tests were successful at separating the Am and Cm from Pu, as there was less than 0.1% of the Pu in the Am-Cm product, and less than 1% of the Am-Cm in the Pu product.

Forty liters of clarified Plutonium Finishing Plant acidic waste were treated at Hanford using the TRUEX process (Schultz and Horwitz, 1988). The process solvent contained 0.25 *M* CMPO in 0.75 *M* TBP and tetrachloroethylene. The applicability of the TRUEX process to several other Hanford waste streams has been studied (Lumetta et al., 1996); however, there are currently no plans to utilize the TRUEX process to treat other waste streams at Hanford.

The Idaho National Engineering and Environmental Laboratory (INEEL) has been testing and evaluating the TRUEX process for the treatment of acidic mixed waste contained in underground storage tanks as well as dissolved HLW calcine. Numerous laboratory batch contact tests with simulated and actual acidic tank waste and dissolved calcine solution, as well as countercurrent pilot-scale flowsheet tests with tank waste and dissolved calcine solutions, have been performed (Law et al., 1999). TRUEX flowsheets have also been demonstrated using actual liquid waste in a 24-stage, 2-cm centrifugal contactor pilot plant (Law, Brewer, and Todd, 1998). A flowsheet of the TRUEX demonstration with actual tank waste is shown in Figure 3.3.1. The flowsheet demonstration was performed on approximately 1 liter of actual waste solution and resulted in the removal of 99.8% of the actinide elements. This is sufficient to allow the waste, as a grout waste form, to meet the NRC Class A non-TRU criteria of <10 nCi/g. Additionally, 74% of the Hg, 42% of the Zr, and 0.7% of the Fe were extracted into the TRUEX solvent. The Fe and Zr exited with the high-activity waste strip product, and the Hg was removed from the process solvent in the sodium carbonate wash stream. Subsequent testing using surrogate tank wastes has demonstrated that 96% of the Hg can be removed and recovered with the TRUEX process (Herbst et al., 2000). This process therefore allows for the removal and partitioning of TRU elements and mercury.

A TRUEX flowsheet has also been developed for the treatment of dissolved INEEL zirconium calcine (Law et al., 1997). This flowsheet has been tested using simulated dissolved calcine spiked with ^{241}Am and ^{95}Zr. With this flowsheet, a removal efficiency of >96.4% was obtained for ^{241}Am. Less than 0.25% of the ^{95}Zr was extracted and exited with the strip product. An ammonium fluoride scrub was effectively used to back-extract the Zr from the TRUEX solvent. Also, only 1.1% of the Fe was extracted with this flowsheet.

In addition to the extensive development efforts carried out in the United States over the past 15 years, the TRUEX process has been evaluated and tested in several other countries, including Japan, India, and Russia.

Strontium Extraction Process (SREX)

The need for removal of ^{90}Sr from aqueous mixed waste solutions has stimulated much research in the area of liquid–liquid extraction. The remediation of mixed wastes may require the selective removal of Sr in the presence of numerous other ions. The aqueous complexation of Sr by macrocyclic polyethers, also called crown ethers, has been studied extensively. The crown ether 4,4′(5′)di-(*t*-butylcyclohexano)-18-crown-6 (DtBuCH18C6) was determined to be a highly selective and efficient extractant for Sr (Horwitz, Dietz, and Fisher, 1990). The term “SREX” process was applied by ANL scientists to the use of DtBuCH18C6 dissolved in 1-octanol in a liquid–liquid extraction process in 1991.

A research program began in 1993 to develop the SREX process for the removal of ^{90}Sr from mixed wastes and dissolved calcine solutions at the INEEL. This research has focused on the use of 0.15 *M* DtBuCH18C6 with a TBP phase modifier (1.5 *M*) in a hydrocarbon diluent (Isopar-L®), as opposed to an octanol diluent. Numerous laboratory batch contact tests, as well as countercurrent pilot-scale flow-

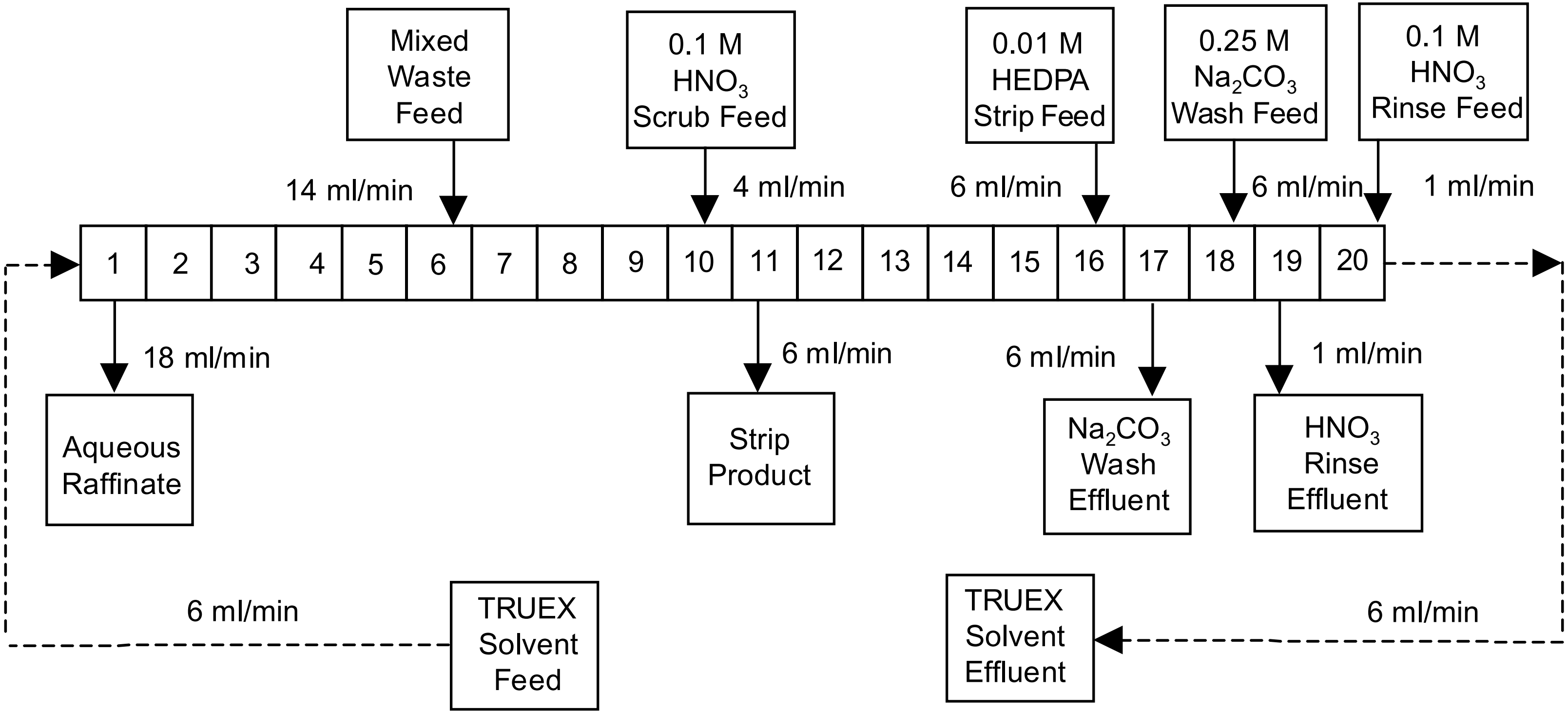

FIGURE 3.3.1 TRUEX flowsheet for the treatment of INEEL mixed waste. (Reprinted from *Waste Management*, 19(1), Development and demonstration of solvent extraction processes for the separation of radionuclides from acidic radioactive waste, 17–27, copyright 1999, with permission from Elsevier Science.)

sheet tests, have been performed with simulated and actual liquid waste and dissolved calcine solutions (Wood and Law, 1997). An SREX flowsheet has also been demonstrated using actual liquid waste solution in a 2-cm centrifugal contactor pilot plant (Wood, Law, and Todd, 1998). A flowsheet of the SREX test with actual tank waste is shown in Figure 3.3.2.

For the SREX flowsheet demonstration with actual INEEL mixed waste, a removal efficiency of 99.994% was obtained for ^{90}Sr. This is sufficient to reduce the ^{90}Sr activity of the waste, immobilized into a grout, to below the NRC Class A LLW criteria of 0.04 Ci/m^3. With this flowsheet, >94% of the Pb, >82% of the Zr, 31.5% of the K, >89% of the Hg, 64% of the Ba, and 1.7% of the Fe were extracted and exited with the high-activity waste strip product. The extracted Pb can be selectively stripped from the solvent using citrate.

An SREX flowsheet has also been developed for the treatment of dissolved INEEL zirconium calcine (Law, Wood, and Todd, 1999). This flowsheet has been tested using simulated dissolved calcine spiked with ^{85}Sr. With this flowsheet, a removal efficiency of 99.6% was obtained for ^{85}Sr. A stage efficiency of 60% in the extraction section of the flowsheet accounted for the reduced removal efficiency for Sr. A sodium nitrate scrub was effectively used to scrub the extracted K from the SREX solvent, thus minimizing the amount of K in the strip product. As a result, only 6.4% of the K was extracted and exited with the strip product.

A similar process to remove strontium and technetium from alkaline wastes, which is based on the use of the same extractant (DtBuCH18C6), was independently developed by scientists at Oak Ridge National Laboratory. This process, referred to as the SRTALK process, has been shown to effectively remove strontium and technetium from alkaline wastes such as Hanford tank waste (Leonard et al., 1999).

Cobalt Dicarbollide Processes (ChCoDiC)

Cobalt dicarbollide was first synthesized and characterized at the University of California (Hawthorne and Andrews, 1965). Rias first reported the applicability of cobalt dicarbollide in liquid–liquid extraction processes (Rias, Selucky, and Kyrs, 1976a). Chlorinated cobalt dicarbollide (ChCoDiC) has been developed as an extractant for Cs from acidic waste solutions in the Czech Republic, Russia, and the United States (Esimantovski et al., 1992). With the addition of polyethylene glycol (PEG) to the ChCoDiC solvent, Sr can also be partitioned from acidic waste streams (Rias et al., 1976b). The acid form of cobalt dicarbollide is completely dissociated in the organic phase; therefore, a polar solvent such as nitrobenzene has been used. The Mayak Production Facility in Russia is currently using the ChCoDiC process, with a nitrobenzene-based diluent, for the treatment of acidic radioactive wastes. Over 800 m^3 of waste has been treated with this process from 1996 to 2000. The facility is currently not in operation, due to limited surge capacity between the separations process, and the vitrification facility which is undergoing installation of a new melter. Safety considerations associated with the use of nitrobenzene derivatives have led to the development of acceptable alternatives to nitroaromatic diluents used in the cobalt dicarbollide process (Todd et al., 1996).

A joint research program with the Khlopin Radium Institute in St. Petersburg, Russia, was initiated in 1993 to develop the ChCoDiC process with a non-nitroaromatic diluent for the removal of ^{137}Cs and ^{90}Sr from acidic radioactive waste at the INEEL. Numerous laboratory batch contact tests with simulated and actual liquid waste solutions, as well as countercurrent pilot-scale flowsheet tests with simulated liquid waste, have been performed. This testing has culminated in the development of ChCoDiC flowsheets (with and without PEG for the extraction of Sr), which have been demonstrated using actual liquid waste solution in a 2-cm centrifugal contactor pilot plant. The flowsheet tested for the demonstrations of the ChCoDiC process (with and without PEG) is shown in Figure 3.3.3.

For the ChCoDiC flowsheet demonstration with PEG, a removal efficiency of 96.2% was obtained for ^{90}Sr and 99.3% for ^{137}Cs. Also, 98.5% of the Pb, 45.2% of the K, 26.4% of the Hg, 2.1% of the Na, 1.4% of the Ca, <5.8% of the Zr, and <2.1% of the Fe were extracted and exited with the high-activity waste strip product.

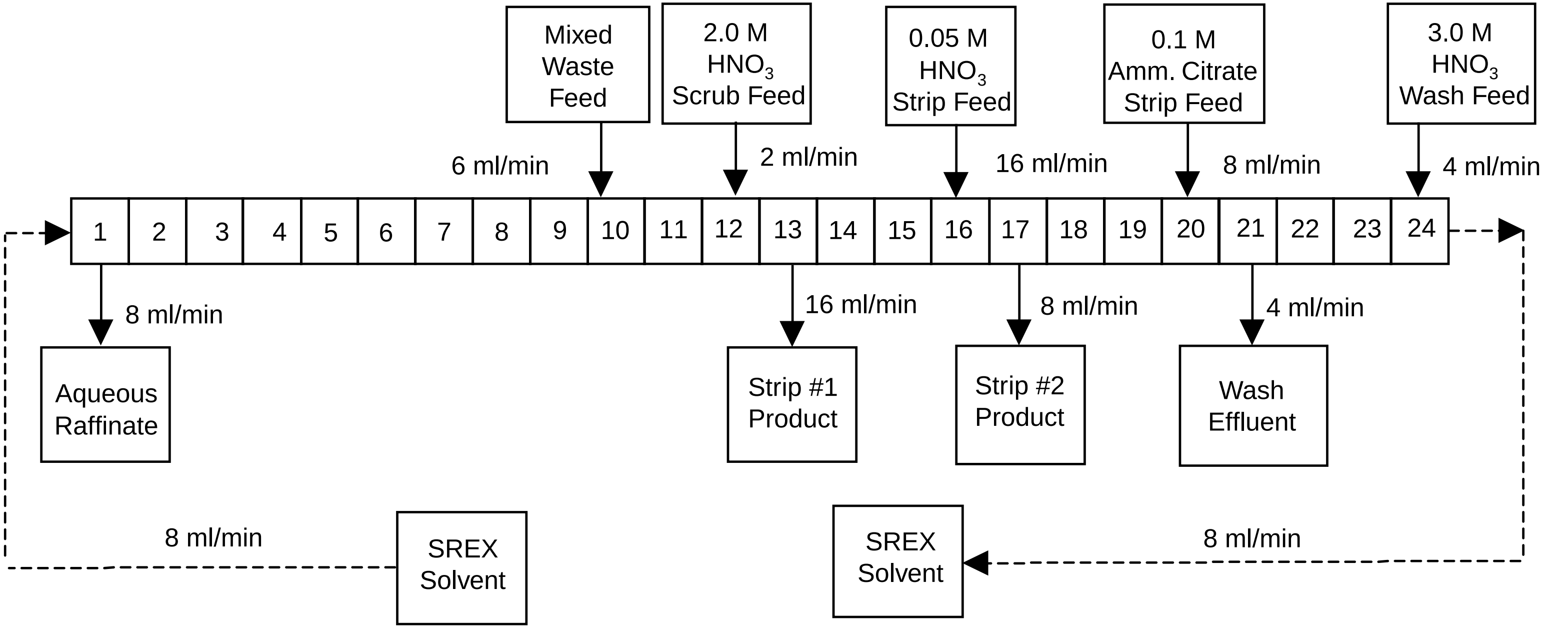

FIGURE 3.3.2 SREX flowsheet for the treatment of INEEL mixed waste. (Reprinted from *Waste Management*, 19(1), Development and demonstration of solvent extraction processes for the separation of radionuclides from acidic radioactive waste, 17–27, copyright 1999, with permission from Elsevier Science.)

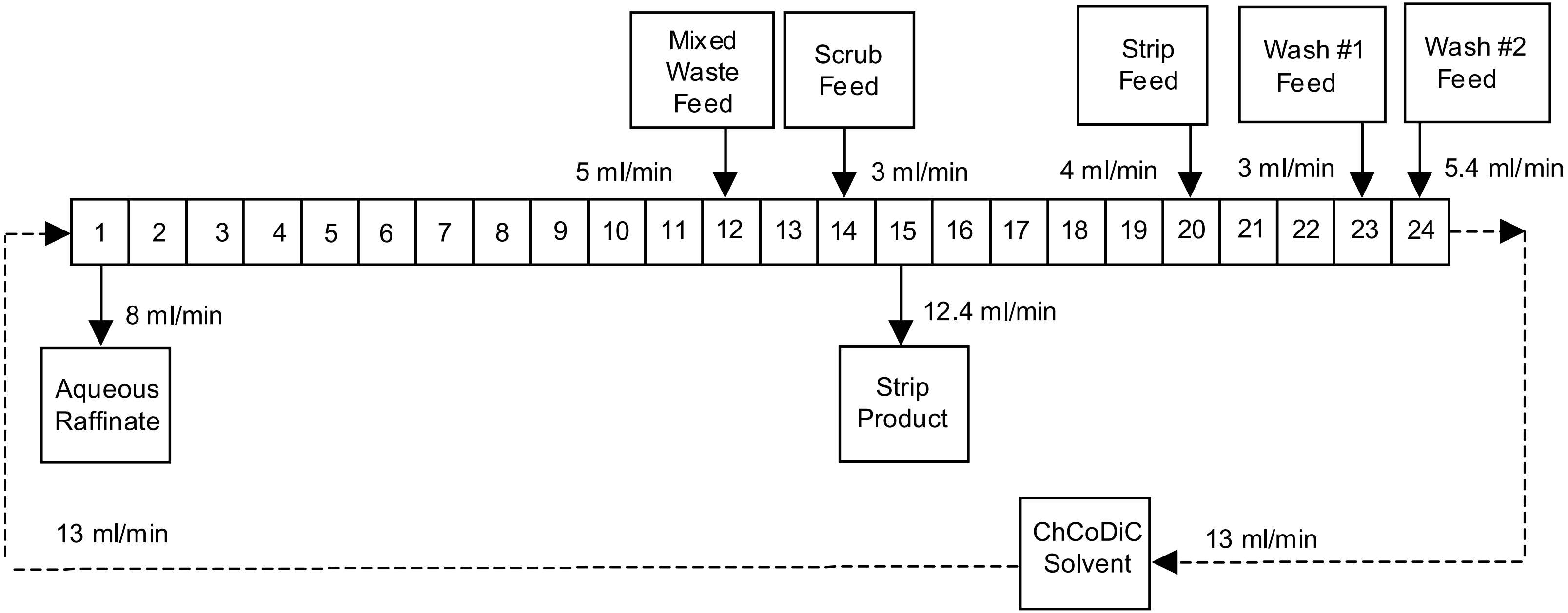

FIGURE 3.3.3 ChCoDiC flowsheet for the treatment of INEEL mixed waste. (Reprinted from *Waste Management*, 19(1), Development and demonstration of solvent extraction processes for the separation of radionuclides from acidic radioactive waste, 17–27, copyright 1999, with permission from Elsevier Science.)

For the ChCoDiC flowsheet demonstration without PEG, a removal efficiency of >99.998% was obtained for ^{137}Cs. Also, 50% of the K, 37.5% of the Hg, 0.7% of the Na, <28% of the Ca, and <40% of the Fe were extracted and exited with the high-activity waste strip product.

Universal Extraction Process (UNEX)

The use of a single liquid–liquid extraction process to remove the desired radionuclides, as opposed to a combination of processes in separate unit operations that remove these same radionuclides in sequential steps, evolved from the previous collaborative work between the INEEL and the Khlopin Radium Institute. The development of a universal extraction (UNEX) process containing ChCoDiC with PEG to remove ^{137}Cs and ^{90}Sr, and a carbamoylmethylphosphine oxide derivative (diphenyl CMPO) to remove the TRUs, was initiated in 1996. Numerous laboratory batch contact tests with simulated and actual liquid and dissolved calcine waste solutions, as well as countercurrent pilot-scale flowsheet testing with simulated liquid waste, have been performed [Law et al., 1999a]. A universal extraction flowsheet has also been demonstrated using actual liquid waste solution in a 2-cm centrifugal contactor pilot plant (Figure 3.3.4.)

For the UNEX flowsheet demonstration with actual liquid tank waste, a removal efficiency of 99.995% was obtained for ^{90}Sr, 99.4% for ^{137}Cs, and 99.96% for the actinides. This is sufficient to reduce the activity of a grout waste form to below the NRC Class A LLW criteria of 0.04 Ci/m^3 for ^{90}Sr, below the NRC Class A LLW criteria of 1.0 Ci/m^3 for ^{137}Cs, and below the NRC Class A criteria of 10 nCi/g for the actinides. With this flowsheet, 87% of the Zr, 98.8% of the Pb, 28% of the K, >99% of the Ba, and 8.3% of the Fe were extracted and exited with the high-activity waste strip product. Aluminum, mercury, and sodium were essentially inextractable.

Summary of Test Results of Liquid–Liquid Extraction Processes

The removal efficiencies obtained for the separation of radionuclides and metals from INEEL acidic mixed wastes are summarized in Table 3.3.1 for comparison purposes. All results presented, with the exception of the TRUEX and SREX results with surrogate calcine, were obtained from flowsheet demonstration with actual, highly radioactive mixed waste. The feed solution for the TRUEX and SREX testing with surrogate calcine was obtained by dissolving nonradioactive pilot plant calcine in 5 *M* HNO_3 at a ratio of 100 g calcine per liter of HNO_3 and a temperature of 90°C.

Other Liquid–Liquid Extraction Processes

Other liquid–liquid extraction processes that have been developed and tested include actinide separation processes based on diethylcarbamoylmethylphosphonate (DHDECMP) and trialkyl phosphine oxide (TRPO) extractants. These extractants belong to the same class of neutral organic compounds as CMPO, but have different extraction characteristics. Research on the DHDECMP process was performed mostly in the 1980s; however, this extractant is no longer produced commercially and there appears to be no further interest in it. The TRPO processes were primarily developed by Chinese and Russian researchers (Song, Wang, and Lian, 1997). French scientists have performed extensive development efforts on bifunctional amides for the extraction of actinides (Nigond et al., 1995). The process is referred to as the DIAMEX process and has the advantage that the process solvent is easily incinerated because it contains no phosphorus component. Americium extraction is not efficient until nitric acid concentrations are quite high (>3 M). This limits the application of the process with americium containing wastes.

Liquid–liquid extraction processes have also been developed for removing cesium from acidic and alkaline wastes using crown ethers and calixarene extractants. The two crown ether extractants that have been utilized for cesium extraction are typically dibenzo-18-crown-6 and dibenzo-21-crown-7. With crown ether extraction processes, the choice of a diluent and/or modifier is extremely important because they have a large effect on complexation reactions. A process utilizing a dibenzo-18-crown-6 derivative was developed at ANL with excellent recovery of cesium; however, the solvent was relatively unstable in nitric acid solutions. Russian scientists have developed a cesium separation process based on

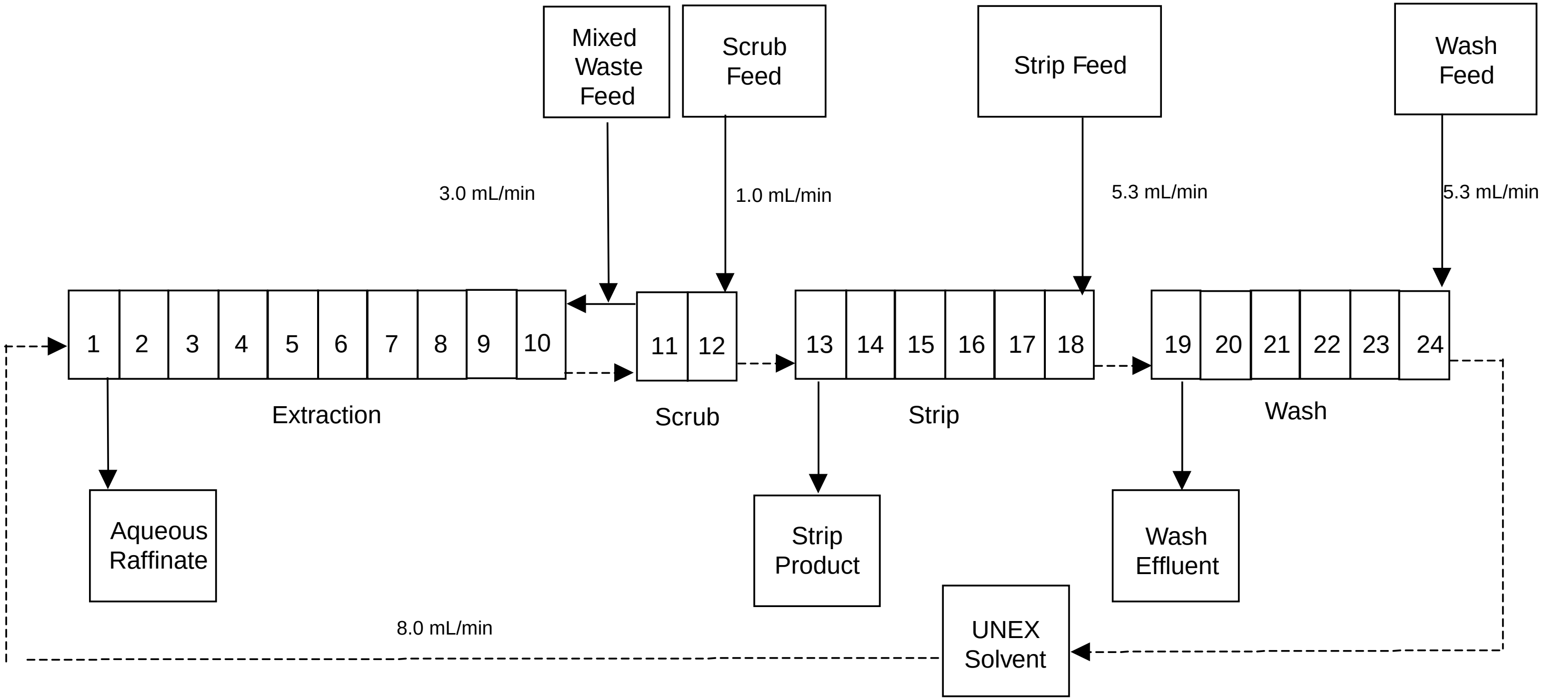

FIGURE 3.3.4 UNEX flowsheet for the treatment of INEEL mixed waste.

TABLE 3.31 Summary of the Removal Efficiencies Obtained from Demonstrations of Solvent Extraction Processes with Actual Acidic Mixed Waste and/or Surrogate Waste

Comp.	TRUEX (liquid waste)	SREX (liquid waste)	ChCoDiC (liquid waste)	ChCoDiC w/o PEG (liquid waste)	UNEX (liquid waste)	TRUEX (surrogate calcine)	SREX (surrogate calcine)
Alpha	99.8%	94.0%	[b]	[b]	99.96%	[b]	[b]
^{241}Am	99.8%	2.0%	[b]	[b]	99.999%	>96.4%	[b]
Pu	99.97%	99.95%	[b]	[b]	99.994%	[b]	[b]
U	99.8%	99.6%	[b]	[b]	[b]	[b]	[b]
^{90}Sr	[b]	99.994%	96.2%	0.09%	99.995%	[b]	99.6%
^{137}Cs	[b]	0.4%	99.3%	>99.998%	99.4%	[b]	[b]
^{99}Tc	89%	[b]	[b]	[b]	[b]	[b]	[b]
Al	[b]	0.4%	0.03%	[b]	0.14%	[b]	<0.5%
B	[b]	<23%	[b]	[b]	[b]	[b]	3.6%
Ba	[b]	63.6%	[b]	[b]	>99%	[b]	[b]
Ca	[b]	5.0%	1.4%	<28%	[b]	[b]	0.007%
Ce	[b]	[b]	[b]	[b]	[b]	>98.7%	[b]
Cr	[b]	[b]	[b]	[b]	[b]	1.1%	<1.7%
Fe	0.7%	1.7%	<2.1%	<40%	6.9%	1.3%	<2.6%
Hg	73.7%[a]	>89.2%	26.4%	37.5%	0.16%	[b]	[b]
K	[b]	31.5%	45.2%	50%	27.9%	[b]	6.4%
Na	0.07%	0.4%	2.1%	0.7%	0.13%	[b]	[b]
Pb	[b]	>94%	98.5%	[b]	98.8%	[b]	[b]
Zr	42%[a]	>82%	<5.8%	[b]	87%	0.01%	<0.25%

[a] Testing of the TRUEX flowsheet, optimized for Hg separation, resulted in 96% Hg removal.

[b] Data were not obtained.

dibenzo-21-crown-7 and a fluorinated alcohol diluent; however, removal efficiencies in a countercurrent process of only about 90% have been achievable with INEEL mixed waste solutions. Recent developments in France and at the ORNL using calixarene extractants have shown very promising results, but the processes are less mature and the extractant costs very high (Bonnesen et al., 1998).

Precipitation Processes

Precipitation processes have been developed from analytical chemistry applications for nearly all TRU elements and fission products. They are typically not preferred for large-scale applications because they are batch processes, require a solid–liquid separation operation after the precipitation step, produce large volumes of waste, and, except for a few select processes, are not able to achieve very high separation factors.

Precipitation of actinides was performed nearly 50 years ago using the $BiPO_4$ co-precipitation process for Pu and Np. This process does not quantitatively remove either element because of solubility limitations, and also precipitates other metals such as zirconium, which forms insoluble phosphates. Oxalates of Pu, Np, and Am are relatively insoluble in 1 *M* HNO_3. However, multiple precipitation steps must be used to meet non-TRU limits and other oxalates (e.g., La, Ca) will also precipitate. Strontium may be precipitated in alkaline solutions by carbonate and, under certain conditions, hydroxide or in weakly acidic solutions by the addition of sulfate ions. The strontium precipitates are all relatively soluble and would require multiple precipitation steps to achieve a high separation factor. Numerous precipitation processes have been demonstrated for cesium, including phosphotungstic acid, ammonium phosphomolybdate, and ammonium phosphotungstate for acidic solutions, as well as sodium tetraphenylborate and nickel hexacyanoferrates for alkaline solutions. With the exception of the tetraphenylborate process, which is capable of decontamination factors of 10^4, the cesium precipitation processes would also require multiple batch precipitation steps. At the current time, the Savannah River site is the only DOE facility evaluating precipitation as a waste treatment process.

Defining Terms

TRUEX process: Liquid–liquid transuranium extraction process.

SREX process: Liquid–liquid strontium extraction process.

Cobalt dicarbollide process: Liquid–liquid cesium and strontium extraction process.

UNEX process: Liquid–liquid cesium, strontium, actinide, and rare-earth element extraction process.

Batch contact tests: Laboratory tests wherein equal volumes of two immiscible phases are mixed and separated, and sampled for solute concentration.

Scrub: A section in a countercurrent liquid–liquid extraction flowsheet where undesired, extracted metals are removed from the solvent.

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Chapter Four

Thermal Treatment Technologies

4.1

Incineration Systems

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Introduction

Incineration has been used by industry since the 1930s to deal with "troublesome wastes" (Cudahy, 1999). At that time, it was developed as a permanent solution for organic industrial wastes that could not be discharged into streams and waterways without noticeable results. With that start, incineration became a process option for industrial wastes, municipal wastes, environmental restoration clean-ups, radioactive wastes, medical wastes, and virtually any organic material that represents an environmental hazard. This chapter section describes several conventional incinerator types, with emphasis on the special issues related to the treatment of radioactive and mixed wastes.

Radioactive waste incineration has been practiced since the 1950s for volume reduction and conversion of slightly contaminated fibrous waste to forms amenable to immobilization (Perkins, 1976). The earliest radioactive waste incinerators were variations on the fixed hearth or controlled air incinerators. These were manual feed/manual discharge systems. In the 1980s, several manufacturers offered radioactive treatment systems based on common incinerator designs for the treatment of wastes from nuclear power stations. With the definition and regulation of mixed waste, the focus has turned to demonstration that these same incinerator designs acceptably address the hazardous and toxic constituents of radioactive waste.

In general practice, incineration is the high-temperature oxidation of a waste material for the purpose of volume reduction, energy recovery, or detoxification. The U.S. Environmental Protection Agency (U.S. EPA) provides a definition in 40 CFR 260.10: "a closed device that uses controlled flame combustion …" This definition has supported the exclusion of some non-flame oxidation systems from the hazardous waste incineration regulations.

Two general introductory topics are briefly covered in this section: the chemistry of incineration and design considerations. These topics support the subsequent specific incinerator discussions by providing general background for the evaluation and selection of specific units for specific applications. The chemistry of incineration topic presents waste oxidation chemistry as the energy content of the materials and the oxidation mechanisms have substantial impact on the selection of a specific incinerator for a task. The second topic, design considerations, details how physical properties of waste affect selection and design of an incinerator.

One of those design aspects is organic destruction efficiency, which is commonly advertised as a performance criteria for an incinerator type. However, it must be recognized that this critical incinerator performance parameter is not solely a function of the primary incineration component. It is controlled by the design and operation of the complete incinerator system; the primary combustion system: the secondary combustion chamber or afterburner, and off-gas treatment system. The U.S. EPA surveyed the performance data from 162 incineration systems in development of the 1999 Combustion Rule. These 162 units all met the applicable destruction and removal efficiency requirements of the Resource Conservation and Recovery Act, at least 99.99% for the tested organic constituents (U.S. EPA, 1995). Therefore, it can be stated that essentially all incinerator types that are designed and operated properly are capable of providing compliant destruction of organic compounds.

Chemistry of Incineration

Basic Combustion Equations

Incineration is defined in general terms as the controlled combustion of organic matter. All organic matter is composed of various elements, including carbon (C), hydrogen (H), oxygen (O), nitrogen (N), sulfur (S), Chlorine (Cl), and other elements. The concentration of each of these elements in the organic matter determines the specific organic compound and its chemical and physical properties that will impact the selection and sizing of an incineration system.

Most analyses of incineration systems can be accomplished based on the laws of thermochemistry and thermodynamics. The reaction mechanisms that occur and the intermediate compounds that form during the combustion process can be very complex. However, the combustion analysis depends predominantly on the initial reactants and the final products of the combustion reactions, and not on the actual path taken to reach the final products. For example, the combustion mechanism for propane (C_3H_8) may be as follows. The propane is first thermally cracked to methane (CH_4) and ethylene (C_2H_6). From these intermediate compounds, the oxidation begins and may first oxidize the organic molecules to carbon monoxide (CO) and subsequently completing the oxidation by converting the CO to carbon dioxide (CO_2). The fact that there were several intermediary products between the propane (C_3H_8) and the CO_2 is generally not significant in the overall analysis of the system thermochemistry.

With this said, environmental regulators have turned their attention from looking at the destruction efficiency of the incinerator to the concentration of the products of incomplete combustion (PICs) from the incinerator and their associated risks to the public. PICs are intermediary organic species and those formed by side reactions in the combustion system. The regulation of PICs from an incinerator plays a significant role in the design of the combustion process to ensure essentially complete destruction of all organic species to form CO_2 and water. In some systems, additional control technologies are added to the gas cleaning system to control PIC emissions to the regulated levels.

The simplest way to evaluate combustion in an incineration system is on a molecular level. As such, one or more of the following generalized reactions may represent the basic combustion reactions:

$$C + O_2 = CO_2 \tag{4.1.1}$$

$$C_3H_8 + 5O_2 = 3CO_2 + 4H_2O \text{ (plus trace CO emissions)} \tag{4.1.2}$$

$$H_2O(l) = H_2O(g) \text{ (liquid to gas phase change)} \tag{4.1.3}$$

$$2C_6H_5NH_2 + 15{}^1\!/_2O_2 = 12CO_2 + 7H_2O + N_2 \text{ (plus trace NO and } NO_2 \text{ emissions)} \tag{4.1.4}$$

$$C_6H_5Cl + 7O_2 = 6CO_2 + 2H_2O + HCl \text{ (example of chlorinated organic)} \tag{4.1.5}$$

$$Cl_2 + H_2O = 2HCl + {}^1\!/_2O_2 \text{ (equilibrium reaction)} \tag{4.1.6}$$

$$S + O_2 = SO_2 \text{ (plus trace } SO_3 \text{ emissions)} \tag{4.1.7}$$

Note that these reactions show sufficient oxygen to complete the oxidation of C to CO_2. If there is insufficient air or oxygen present, only partial oxidation (e.g., C to CO, etc.) will take place. As discussed previously, partial oxidation can result in higher levels of PICs. However, a number of systems are designed to meet the emissions standards operating in the pyrolytic mode in the primary combustion chamber and completing the oxidation in the secondary combustion chamber.

The carbon component of organic waste can be either as a volatile or fixed carbon. The volatile portion of the organic is vaporized in the combustor at temperatures less than 800°C. For example, turpentine represents the condensed volatiles from the destructive distillation of wood. The volatiles are combusted either immediately, as is the case with an oxidative combustion chamber, or are carried away with the flue gas into a secondary combustion chamber (SCC) for oxidation in the gas phase. The fixed carbon is the non-ash residue that remains in the waste after the volatiles have been driven off. Typically, the fixed carbon consists almost entirely of combustible carbon. Coke and charcoal are typically encountered forms of fixed carbon. The fixed carbon is more difficult to oxidize and can be the limiting design parameter for solid residence time in solid waste incineration.

The amount of fixed carbon in waste can be an issue in the selection and design of an incineration system. For example, when processing wastes in a fixed hearth furnace, very little of the fixed carbon is typically oxidized. This could result in an ash material with a high loss on ignition (LOI) measurement, and analysis of residual combustible material in the ash. In some applications, the LOI of the ash residue from the combustor is a design and performance requirement mandated either by the client or a government regulatory agency. High residual carbon in the ash may be detrimental if ash immobilization is planned, as is the case for most mixed waste applications. Many of the immobilization agents are sensitive to carbon content.

Inert matter, also referred to as ash, in the waste feed to the combustor essentially passes through the combustion process either unchanged or is converted to solid oxides or salts. Depending on the physical form of the waste, the ash can be exhausted from the combustor as particulate matter (called particulates or fly-ash) in the flue gas or discharged from the combustion chamber as bottom-ash. The quantity and physical form can have substantial impact on system selection, as some systems can process noncombustible items such as metal parts, whereas other systems would simply accumulate these items until shutdown. Ash constituents also significantly impact the design of the incineration system. For example, wastes containing sodium, potassium, and silicon in the necessary proportions could soften, melt, and agglomerate in systems when the ash is raised to high temperatures. If the selected system is a “slagging” unit or a melter design, then the melted ash is easily processed. Ash softening in non-slagging systems can lead to process plugging and eventual shutdown for removal.

The flue gas from a combustion system designed to process solids and sludges will typically contain particulates. These particulates will be ash or unburned organic material that is entrained in the flue gas. Depending on the type of combustion system, the entrainment of the ash in the flue gas could be 5 to 20% of the ash in the waste feed.

Particulates in the flue gas will also result from the combustion of liquid wastes in a burner or the atomization of liquids in the combustor. Almost all of the inert material in the liquid wastes atomized in a combustion system will result in particulates in the flue gas. The particulates from the atomization of liquid wastes in a burner are typically the most difficult to treat and remove in the downstream gas cleaning system because of their tendency to form submicron-sized particulates. Because of the high flame temperatures in liquid waste burners, these particulates may be in a melted form, which also challenges system design.

Trace Emissions

The combustion of waste materials will almost always result in a flue gas that contains low concentrations of various pollutants. Many of these trace emissions are regulated and therefore must be controlled. The primary control method is to minimize the initial formation of the pollutant with specific designs of the combustion system. Gas cleaning technologies are then added downstream of the combustion process to remove the remaining pollutants before the flue gas is exhausted to the atmosphere. Some of the more frequently encountered trace emissions include HCl, SO_2, NO_x, CO, particulates, metals, and PICs.

Trace emissions can be the result of a number of factors, including the combustion technology selected, the design of the combustion system, the presence of pollutant progenitors in the feed, and the system operating conditions. Carbon monoxide, for example, is typically formed in the combustor due to low combustion temperatures, poor mixing, insufficient excess air, or very short residence times. The trace emissions can also be formed in the downstream equipment, such as in an energy recovery boiler. Off-gas treatment systems and boilers that provide long residence times within a certain temperature range can promote the formation of various trace emissions such as polychlorinated dibenzo-dioxins (PCDD) and polychlorinated dibenzo-furans (PCDF). Much work has been done to study the formation mechanism of dioxins from combustion systems. Data has shown a direct relationship between the residence time of the gases at intermediate temperatures after the combustion chambers and the concentration of dioxins in the flue gas. (Acharya, 1999).

Typical Combustion Gas Composition

The typical composition range of the gases from the combustion of waste in an incinerator is illustrated in Table 4.1.1. The compositions shown in this table are for the gas leaving the combustion system and entering the downstream off-gas cleaning system. It should be noted that the flue gas composition is directly related to the waste feed materials and operating conditions of the incinerator.

TABLE 4.1.1 Typical Secondary Combustion Chamber Off-gas Composition and Conditions

Off-gas Constituent	Range
Nitrogen (N_2)	60–85%
Water vapor (H_2O)	6–30%
Carbon dioxide (CO_2)	5–15%
Oxygen (O_2)	3–14%
Acid gas (HCl)	0–100,000 ppm_v
Acid gas (SO_2/SO_3)	0–100,000 ppm_v
Nitrogen oxides (NO_x)	15–300 ppm_v
Carbon monoxide (CO)	0–100 ppm_v
Particulates	20–24,000 mg/dscm

Note: All values in above table except water vapor are on a dry gas basis.

Design Considerations

Incinerator selection is actually the specification of a complex array of interrelated components, of which the primary combustion chamber is only one part. A complete incineration system is typically composed of the following components:

1. Waste receipt system to confirm compliance with the waste acceptance limits and capabilities
2. Waste feed storage and preparation (tanks for storing and blending liquid wastes; pits or storage buildings for solid wastes; shredders and other size reduction operations for solid wastes; tanks and special pumps for processing sludges and thick liquid wastes; etc.)
3. Primary combustion chamber selected to address the waste type, quantity, and composition (rotary kiln, fixed hearth, etc.)
4. Secondary combustion chamber or afterburner to complete oxidation of gases and comply with emission requirements for unburned hydrocarbons (the secondary combustion chamber can also be used for liquid waste incineration)
5. Ash removal system to remove ash and non-combustibles from the primary chamber, and cool it for subsequent handling and treatment
6. Ash and non-combustibles treatment system for immobilization or other treatment required to meet disposal site requirements
7. Gas cleaning system to control particulate, acid gas, and other emissions
8. Energy recovery (e.g., steam generation) and plume suppression may also be included in the design of an incineration system
9. Utility systems providing power, water, and process consumables

In the primary and secondary combustion systems, complete oxidation of waste is achieved by close attention to the “3 Ts” of incineration design: Time, Temperature, and Turbulence. Sufficient air or oxygen must be intimately mixed (turbulence) with the organic material to complete the oxidation, with sufficient reaction time (time) available to complete the oxidation reaction. As discussed, this time factor is relevant to both the incineration of volatiles in the gas phase and the fixed carbon remaining in the solid phase. As for temperature, the oxidation reaction is generally faster at higher temperatures, but higher temperatures can lead to melting of noncombustibles and residuals. Designers must also focus on providing adequate turbulence in solids combustion systems as that has been found to be a more difficult design factor than time and temperature on the destruction of volatile organics in an incinerator (Lee, 1988).

Impact of Waste Types

A key aspect to the selection and operation of an incineration system is the nature of the wastes and how they can be prepared and fed to the combustion system. In general, designers strive to provide the incinerator a waste feed that is uniform in size, composition, and feed rate. This leads to controlled, steady operation and high oxidation efficiencies. In the subsequent discussions of specific incinerators, the particular waste types appropriate for each incinerator design are indicated.

Gaseous Waste

Vapors from process vents and other such sources can be treated by incineration. Technologies other than incineration for handling this type of waste stream include adsorption on activated carbon, chemical absorption in packed towers, UV photolysis, and flameless thermal oxidation.

Liquid Wastes

Liquids are normally atomized or sprayed into a high-temperature combustion chamber for complete oxidation. If the liquids have sufficient heat content, 3×10^6 to 4.5×10^6 cal/kg (5000 to 8000 Btu/lb.), they are fed through a burner and can supply the heat or ignition source to support incineration of other less energetic wastes such as aqueous liquids or sludges. These high-energy liquid wastes can be fired in either a primary or a secondary combustion chamber, depending on the energy requirements in those subsystems. Alternatively, waste solvents or oils with higher heating values can be mixed with other low-energy wastes to provide a blend appropriate for good combustion.

The viscosity of wastes fired through a burner must be low enough for proper atomization in the burner. Liquids with viscosities below 750 SSU (165 centistokes) can be atomized, but proper atomization can only be achieved by many burners when the liquid viscosities are below 100 SSU. Blending of the wastes is frequently used to meet the viscosity requirement. Nozzle openings for burners are small, so strainers are necessary in most waste liquid systems to prevent plugging. Nozzle selection is specific to the liquid properties to ensure proper atomization and combustion.

Aqueous Wastes

Aqueous wastes and other liquids with low heat values are frequently atomized through “slave” or secondary atomizers located near the primary burner or other heat sources where the aqueous waste is evaporated and organic contents oxidized. Aqueous wastes are sometimes used to provide a “heat sink,” a way to help control the temperature within the combustion system when high-energy wastes are being burned.

Solid Wastes

Solid wastes can be fed to incinerators in large packages or shredded and metered into the primary chamber. The mechanical reliability of the solids feed system can become a process-limiting parameter for incineration system operation and particularly important for mixed waste systems. Therefore, much effort is spent on evaluating and designing the receiving, storage, preparation, and feeding of solid wastes. Solids can be received in bulk, boxes, drums, and other containers of varying sizes. The preparation (size reduction, mixing, and blending) of these solids is critical for successful system operation.

For many incineration systems, it is advantageous, and frequently necessary, that large solids be size reduced by shredding in order to be fed to the system and properly combusted. Smaller sized solids are more easily oxidized than larger materials. Containers, such as drums, are generally emptied and/or shredded before being fed. Large rotary kilns and fixed hearth incinerators can be designed to accept drums and large packages. However, design and feed composition limits must be imposed on these packages to avoid overpressures in the system or the release of incompletely oxidized organics.

To address the issue of feeding solid wastes of varying composition and energy contents, most applications require waste screening and blending. Because of differing energy and volatiles contents, solid wastes may also need some level of blending. For example, a sudden change in the feed from a slow burning, low heat value wet waste to a rapid burning, high heat value plastic waste could challenge control systems to maintain proper incineration conditions and subsequently impact the gas cleaning system performance.

Sludges

The term "sludge" can refer to any waste that is viscous or that contains too much solid to be considered a liquid waste, yet which is too fluid or sticky to be handled as a solid waste. Sludges are stored in tanks, pits or drums and are fed to the incinerator using special equipment (pumps, extruders, or conveyors) designed to handle dense materials containing relatively large solid particles. Blending with other liquid wastes to modify handling properties is also a common production process. These wastes may have high or low heating values. One design challenge for sludge incineration is proper atomization or dispersion in the incinerator to ensure good drying and combustion.

Combustion Efficiency

As discussed, one object of incineration is to volatilize and oxidize the organic constituents in the waste. Volatilization is enhanced by the atomization of liquids and by the high temperatures achieved by the burning process. The remaining fixed carbon oxidation is a much slower process than the gas-phase oxidation of the volatiles. An element of incinerator design is proper primary chamber operating temperature, residence times, and sufficient air/waste contact to support combustion of the fixed carbon.

Complete oxidation of volatile organic components is not always achieved in the primary combustion chamber, especially in rotary kiln systems where combustion air is seldom introduced into the system in such a manner as to pass through the bed of waste material. For this reason, afterburners or secondary combustion chambers (SCCs) are used in many incineration systems to complete the oxidation of the organic materials that were vaporized and/or partially oxidized in the primary combustion chamber.

A well-designed SCC achieves good turbulence by mixing the primary chamber off-gases with additional combustion air to complete the oxidation process. The temperature in the SCC is frequently higher than the temperature achieved in the primary chamber because the temperature in the primary chamber is controlled to minimize melting or slagging of the solids and ash residues. Slag can plug air inlets, form dams that hold back solids, chemically attack the refractory, and create other problems in the combustion system. An exception to this design practice is for those incineration systems that are designed to operate at high temperatures in the "slagging" mode to melt and glassify the ash that is discharged. Although laboratory data indicates that complete volatile organic oxidation can be achieved in less than a second under good mixing conditions with a high enough temperature, many incineration systems are designed to provide a minimum of a 2-second retention time of the gases in the SCC (based on off-gas conditions).

The design of the SCC is primarily based on achieving good mixing of combustion air with the primary off-gases. The SCC can be "upfired," a vertical system in which the primary off-gases enter at the bottom and SCC off-gases exit at the top. Downfired and horizontal SCCs are also used. Slagging can also occur in the SCC because of solids entrainment from the primary off-gases and ash melting (from ash constituents in the liquid wastes being fired). Vertical SCCs are typically used in these applications to allow the slag to flow down and out of the SCC. Where slag can flow out, the bottom of the SCC must be designed for the removal of this material.

Controlled Air Combustion

The quantity of air introduced into a combustion chamber is controlled. The dual function of air in the incinerator is to provide both oxygen for combustion and cooling/temperature control for high-energy wastes. Too much air will lower the combustion temperature and reduce combustion efficiency. Too little air can result in higher temperatures than desirable for the combustion chamber or insufficient oxygen to complete the oxidation of the waste materials.

A combustion system that is operated "controlled-air" is sometimes referred to as a pyrolytic, starved air, or substoichiometric operation. A primary combustion chamber that is operated with excess air is typically referred to as oxidative operation. In all cases when controlled air combustion is used, there is at least one additional oxidation stage (secondary combustion chamber) to complete the oxidation of the organics, carbon monoxide, and hydrogen.

Controlled air combustion has been used in the incineration industry to optimize the combustion process for the treatment of solid and sludge wastes and also to control NO_x emissions. The combustion air and operating temperatures are controlled in the primary combustion chamber to dry wastes and drive off volatiles at a controlled rate. As the name implies, it is important in a controlled air combustion system to limit the amount of air that is allowed to enter the primary combustion chamber and react with the organics. There are several benefits to operating with controlled air combustion, including:

1. The dual temperature regimes between the primary and secondary chambers facilitate good organic destruction at the high-temperature secondary chamber while avoiding melting of ash and non-combustibles in the lower-temperature primary chamber.
2. Energy released from the partial combustion and volatilization of the waste in the first stage combustor is less than if the wastes were completely incinerated.
3. The volume of flue gas exiting the first stage combustor is reduced because the amount of combustion air is less than that required for complete oxidation of the organics.
4. Flue gas from the first stage combustor will include partially oxidized compounds such as carbon monoxide and hydrogen gas that provide significant energy to increase the temperature of the flue gas up to the operating temperature of the SCC.
5. The volume of flue gas exiting the SCC in a controlled air combustion system can be significantly less than the flue gas from a similarly designed oxidative system. The amount of reduction depends on the quantity of volatile organics in the waste. The more volatiles in the waste, the greater the reduction in flue gas volume. This is because in the controlled air combustion system, many of the volatiles in the solid and sludge wastes are not burned until they reach the SCC, where they are oxidized and the energy is released.
6. Flue gas exiting the primary combustion chamber contains very little oxygen. Typically, at temperatures above 650°C, any oxygen that enters the flue gas will react immediately with volatile organics. With the amount of oxygen controlled in the primary and secondary combustion chambers, side reactions are greatly reduced. For example, controlled air combustion is used to limit the formation of NO_x emissions in combustion processes.

Control of combustion air is also a significant design parameter for mixed wastes containing toxic metals. Common mixed waste contaminants include toxic heavy metals such as arsenic, mercury, lead, and chromium. If an incinerator is operated at high temperatures, the quantity of heavy metal vaporized from the ash and leaving the combustor in the exhaust gas tends to be higher relative to a system operating at a lower temperature. These metal emissions must then be removed by additional components in the gas cleaning system.

Essentially, all incineration systems are operated under a slight negative pressure so that air leaks into the system rather than having partially oxidized vapors and particulates leaking out. This is especially important for mixed waste incinerators where the particulate matter may be radioactive. Therefore, control of air infiltration must also be considered in the design of waste feed and ash removal systems.

Incinerator Sizing

Incineration systems are sized primarily according to the amount of heat released in the combustion chambers. Approximately one cubic meter ($1\ m^3$) of combustion air is required for each 890 kilocalories (kcal) of heat released by the burning of waste and auxiliary fuels (North American, 1965). Thus, a specific volume of combustion off-gas is generated for a specific quantity of heat released, with relatively small variations caused by water evaporation and other constituents. The gas cleaning system and other downstream unit operations are sized according to the volume of off-gas generated, and are therefore sized in relation to the amount of heat released.

The turndown capability of an incinerator to operate at less than the design feed/energy input rate is an important design and system selection consideration. An incinerator operates most efficiently near its design conditions. Some incineration systems can be operated at about 50% of their design, depending on the type of incinerator. The requirement to run at less than design capacity may be costly from an energy perspective. Most incineration systems are designed to operate 24 hr a day, rather than being operated for only a portion of a day or week. This avoids the time loss for programmed heat-up and cool-down of the refractory lining.

Conventional Mixed Waste Incineration Systems

The following subsections present general design concepts on a few specific conventional incinerator types with a focus on those used for mixed waste incineration. The principal design differences between conventional and radioactive/mixed waste incineration systems are in two areas. The combustion chambers must be of designs that preclude fugitive emission of radioactive particulate matter. For this reason, many of the simpler incineration designs for municipal waste have not found favor in the radioactive/mixed waste arena. A second feature that drives system selection is the need for a low carbon residual ash. The ash from a radioactive waste processing system is generally immobilized prior to disposal. Many solidification agents are sensitive to residual carbon, so the incinerators themselves must provide a low carbon ash.

Table 4.1.2 provides a brief introduction to the applications and issues of the selected incinerator types.

TABLE 4.1.2 Mixed Waste Incinerator Types and Applications

Incinerator Type	Waste Types Accepted	Applications
Liquid injection	Liquids	Small or large industrial
Fixed hearth	Packaged solids in primary chamber and liquids in secondary chamber	Used for small packaged mixed waste applications
Rotary kiln	Liquids, sludges, solids	Used on large mixed waste applications with multiple waste types
Fluidized bed	Liquids, sludges, shredded solids	Specialized applications in High Level Wastes
Multiple hearth	Sludges, solids	Potential waste applications identified
Car-bottom furnace	Large metallic solids	Potential waste applications identified

Liquid Injection Incinerators

A liquid injection incineration system is generally the simplest of combustion systems, as it can be a single burner mounted in a refractory combustion chamber (Aident, 1998). Liquid wastes are also fired in the primary and secondary combustion chambers of other incineration systems. A liquid incineration system is typically used when other waste treatment or disposal options are unavailable or when the liquid wastes may be problematic for other treatment systems. Liquid wastes with relatively high concentrations of halogens or ash, for example, may not be acceptable for boilers or cement kilns. Figure 4.1.1 is a schematic of a typical liquid injection incinerator.

Because of the high temperature of a burner flame, the “ash” (metals, salts, etc.) constituents in the liquid wastes can vaporize as the liquid is burned. The ash vaporization, however, depends on the ash elemental composition. The condensing of these vapors will result in submicron particulate that must be considered in the selection and design of a gas cleaning system. Alternatively, the ash in the waste liquid could melt and form sticky particulate that could adhere to the walls of the combustion system

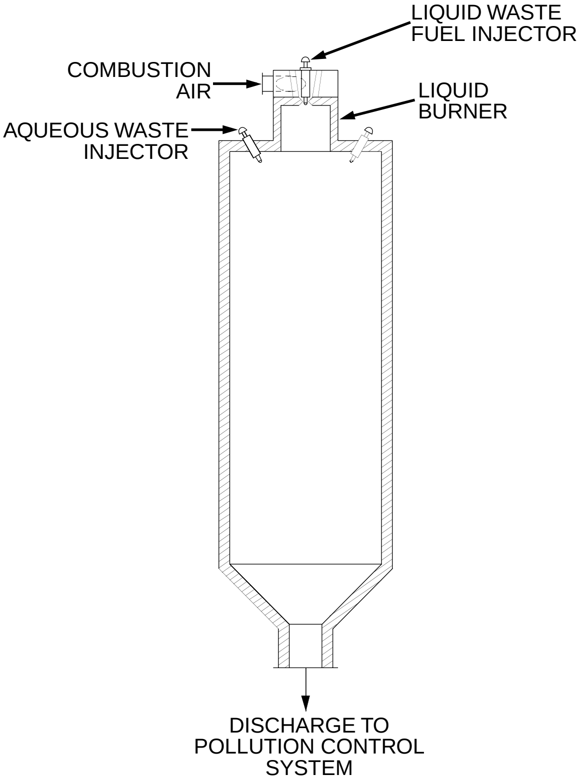

FIGURE 4.1.1 Liquid injection incinerator schematic.

or on the walls and other components of the gas cleaning system. The ash can also form eutectic mixtures that attack, weaken, and ultimately destroy the incinerator refractory.

Larger liquid incineration systems frequently have multiple burners. At least one of the burners will be fired with good fuel value liquids, but the other burner(s) may be firing wastes that will not independently support a flame. The primary burner may be fired with auxiliary fuel. The secondary burners, sometimes called "slave burners," may be processing aqueous wastes or poor-quality burner fuels. The atomization of these wastes in the combustion chamber enhances the evaporation of the water component and provides for destruction of the organic species.

Unlike most other incineration systems, liquid incineration systems can be designed to operate under pressure. One type of liquid incineration system is a down-fired unit where the burner is mounted on top of a vertical combustion chamber and the bottom of the chamber is submerged several inches in a water sump. As the combustion off-gases pass through the water in the sump, they are quenched to their adiabatic saturation temperature. The gases then pass into the gas cleaning system. It is not unusual in this type of system for the combustion air blower and combustion chamber to operate at pressures as high as 1.3 atmospheres, thereby providing the motive force for flow through the gas cleaning system and eliminating the need for an induced-draft fan.

Table 4.1.3 lists the advantages and disadvantages of liquid injection incinerators.

Fixed Hearth (Controlled Air) Incinerators

In the development of incinerators, the simple fixed hearth has occupied a continuing role for small applications, including mixed waste. One of the simplest fixed hearth incinerators is a rectangular, refractory-lined chamber (firebox) where a door is opened and waste is manually placed onto the floor of the firebox. The door is closed and a burner is turned on to heat up the firebox to temperatures in the range of 1000°C (1800°F). With the firebox at temperature, air is injected into the firebox from the

TABLE 4.1.3 Liquid Injection Incinerators: Advantages and Disadvantages

Advantages	Disadvantages
Efficient method for disposal of liquid wastes, especially hazardous waste solvents	Limited to liquids that can be atomized or sprayed through burner nozzles
Very simple design	The high temperature in the liquid burner flame can melt the ash and impact gas cleaning system performance and refractory life
Low maintenance	

sides and from beneath the bed of solid wastes. In many fixed hearth incinerators, the amount of air injected into the firebox for combustion with the wastes is controlled to be less than stoichiometric. The low air flow is intentional, resulting in very low gas flows from the combustor and therefore low particulate entrainment.

During the initial stages of waste incineration, the off-gases will contain a certain amount of unburned or partially oxidized organics. These gases are then treated in a secondary combustion chamber (SCC) to complete the oxidation of the organics. As the wastes continue to burn, there is a time in the batch process when the amount of air injected into the firebox exceeds the air required for combustion, resulting in a drop in temperature. When the temperature starts to drop, the burner automatically comes on to maintain the system temperature. Once the solids have completely burned out, the incinerator is allowed to cool down and, when safe, the door to the firebox is opened and the ash is removed manually.

Because fixed hearth incinerator technology limits the amount of air injected into the firebox, the technology is also referred to as a controlled air incinerator. Additionally, many of these systems are relatively small and easily shop-fabricated for shipment to the site. As such, these fixed hearth incinerators have become more commonly referred to as "modular controlled air incinerators." Figure 4.1.2 is a schematic of a common design that has been configured for continuous operation.

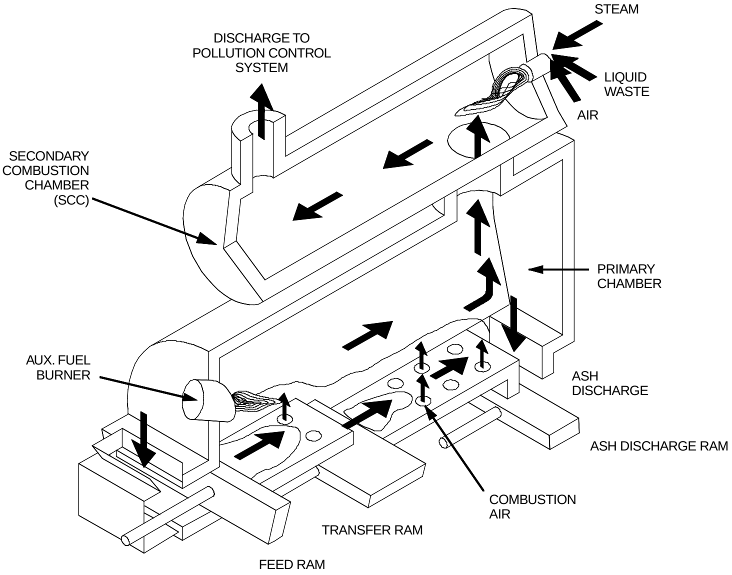

FIGURE 4.1.2 Fixed-hearth incinerator schematic.

As seen in Figure 4.1.2, packaged waste is fed into the primary chamber through a charging door to the feed ram. In this nonturbulent area, the packaged waste heats up relatively slowly and volatiles are driven off at a controlled rate. Because the primary chamber is operated in an oxygen-deficient mode, the gases leaving the primary chamber are combustible and are ignited when contacting excess air in the secondary combustion chamber. In continuous operation, the primary chamber is maintained at a relatively low temperature throughout the feeding operation by injecting more waste when the chamber temperature gets too high. Because of the substoichiometric conditions, adding more waste cools the chamber and reduces the temperature. A supplemental fuel burner controls the secondary chamber temperature. The fixed carbon material remaining in the primary chamber must be periodically burned off by ceasing feed and allowing the chamber to slowly advance from oxygen deficient to oxygen rich. In this fashion, the fixed carbon content of the ash is reduced, although not to the same level that is commonly achieved by systems with agitation and mixing of the solids in the primary chamber.

In one fixed hearth application processing mixed waste, the waste is packaged and fed to the firebox via a ram. The bottom of the firebox is sloped to two augers that continuously convey the solids and ash from the firing end of the unit to the ash end. The solids' residence time in the incinerator is approximately 16 hr allowing for complete oxidation of all organics and fixed carbon in the waste. This system was designed in Denmark by Studsvik and is now being used by GTS Duratek in Oak Ridge, Tennessee to treat low-level radioactive contaminated waste.

The advantages and disadvantages of fixed hearth incinerators are listed in Table 4.1.4.

TABLE 4.1.4 Fixed Hearth Incinerator: Advantages and Disadvantages

Advantages	Disadvantages
Accepts packaged waste and still provides well-oxidized off-gases	Batch operation may require periodic cooling for manual ash removal
Inexpensive simple design, commonly shop-fabricated	Low throughput leads to high unit treatment cost
Low particulate emissions	Ash quality typically not as good as other incineration technologies

Fixed hearth incinerators have historically been used in applications where the quantity of waste is relatively small. These systems have been used to treat medical waste, trash, rubbish, garbage, and pathological human and animal remains. Several companies market this technology, including Consutech Environmental Systems, Inc., Richmond, Virginia; Incinerator International, Inc., Houston and Trecan Combustion, Inc., Halifax, Nova Scotia.

Rotary Kiln Incinerator

The rotary kiln is a mature and established high-temperature solid processing technology. One of the first commercial applications for the rotary kiln was for the processing of ores. They are extensively used around the world in the manufacture of cement. The Dow Chemical Company transferred the knowledge base for the design and operation of rotary kilns in these industries to the processing of solid wastes in the late 1950s. Since that first rotary kiln incinerator, the rotary kiln has demonstrated good, long-term, reliable operation on waste streams that include industrial waste, municipal trash, hazardous, mixed and radioactive wastes, and contaminated soils. For example, in the thermal remediation of soils, the rotary kiln design has processed more wastes than all other technologies combined.

The kiln is a refractory-lined rotating cylinder installed at a slight slope (typically between 1 and 3°). The primary combustion chambers are frequently sized with a 3:1 length:diameter ratio, but longer rotary kilns are specified when excess moisture from wet wastes is present or there is an excess of slow-burning fixed carbon. Figure 4.1.3 provides a schematic of a common rotary kiln configuration.

Rotary kilns are used in the waste processing as the primary (first stage) combustion chamber for liquids, solids, and sludges. Combustion gases and volatilized wastes are then treated in a downstream secondary combustion chamber. The kiln is typically operated at relatively high temperatures, 700 to 1300°C (1300 to 2400°F). Tumbling action in the kiln continually exposes fresh waste surface to the high-

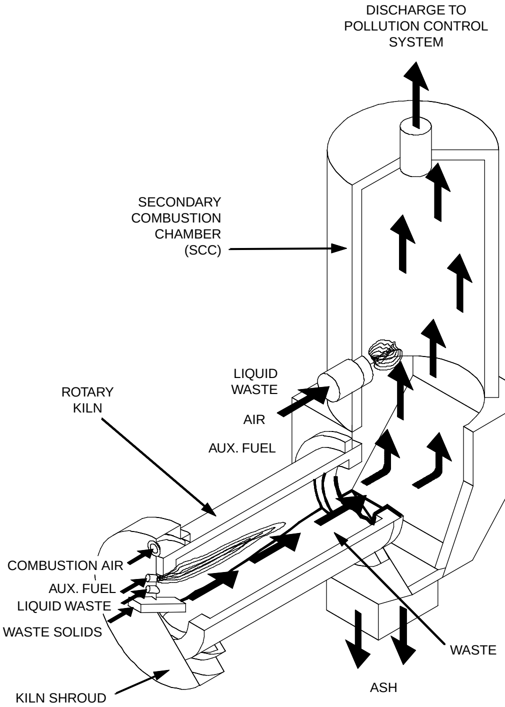

FIGURE 4.1.3 Rotary kiln incinerator schematic.

temperature radiant heat from the burner and refractory walls and to the oxygen in the combustion air. Rotary kilns do not require internal moving parts because of the intrinsic solids-conveying capability of the inclined rotating cylindrical chamber. Ash is continuously discharged into an ash handling system. Combustion products and volatilized organics are exhausted from the rotary kiln into a secondary combustion chamber where gas-phase oxidation reactions are completed. Seals are provided at both ends of the kiln shell to minimize air in leakage. In mixed waste applications, particular attention must be given to design and maintenance of these seals to minimize the potential for fugitive emissions or radioactive particle release.

There are several types and configurations of rotary kiln incinerators, each providing specific operating advantages and disadvantages. These general categories include:

- Co-current or countercurrent
- Ashing or slagging
- Controlled air or excess air

Co-current or Countercurrent Design

In a co-current (sometimes called parallel flow) kiln, combustion gases and wastes travel in the same direction. In countercurrent kilns, combustion gases travel in the opposite direction to the wastes. Typically, counter-current kilns are used in applications where the burning of organics in the waste can be used to evaporate moisture. As the hot flue gas travels through the kiln, it passes over the wet waste, transferring some of its heat to the solids. Careful attention must be placed on the rotary kiln design to ensure that the wastes do not melt and cause conveying problems for the waste and ash.

Countercurrent kilns allow for independent control of the ash temperature exiting the kiln in applications that require specific ash temperatures. The co-current kiln ash temperature is typically about the same as the temperature of the kiln off-gas. A key advantage of the co-current kiln is that the feed systems are at the cool end of the kiln where the materials of construction and system design are typically not as difficult. Additionally, in a co-current kiln, any air in-leakage to the kiln from the solids feed system can be used for waste combustion. In the countercurrent kiln, the air in-leakage through the waste feed system is immediately exhausted out of the kiln and into the downstream equipment.

Ashing or Slagging Operation

In an ashing kiln, inert material in the waste (ash) is heated to temperatures sufficient to achieve the required ash quality without melting the ash. Properly designed ashing kilns produce a hot, dry, free-flowing, low-carbon, friable ash. In an ashing kiln, the organics can be oxidized from the waste but the metals may remain in the ash. If the metals that remain in the ash after treatment do not pass the relevant leachate tests, then additional processing will be required to stabilize the metals.

Slagging kilns must operate at higher temperatures and typically must use additives to melt the inert waste materials to form a molten slag pool in the kiln. These additional reagents for the slagging kiln will add to the quantity of ash that is ultimately landfilled. A slagging kiln is typically operated at temperatures in the range of 1100 to 1300°C (2000 to 2400°F), in comparison with an ashing kiln, which typically operates in the range of 700 to 900°C (1300 to 1650°F).

Controlled Air and Excess Air Operation

Rotary kiln incinerators can be designed to operate either in a controlled air or excess air mode. The advantages and applications of these modes of operation were previously discussed for the fixed hearth incinerator and apply equally to rotary kilns.

Rotary kilns are the workhorse of the hazardous waste incineration industry because they can accept solid, liquid, and sludge wastes in a single-unit operation. In some large commercial incineration systems, 200-L drums filled with waste can be fed into the rotary kiln. Design for injection of whole drums into the rotary kiln is a challenge, both mechanically and operationally. The operational challenge is to maintain good destruction conditions with the instantaneous input of energy from the volatilization and subsequent combustion of the wastes. Additionally, the drums could damage the refractory as they fall into the kiln. The U.S. Department of Energy operates rotary kiln mixed waste incinerators at the Oak Ridge and Savannah River sites.

Table 4.1.5 provides a listing of the advantages and disadvantages of rotary kiln incinerators.

TABLE 4.1.5 Rotary Kiln Incinerators: Advantages and Disadvantages

Advantages	Disadvantages
Accepts all waste forms	Kiln seals must be carefully designed and maintained
Large continuous systems are economical	Not amenable to routine cycling
Well-developed technology	

A number of companies design and fabricate rotary kiln incinerators, including Vulcan Iron Works, Inc., Wilkes Barre, Pennsylvania, Svedala Industries, Inc., Waukesha, Wisconsin; ABB, Inc. Norwalk, Connecticut, and Von Roll, Switzerland.

Fluidized Bed/Circulating Bed Incinerators

Fluidized bed furnaces were first developed for catalyst recovery in the oil refining industry in the early 1940s as a process operation that provided excellent mixing and good air/solids contact (Kunii and Levenspiel, 1991). Subsequently, fluidized beds were developed and marketed for sludge incineration (Brunner, 1991) and have since found application in the waste market for both waste destruction and energy recovery. Freeman (1988) reported that over 1000 fluidized bed combustion units are operating worldwide, with 20 of them destroying hazardous and toxic wastes. The Amoco fluidized bed incinerator at Whiting Indiana has destroyed hydrocarbon wastes for 26 years and operates with 98% availability (Bunk and D'Acierno, 1999). In the 1970s, two fluidized bed systems were developed and offered to commercial power stations for volume reduction of radioactive wastes. More recently, fluidized bed gasification systems have been offered.

Two fluidized bed configurations have been used in waste applications: the classical bubbling bed and the circulating bed design. Classical bubbling bed designs generally include a primary combustion area, the dense-phase fluidized bed, and a secondary combustion zone that provides for secondary combustion and bed medium disengaging. Circulating bed designs use a dilute-phase fluidized bed for the primary chamber, and may include a secondary combustion chamber after a cyclone separator.

Fluidized bed operation is best described by considering the action of the bed of sand-like medium when fluidizing air velocity is slowly increased, starting at a very low value. Figure 4.1.4 shows the expected pressure differential measurements as the air flow is increased. At low air velocities, the bed medium acts as a fixed bed of solids and air simply flows between the particles. The linear region of Figure 4.1.4 is that of a pressure drop for gas flow through a packed bed of solids (packed bed region). As air velocity increases, it reaches the point where the bed particles are actually supported by the air. Pressure differentials across the bed medium at that point are such that the entire weight of the bed is supported by the fluidizing air. In appearance, the bed may initially make a slight movement as the smaller bed particles move to fill voids. After this initial movement, the bed remains static and there is no physical growth in size, although the bed particles can be seen to be vibrating in place. In this state, the medium would yield to the touch and a heavy object dropped on the bed would sink to the bottom. This point is called incipient fluidization.

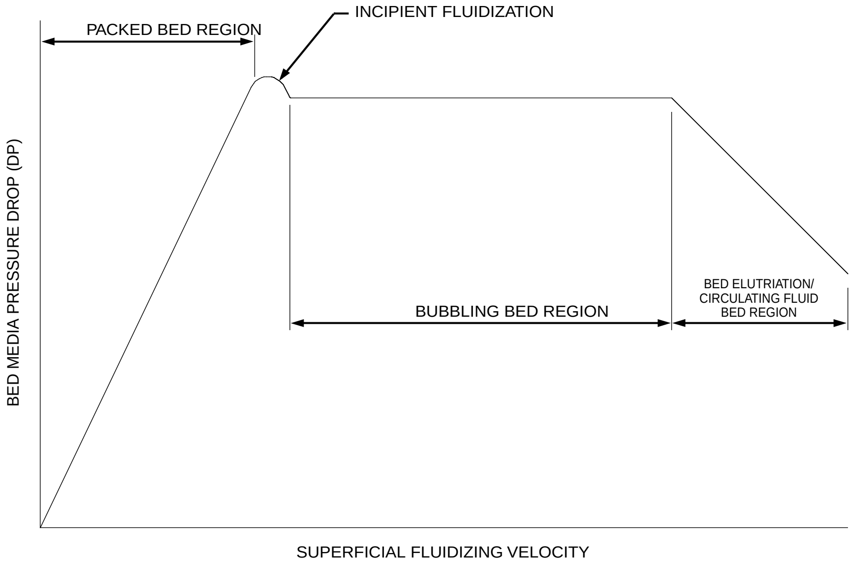

FIGURE 4.1.4 Fluidizing modes.

Increasing the air velocity above incipient fluidization, the bed medium takes on the appearance of a boiling liquid and grows in volume. A growth of 30 to 60% is common. The medium is very active and movement in all directions is visible. This mode of fluidization is that used in bubbling bed incinerators. It is a very well-mixed environment with high gas/solid contact. The flat portion of Figure 4.1.4 is the bubbling bed portion of the curve. If the air velocity is increased even further, all of the bed particles become entrained and are carried out of the chamber. This latter mode of operation is that associated with circulating bed combustors. This mode is also characterized as well-mixed and abrasive to any solid waste.

Bed medium selection is based on the waste to be treated and the design objectives. In some very specific applications, the waste itself may be the bed medium; but in general, the medium is either an inert material resistant to the combustion environment or a specially chosen absorbent medium that actively removes pollutants. Sulfur oxides, halogens, and phosphates are a few materials that can be absorbed or reacted by an active bed medium. It is also necessary to carefully select the bed medium size and density to ensure proper assimilation of the waste into the bed.

Note that bed chemistry control is very important where melting of the bed/ash is possible. In fluidized beds using active media, bed composition must be monitored to avoid melting of eutectic mixtures and system shutdown. Additives, such as kaolin clay, have historically been used to address this problem.

Figure 4.1.5 shows a common cylindrical design for a bubbling bed. The fluidized bed medium is supported by a distributor plate or above a distribution manifold. Simple perforated plates can be used for air distribution if the waste does not contain any oversized noncombustible material. Manifold distributor systems are chosen if the non-combustible material must be removed during operation. The disengaging space or secondary combustion area can be of the same diameter as the bed, or can be expanded to a larger diameter. A supplemental fuel burner can be included in the secondary chamber. In almost all applications, a cyclone is used on the bed exit to capture particulate matter consisting of the noncombustible ash as well as any abraded bed medium.

In bubbling bed applications, the medium is heated with hot fluidizing air or an in-bed burner to bring it to the ignition temperature of the waste. In this condition, solid waste added to the medium is ignited and burns in the bed medium. Even large solid waste items can be seen to travel into and around the bed as they are agitated and abraded by the active bed medium. Depending on the waste energy content, the preheat burners can be turned off after waste feed is initiated.

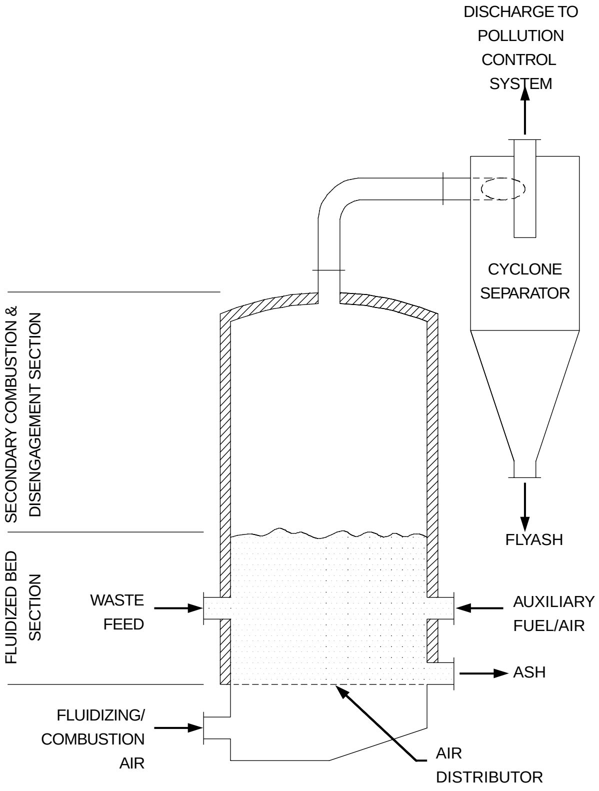

FIGURE 4.1.5 Fluidized bed incinerator schematic.

Temperature control can be very precise because the bed medium provides a large "thermal inertia" that changes temperature slowly in comparison to many waste-burning systems. The highly agitated medium is also effective in abrading waste material to fresh surface areas and rapid combustion of fixed carbon. The uniform temperature in the bed medium also results in reduced NO_x.

Bubbling fluidized bed applications include solid, liquid, and sludge wastes. Solid wastes must be size-reduced to permit injection into the combustion chamber and to ensure good mixing in the bed medium. Rapidly burning gaseous wastes are not good candidates for fluidized beds because the gases can transport through the bed without complete combustion. Fluidized bed systems have been widely used in wastewater plant sludge incineration and have been used in specific hazardous waste applications. Energy recovery from the hot off-gases is common as well, including in-bed heat transfer tubes to recover energy and reduce excess oxygen during incineration of high-energy wastes.

The advantages and disadvantages of fluidized bed incinerators are summarized in Table 4.1.6.

TABLE 4.1.6 Fluidized Bed Incinerator: Advantages and Disadvantages

Advantages	Disadvantages
Well-mixed environment leads to reduced temperatures for equivalent destruction and therefore lower NO_x	Solids must contain minimal large non-combustibles to avoid bed removal/recycle systems
No moving parts or seals for maintenance	Large solids must be size-reduced
Thermal inertia of the bed medium enhances temperature control	Bed/ash composition control is necessary to avoid melting
Bed additives can absorb or neutralize pollutants	Turndown ratios below approximately 0.5 of the design are not possible without complex air control systems

In the circulating bed configuration, as shown in Figure 4.1.6, both the waste and bed medium are entrained in the combustion chamber in a dilute-phase fluidization mode. Gases and particulate solids exit the primary chamber into a cyclone separator. The cyclone captures the bed medium and large waste particles for re-injection into the primary chamber. In this fashion, the solid waste is re-injected until it is completely burned and bed medium is continually re-injected. Power generation fluidized beds frequently use the circulating bed process.

The bed medium selection for circulating fluidized beds is similar to that for bubbling beds. Circulating beds are somewhat less sensitive to waste size and turndown ratio. Although theoretically possible, no applications for sludge treatment in a circulating bed configuration has been identified. Liquids can be injected into the primary chamber.

The advantages and disadvantages of a circulating bed incinerator are listed in Table 4.1.7.

TABLE 4.1.7 Circulating Bed Incinerator: Advantages and Disadvantages

Advantages	Disadvantages
Well-mixed environment leads to reduced temperatures for equivalent destruction and therefore lower NO_x	Solids must not contain large, dense particles resistant to transport in the air
The thermal inertia of the bed medium enhances temperature control	Bed/ash composition control is necessary to avoid melting
Bed additives can absorb pollutants	
No moving parts or seals for maintenance	

Multiple Hearth Incinerator

The multiple hearth incineration system has been commonly used for sludge incineration. The multiple hearth is a vertical, round system that typically contains five to nine hearths; see Figure 4.1.7 for a schematic of a common multiple hearth design. Rabble arms above each hearth are attached to a slowly rotating (e.g., 1 rpm) center shaft. The sludge or waste material is introduced onto the top hearth. The

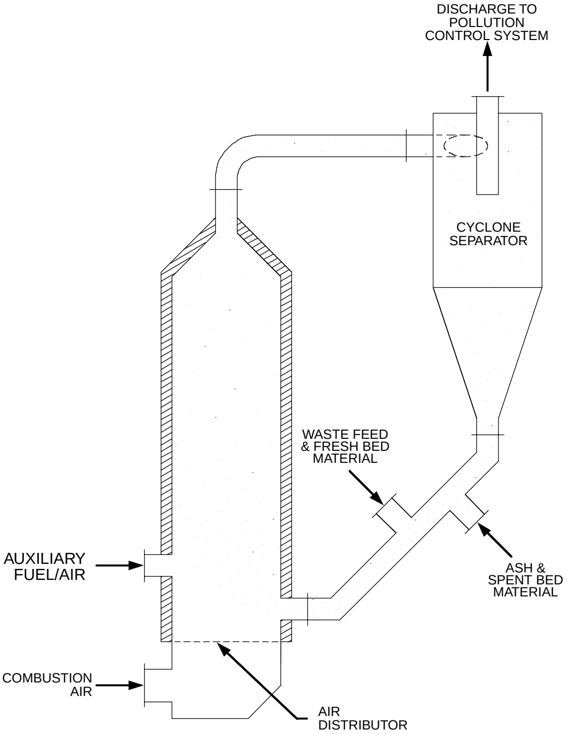

FIGURE 4.1.6 Circulating fluidized bed incinerator schematic.

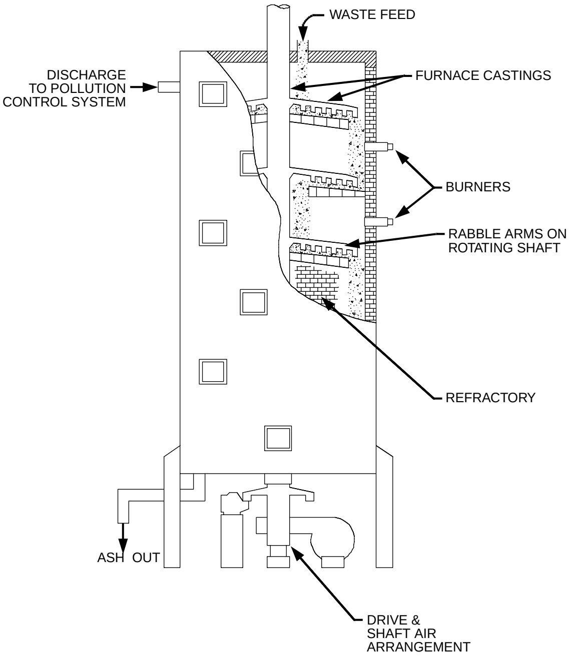

FIGURE 4.1.7 Multiple hearth incinerator schematic.

rabble arms are shaped to slowly move the waste either toward the center or toward the outside on alternating hearths so that waste and ash pass downward from one hearth to the next. Movement of the material by the rabble arm helps to expose fresh surface to complete oxidation and destruction of the waste.

Combustion air is introduced above the bottom hearth and passes upward through the system countercurrent to solid materials coming down, passing from center to outside and outside to center on succeeding hearths in opposite direction to the solids. Air passing over the ash on the bottom hearth cools the ash before it is discharged from the system. Burners are installed at the next hearth, or at other hearths, to augment the ignition of the waste. The temperature at the center hearths can be 900 to 1000°C (1700 to 1800°F), and the temperature of the off-gases exiting the incinerator at the top can be 400 to 550°C (800 to 1000°F).

The hearths and walls of the system are refractory lined. The central shaft is typically hollow and internally air-cooled. Wastes other than sludges can be processed in a multiple hearth incinerator, but they must be shredded or of a size and form such that they will not hang up or jam the rabble arms. High levels of halogens or salts can cause severe corrosion of the rabble arms and central shaft. Applications for the multiple hearth are therefore somewhat limited. Table 4.1.8 provides the advantages and disadvantages of multiple hearth incinerators.

TABLE 4.1.8 Multiple Hearth Incinerator: Advantages and Disadvantages

Advantages	Disadvantages
High energy efficiency	Waste feeds limited to non-acid-producing waste to avoid metal part corrosion
Low carbon in the ash	Limited waste applications
	Mechanically complex and high maintenance

Car-Bottom Furnace or Metal Parts Furnace

Mixed waste inventories contain contaminated metal parts that are a material handling problem to continuous throughput incinerators. Issues with these items include the very low average heat of combustion contributing to the incineration process and the likelihood that any handling of the metal parts for size reduction is a substantial safety issue. Containers and metal parts contaminated by propellants, explosives, and chemical agents are being treated in furnaces designed with large doors to batch-wise roast the parts according to a prescribed temperature regime. The car-bottom furnace is a batch-fed furnace with a door or opening that accepts a wheeled cart holding the waste or contaminated items. Large waste items or contaminated metal parts are placed in the cart, which is rolled into the chamber and heated to the appropriate temperatures to volatilize and oxidize the contaminants. One variation is a unit in which the cart seals up against the bottom of the furnace and becomes the furnace bottom. The timing of the heating cycle is variable to facilitate complete decontamination of small or large items. Car-bottom furnaces utilizing two carts are common; one cart can be in the cool-down and recharging mode while the other is in the heating cycle.

The primary application of car-bottom furnaces is in areas where size reduction or handling of the metal parts is hazardous, such as decontamination of metal components of weapons systems. Weapons or weapon parts contaminated with chemical agents are treated in similar systems that move the metal parts through a zoned furnace on trays supported on rollers. Units of this design have a relatively low mass throughput capacity because of their batch nature.

The U.S. Army Evaluation Center has demonstrated a hot gas decontamination system to remove residual propellants and explosives from weapon parts. The furnace was demonstrated to be effective in the 150 to 340°C (300 to 650°F) range for a 0- to 12-hour temperature soaking time (Huhyh and Parker, 1996).

A metal parts furnace at the U.S. Army Chemical Agent Disposal System (USACAMDS) at Tooele, Utah, decontaminates metal parts and ton containers used to store chemical agents. Figure 4.1.8 shows

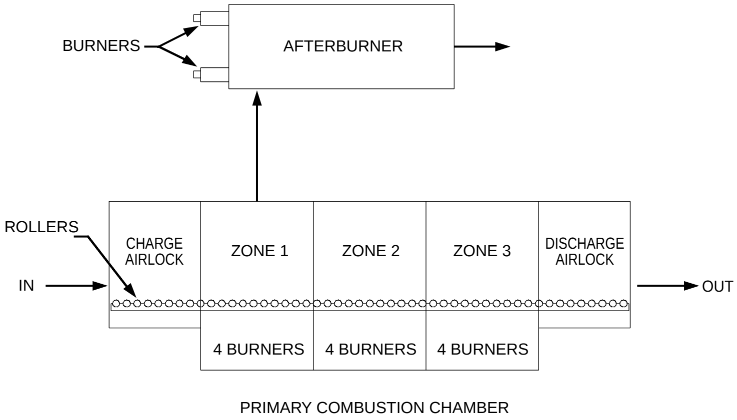

FIGURE 4.1.8 Metal parts furnace schematic.

a primary/secondary furnace system that volatilizes the agent in a three-zone furnace heated by gas burners and a secondary combustion chamber to support essentially complete agent destruction. This unit was demonstrated to provide 99.99999% destruction on the agent during testing. The Zone 1 temperatures varied from 750 to 850°C (1,400 to 1,550°F) during the 38-minute charging time. The primary chamber exhaust temperatures ranged from 750 to 900°C (1,400 to 1,650°F) in this time period. (Booth et al., 1997; Young et al., 1999).

The advantages and disadvantages of car-bottom furnaces are listed in Table 4.1.9.

TABLE 4.1.9 Car-Bottom Furnace: Advantages and Disadvantages

Advantages	Disadvantages
Designed to accept any size metal part or item	The batch nature leads to low throughput and high cost
Simple design	Wheeled cart and charging door are mechanical complexities
Flexible temperature programs for destruction requirements	Limited application to contaminated large metal parts

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4.2

Vitrification

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Introduction

Vitrification is the process of converting a material to a glassy form. The origin of the word (from the Latin *vitrum*, meaning glass) already suggests the fact that glassy materials and the art of glass-making have been known for thousands of years. The long history of this versatile material spans such diverse areas as art and ornamentation, containers, windows, optical components, fiber reinforcement, fiber optics, and electro-optics. However, glass as a waste form — that is, a material form in which to safely stabilize waste substances — is a relatively recent application with origins in the 1950s in the United States, Canada, and the United Kingdom.

The application of glass as a waste form depends on several key factors: (1) Glasses can be made extremely resistant to aqueous corrosion, as evidenced by the fact that man-made and natural glasses have survived in the environment for thousands to millions of years, respectively; (2) glasses can be made over wide ranges of composition and can therefore tolerate correspondingly wide variations in waste composition; and (3) the basic glass-making process is relatively simple and robust, making it well-suited to hazardous and radioactive production environments. For these and other reasons, vitrification has become the international method of choice for the treatment of extremely radioactive high-level nuclear wastes that are generated from the reprocessing of spent nuclear fuels and, in fact, that application has been the primary driver for the development of waste vitrification technology over the past few decades. However, this substantial technology base has also provided the impetus for interest in vitrification as a potential treatment technology for numerous other waste management problems, including other types of radioactive wastes as well as hazardous wastes.

The process of vitrification is attractive because it can destroy hazardous organics present in the waste and chemically incorporate the radioactive and hazardous inorganic constituents into a stable glass product while often providing significant volume reduction, which contributes to reduced disposal costs. Furthermore, unlike the case with radioactive wastes, for which the glass product is still radioactive and must be disposed accordingly, vitrification can render hazardous wastes non-hazardous, which opens up the additional possibility of product reuse; typical uses of the product include aggregate, abrasives, coatings, fibers, insulation, and tiles. Clearly, such beneficial reuse offers the possibility of offsetting some of the waste treatment costs, which can be a significant factor in selecting a treatment technology.

This section presents a discussion of the basic elements of waste vitrification technology, including glass chemistry considerations and waste glass melter characteristics. Important areas such as off-gas treatment, waste characterization, and plasma vitrification are not discussed in any detail because they are reviewed elsewhere in this handbook. In general, the hardware focus is on the glass melter itself and specific examples often relate to the widely used joule-heated waste glass melter approach. The section concludes with a summary of each of a number of specific and diverse applications of vitrification technology.

Fundamentals

A vitrification *system* can be considered to be composed of the engineered unit operations that constitute the "hardware" and the underlying glass chemistry that dictates the process controls that must be implemented ("software") to ensure that the overall system performance criteria are met. Failure of vitrification systems can often be traced to an overemphasis of one of these components at the expense of the other and/or to poor integration of these elements of the overall system. Each of these aspects is discussed below.

Basic System Components

Vitrification hardware can be divided into four main operations: feed preparation/pretreatment; glass melter; off-gas system; and product handling.

Feed Preparation/Pretreatment

This may include some or all of the following: waste feed handling, size reduction, drying, **calcining**, blending with **glass forming chemicals** (GFCs) and other feed additives, and transport to the glass melter. More extensive pretreatment steps can also be included, such as the removal of troublesome waste constituents (such as sulfur or halogens) to increase waste loadings, as discussed below. Feeds to the waste glass melter can range from dry powders to wet slurries to aqueous solutions. Drying or calcining of the feed is sometimes performed in a separate unit operation prior to vitrification to reduce the evaporative load on the melter and thereby increase the processing rate. Disadvantages of calcining include the maintenance and contamination concerns associated with the additional equipment and the fact that many waste types (particularly high-alkali, low-melting wastes) are not suitable for calcining.

Glass Melter

In the melter, the feed is heated to temperatures typically in excess of 1000°C and undergoes a series of reactions, including drying, calcining, and melting, to form the molten glass product. These processes evaporate water and evolve gases as a result of the decomposition of the various salts and organics that are present in the feed (e.g., nitrates, carbonates, hydroxides, etc.). The remaining constituents of the feed are thereby converted (predominantly) into the corresponding oxides, which are then incorporated into the glass melt. In joule-heated melter systems, the feed is introduced directly onto the surface of the pool of molten glass in the melt cavity and this sequence of reactions occurs in a stratified layer of reacting feed referred to as the cold-cap. Because the conversion of feed to the glass product occurs essentially as a reaction at a surface, the maximum melting rate for a given set of operating conditions is expected to be proportional to the surface area of the melt, and the capacity utilization is roughly proportional to the fraction of that area covered by cold-cap. These relationships are found to hold reasonably well in practice, except for very small systems for which wall effects become important.

Off-Gas System

The function of the off-gas system is to render the gaseous and particulate emissions from the melter suitable for safe and compliant discharge to the atmosphere. Vitrification off-gas systems vary considerably in complexity, depending on the application and the amounts and types of hazardous constituents present in the waste. However, they are typically composed of a train of standard gas cleaning operations and may involve various types of quenchers, scrubbers, filters, electrostatic precipitators, catalytic convertors (e.g., reduction or oxidation), or secondary combustion units. Off-gas treatment is discussed in detail elsewhere in this handbook.

Product Handling

The molten glass may be discharged from the melter into containers, where it cools to form a glass block, or may be discharged into a mechanism that produces some other finished form of the product that may be better suited for storage or reuse. Examples include cullet, marbles, gems, fiber, and tiles. In radioactive systems, the product handling system would also include closure and decontamination of the product container.

Operation and integration of these four main areas of the vitrification systems also involve process control systems, instrumentation and monitoring, and a variety of support systems and services, including the power supply and control systems and services and utilities. Key process variables include temperatures, pressures, flow rates (gases, feed, and glass), furnace atmosphere, glass level, supplied power, etc. However, as discussed below, one of the most important parameters is the glass composition because that affects the processing characteristics and determines the properties of the product. The glass composition is typically controlled by controlling the proportion and composition of the glass-forming additives.

Types of Melters

The variety of different types of waste glass melters can be conveniently organized in terms of the method by which energy is introduced into the system to effect the conversion of the melter feed to glass. A further division can be made on the basis of whether the melting of the waste is performed *in situ* or *ex situ*. While the primary focus here is on *ex situ* systems, the existence of parallel *in situ* systems is also noted. A brief summary of the principle of operation of each type of melter is presented below.

Electric Melters

Joule-Heated Melters (JHM)

This design relies on the fact that molten glass is electrically conductive and, therefore, if suitable electrodes are located in the glass melt, sufficient alternating current can be passed to dissipate energy in the melt at the rate required to convert the feed stream to glass. Plate or rod electrodes are usually used and the feed is deposited directly onto the surface of the pool of molten glass contained in the melter. The basic concept is extremely flexible and has been deployed in systems with capacities ranging from a few kilograms to hundreds of tons of glass per day. Joule-heated melters are discussed in some detail below. The joule-heated vitrification method has also been employed in *in situ* systems.

Induction Melters — Hot Wall

The melter unit consists of a metal crucible (typically cylindrical or of elliptical cross-section), the wall of which effectively forms the secondary of a transformer. The crucible sits inside the primary winding of the transformer that is connected to the power supply. In this way, a current is induced to flow around the wall of the crucible, which causes resistive heating. Heat is transferred from the walls to the glass melt contained in the crucible by conduction and supplies the energy required to melt the feed. Because in this system, energy is supplied at a surface to heat a volume, scale-up is limited and is typically accomplished by use of multiple units.

Induction Melters — Cold Wall

The principle of operation resembles that of the hot-wall induction systems except that, in this case, the wall is segmented with dielectric materials to *prevent* the flow of current around the wall of the crucible. In addition, the wall is actively cooled to freeze a layer of glass on the interior surface, which provides containment of the glass melt and the ability to operate at much higher temperatures than is typically the case with hot-wall melters. In this case, it is the electrical conductivity of the glass melt that acts as the secondary of the transformer and the current is induced in the glass melt itself instead of the wall. However, the power profile decays exponentially with distance from the wall and, therefore, most of the power is still delivered to the glass that is closest to the (cold) wall, with the result that the potential for scale-up is still limited.

Resistance Heated Melters

The general design is similar to that of the hot-wall induction melters except that, in this case, the wall of the crucible is heated by external electrical resistance heaters instead of by induction.

Plasma Torch and Arc Melters

These systems are discussed in detail elsewhere in this handbook. Plasma torch systems involve the conversion of a gas stream to an extremely high-temperature plasma by passing an electric discharge through it in a plasma torch. The plasma is then directed onto the waste feed to provide the energy required for melting. Either both electrodes can be in the torch, or one can be in the torch while the second is provided by connection to the glass melt, resulting in "non-transferred" and "transferred" modes of operation, respectively. Arc systems involve striking an arc either between electrodes or between an electrode and the glass melt. These systems are capable of achieving very high temperatures. Plasma torches have also been employed in *in situ* treatment systems.

Microwave Melters

Microwave radiation can also be used to dissipate energy into molten glass. In these systems, a waveguide is used to direct microwave radiation from the generator into the melt cavity. Again, the power profile decays exponentially with distance from the glass surface (typically over a few inches), which limits the practical size of these systems. Ideally, the microwave energy is introduced under the melt because gaseous emissions from the melt (particularly water) can strongly absorb the microwave radiation, resulting in dielectric breakdown (arcing) that can damage the generator.

Combustion Melters

Commercial Glass Melters

Commercial gas- or oil-fired combustion melters have also been modified for waste glass melting. The waste feed is introduced onto the glass pool, which is contained in a refractory-lined cavity. Burners are directed at the waste feed to provide the energy required for melting.

Cyclone Melters

The melter system consists of a cyclone unit in which the particulate waste feed is entrained in flowing combustion gases that are caused to spiral around the inside of the cyclone. The particulates are melted and deposited on the wall of the cyclone, and the resulting glass melt runs down to a collection orifice at the bottom. Because of the short residence time and relatively small glass inventory, these units can have high processing rates for their size. However, these same features can also lead to poor product quality without proper control of composition and other processing parameters.

Melter Features

Basic features and design considerations are discussed in this subsection with particular reference to joule-heated melters (JHMs). Not all of the features discussed are relevant to every type of melter.

Joule-Heating

Many electric melters rely on the ability to joule-heat the glass melt by various means, including with electrodes, by induction, or through a transferred arc. The basic joule-heating phenomenon in glass melting relies on the fact that glass melts are typically electrically conductive over the temperature ranges that are relevant for processing. Glass melt compositions of importance for waste processing are ionic, rather than electronic, conductors. The principal current carriers in such melts are the alkali metals, whose effectiveness is greatest for lithium and least for cesium on a mole basis; the alkaline earths are a distant second in terms of their impact on electrical conductivity. As the temperature is increased, oxygen ions become an increasingly important current carrier. The electrical conductivity of glass melts, σ, increases with temperature T; it behaves as a typical activated process and therefore follows the usual Arrhenius form ($\sigma = \sigma_0 \exp(-E_a/RT)$) reasonably well. A typical glass melt suitable for JHM processing would have an electrical conductivity of around 0.1 to 0.6 S/cm at the processing temperature.

Joule-heated melters therefore employ some means of bringing the initial charge of glass up to the temperature range in which it is sufficiently electrically conductive. Electrodes that are immersed in the glass melt are then energized, causing current to flow through the glass melt. “Joule” or resistive (I^2R) heating occurs and power is dissipated *throughout the volume* of the melt. This is one of the major advantages of joule-heated melting because, in principle, this makes it infinitely scalable. Any type of heating that relies on the dissipation of power at a surface, and conductive or convective heat transport into the melt volume, tends to suffer from local overheating and inefficient heat transport into the bulk of the melt. The maximum practical size of such systems is therefore limited by heat transport considerations; examples are induction heating, resistive heating of the melter wall, plasma or combustion heating of the melt surface, and, to a lesser extent, cold-crucible melting.

The electrical supply is alternating current so as to avoid electrolysis of the glass melt and inefficient power dissipation as a result of the electrode polarization effects that would occur with direct current. The power supply specifications are determined, in the first instance, by simple geometric consideration of the melt pool and electrode combination (i.e., the resistance between the electrodes) and the power dissipation required to sustain the design melt rate, allowing for thermal losses. The power and resistance are sufficient to determine the required supply voltage and current. Actual values obviously depend on the particular configuration and melt characteristics, but voltages are usually in the range of tens to a few hundred volts and currents are hundreds to thousands of amps.

Start-up of a JHM is usually accomplished by preheating the melt cavity using electrical radiant heaters installed through the roof or by means of a temporary burner. Glass frit is then introduced, which ultimately melts to form a conductive path between the electrodes; joule-heating can then be initiated.

Once a pool of molten glass has been formed and joule-heating has been initiated, the glass pool itself becomes the source of heat for melting the feed to the melter. The feed is introduced directly onto the melt surface and may be solid, liquid, or both. The region in which the feed accumulates on top of the molten glass is referred to as the “cold-cap” (when this is very thick, as is often the case in commercial glass melting, it is also referred to as a “feed pile” or “batch blanket”). In this dynamic, highly stratified region, cold feed meets hot glass and, consequently, very large temperature gradients are present. Water is evaporated and salts (carbonates, nitrates, hydroxides, etc.) are decomposed to their corresponding oxides, either with or without melting. Deeper into the cold-cap, fluxes and refractory oxides begin to combine to form the glass melt that is ultimately incorporated into the pool below. The processes occurring in the cold-cap region have been the subject of considerable study but remain relatively poorly understood. The rates of the physical and chemical changes taking place in the cold-cap region can determine the overall melting rate. Because the rates of these processes are temperature and concentration dependent, the rates of heat and mass transport to and from the cold-cap region can also be potentially melt rate limiting. Traditional JHMs have relied on passive conductive and convective transport processes, but actively stirred melters have also been developed with a view to increasing throughput rates (notably the Stir Melter and the DuraMelter™).

The selection of electrode materials and an appropriate electrical configuration for JHMs depend on a number of factors, including operating temperature; melt chemistry; the physical, chemical, and electrochemical rate of erosion/corrosion of the electrodes; and the ability to replace them in service given the melter design and the particular application. The interplay and relationships between these factors are discussed below in specific instances of electrode materials and configurations that have been employed in glass melting processes.

Both rod- and plate-type electrodes have been used in both single-phase and three-phase arrangements. Commercial glass melters typically use rod electrodes, often arranged in triplets placed throughout the melt pool, that are powered by a three-phase supply. The West Valley HLW melter uses three plate electrodes in a three-phase arrangement with two on the sides and one on the bottom of the melt cavity; the Japanese TVF melter uses a similar arrangement. The DWPF melter uses two pairs of plate electrodes arranged one above the other. The DuraMelter™ 5000A used at M-Area is unique in its use of a center electrode to reduce the separation between the electrodes on scale-up; increased electrode separation results in increased supply voltages and increased potential for shorting due to high-temperature dielectric breakdown. The melter was powered by a two-phase supply that was derived from the three-phase line using a Scott-Tee transformer.

It is useful at this point to introduce the concept of the current-density capability of electrode material because this is one of the less obvious but important design considerations. For a given electrode material, melt chemistry, and temperature, the rate of corrosion of the electrode depends on the electric current density at the electrode surface, even under ac conditions. The corrosion rate increases with current density and often exhibits a "threshold" behavior, with the corrosion rate being relatively insensitive to current density at low values but rising rapidly at higher values (Wang et al., 1996). There are some indications that the "threshold" may decrease somewhat with temperature and studies have shown a weak increase with ac frequency (Gan et al., 1996). The detailed behavior as well as the location of the threshold is, of course, also dependent on the electrode material and, other things being equal, materials with high thresholds are desired.

Because the electrodes are required to deliver a certain power P to the melt pool, which in turn has a certain resistance R (determined by the melt chemistry and the electrode configuration), the current is determined by $P = I^2R$. Furthermore, if the selected electrode material has a design current density limit of C, then the area of each electrode must be at least $A = I/C = (P/R)^{1/2}/C$. If it is assumed that the electrodes span the length L of opposite walls of the melt cavity, as is often the case, and that the separation between them is D, then the surface area of the melt is $S = LD$ and the area of an electrode is $A = Lh$, where h is the height of an electrode. The resistance of the melt pool is $R = D/\sigma A$, where σ is the electrical conductivity of the melt. The required power is roughly proportional to the melting rate (for a given feed), which is roughly proportional to the surface area of the melt; thus, P Ý αLD, where α is a constant for a given feed type, temperature, bubbling rate, etc. Combining these results, the required minimum area of an electrode is given by $A = \alpha L\sigma/C^2$ and the required minimum height of the electrodes is $h = A/L = \alpha\sigma/C^2$. Because the surface area of the melt is determined by the required production rate, the minimum value of h then fixes a minimum melt volume and therefore a minimum residence time. This simple illustration shows the important design constraints that are imposed by the value that is assumed for the electrode current density threshold C. Note that because it is the ratio σ/C^2 that determines the minimum height, a small value of C can be offset by using a small value of σ. However, because σ is determined by the melt composition (and the operating temperature), this imposes an additional constraint on the glass formulation, which may translate into reduced waste loading, particularly for high alkali wastes. Furthermore, if the electrical conductivity of the melt becomes too small, electrical conduction through the refractories that form the melter walls becomes the dominant path (at the temperatures of interest, all viable candidates for such refractories have non-zero electrical conductivities). This can lead to increased refractory corrosion and also moves the system toward undesirable surface heating rather than the preferred bulk heating of the glass pool.

Commercial glass melters are predominantly combustion fired but joule-heating — either as the sole means of heating or as a supplemental heat source ("joule-boosting") — is also extensively employed. The processing temperature of typical commercial glasses (1400 to 1600°C) places limits on the materials that can be used for electrodes. Molybdenum is most often used, although tin oxide is also employed. Molybdenum has a relatively high design current density limit in commercial glass use; a typical value is 20 A/in.^{2}, which is sufficiently high to make rods, rather than large plates, practical. Because molybdenum will spontaneously ignite in air at these temperatures, water-cooled electrode holders are employed between the interior melter wall and the point at which the molybdenum electrodes exit the melter wall. The molybdenum rods are sealed to the holders by frozen glass. Because the molybdenum rods are gradually consumed by the glass melt, they are periodically rotated to crack the glass seal and pushed into the melt pool; additional segments of rod are screwed onto the end extending out of the melter as needed. While molybdenum has the advantage of a very high melting point (2610°C), it is relatively easily oxidized and the oxide product is dissolved into the glass melt. Commercial glass melts, which typically contain few easily reducible species (the major constituents are Si, Na, Ca, Al, B), can tolerate the relatively reducing conditions that favor increased molybdenum electrode lifetime. However, this is a considerable disadvantage for waste glass melts that frequently contain not only easily reducible species (e.g., Pb, Cu, Ni, S, etc.), but also significant amounts of multivalent species (particularly Fe) that react readily with molybdenum. The net result is significantly increased rates of electrode corrosion and the production of reduced reaction products such as metallic Pb, Cu, Ni, and/or metalloid sulfides such as Fe-Cu-Ni-Co-S alloys. If the melt is maintained more oxidizing to avoid the production of such products, the rate of electrode oxidation is increased; if the melt is maintained more reducing to prevent electrode oxidation, molten metal or sulfide phases can be formed. Even under relatively oxidizing conditions in the glass melt, reduction reactions still occur on the surface of the molybdenum electrodes, many of which produce low-melting molybdenum eutectics. In summary then, there is a basic redox incompatibility of molybdenum electrodes with most waste glasses, which must be considered in waste glass melters that employ molybdenum.

Tin oxide (SnO_2) ceramic blocks are also used as electrodes in commercial JHMs because they are sufficiently electrically conductive at high temperatures. One of the design challenges with such materials is that the electrical connection must also be made in the high-temperature zone. The standard approach is to use internal cavities in the blocks that are filled with molten silver which, in turn, can be connected to a conventional lower-temperature electrode bus. While SnO_2 is relatively insoluble in silicate melts, SnO is very soluble so that tin oxide electrodes can only be used for oxidizing melts because the electrodes are not feedable and replacement typically requires a rebuild of the melter. Tin oxide electrodes are often used for commercial glass melting of high-lead glasses, which also must be maintained oxidized to avoid the formation of molten lead. Work in Russia has investigated tin oxide electrodes for waste glass melters; and a melter with tin oxide electrodes was tested for 4 years at Mol, Belgium, in the early 1980s.

The basic JHM technology developed for the U.S. Department of Energy (DOE) HLW program by Pacific Northwest Laboratory (now PNNL), and subsequently adapted and extended by others, employs non-replaceable plate electrodes (Chapman, 1975; Chapman et al., 1986). The use of relatively low-melting (around 1150°C) borosilicate waste glasses significantly expands the number of potential electrode materials and reasonably extensive test programs led to the selection of Inconel 690 as the material of choice over two decades ago. This material is in use at West Valley, at DWPF, in the derivative Japanese and German HLW JHM systems that have been operated, and in all of the DuraMelter™ systems, except the high-temperature DuraMelter™ HT, which used molybdenum. The melting point of Inconel 690 (1330 to 1360°C) limits the ultimate maximum operating temperature but other considerations, including increased corrosion rate, softening, and conservative margins for operating errors have led to specified maximum operating temperatures of around 1200 to 1250°C; the standard nominal operating temperature is 1150°C. At these temperatures, Inconel 690 is extremely resistant to corrosion by molten glass. Because the most extensive corrosion typically occurs at the glass/air interface, the plate electrodes are usually completely submerged in the glass melt. While Inconel 690 is somewhat susceptible to sulfidation, chloridation, and phosphidation, these modes of attack are much more prevalent in the vapor phase than in molten glass and, in fact, small amounts of these species in the glass melt appear to have little deleterious effect. Higher concentrations of sulfur (as in the case of molten sulfate salts or sulfides) ultimately lead to relatively rapid attack (with rates on the order of inches per year). As examples of the potential longevity of Inconel 690 electrodes, the full-scale West Valley test melter was at temperature with molten glass and operated periodically over a period of 5 years before being shut down and dismantled. The electrodes, which were air-cooled by means of interior channels, were found to still have sharp edges and machining marks evident on the metal surface. Similarly, test melters at the Vitreous State Laboratory (VSL) and PNNL that do not have cooled electrodes have been held at temperature for many years with no apparent signs of degradation.

As shown in Figure 4.2.1, melting rates typically increase rapidly with processing temperature, which, together with the potential for increased waste loadings, provides the prospect of significant advantages for higher temperature vitrification. The disadvantages include increased materials corrosion and volatilization. Both PNNL and VSL have developed and tested JHM systems that have extended high-temperature capability by employing conductive ceramic electrodes, but these are considerably less developed than their lower-temperature Inconel-690 counterparts. While the results obtained to date are encouraging, both the PNNL and VSL tests observed eventual cracking and hole-burning through the

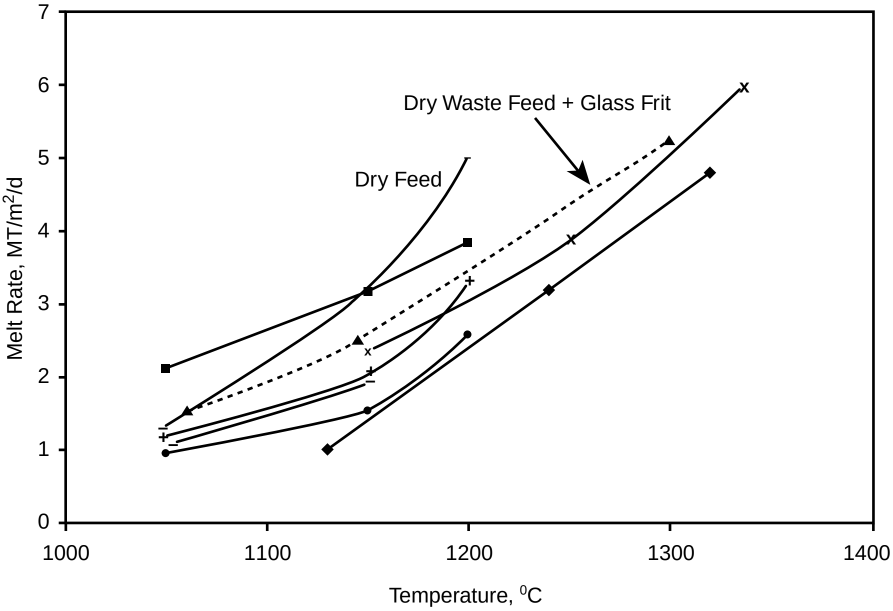

FIGURE 4.2.1 Effect of temperature on melting rate (metric tons per square meter per day) for agitated joule-heated melters with a variety of feed compositions. Data are for slurry feeds except where indicated. Note: The plotted values are one-fifth of the measured melt rates for the dashed line. (From VSL, unpublished data.)

ceramic electrodes. Both systems make use of the fact that several commercially available high-chromium refractories have sufficiently high electrical conductivities to be employed as electrode materials. PNNL used Monofrax E and VSL used both Monofrax E and Corhart 1215Z. The basic challenge is then the method by which the electrical connection is made to the electrode because the material is conductive only at high temperatures. PNNL addressed this by use of a molybdenum backplate that is pressed against the electrode, and a proprietary means of improving the electrical contact. VSL used a three-chamber approach in which the ceramic electrodes formed the two dividing walls between the chambers. Molybdenum electrodes with water-cooled holders, as used in standard commercial glass melting, are installed into each of the end chambers, which are loaded with a simple high-conductivity glass that is free of transition metals or reducible species. The center chamber contains the waste glass melt and feed is introduced onto that pool. Glass frit is added periodically to the end chambers because the partition walls cannot provide a tight seal between the chambers. Joule-heating is effected by conduction from one end chamber to the other by way of the main chamber. However, because most of the resistance is in the center chamber, that is where most of the power is dissipated. The advantages of this system are that the molybdenum electrodes are in a relatively cool, locally reducing environment that has a low concentration of transition metals and reducible species, while the center chamber is much hotter and can be vigorously agitated with air without rapidly dissolving the molybdenum electrodes.

Melt Pool Containment

Many melter designs, including JHMs, employ a pool of molten glass that is contained in a cavity within the melter unit. The various methods of containment of the molten glass within that cavity can be broadly, and somewhat loosely, classified as “hot-wall” and “cold-wall” approaches. Induction and resistance-heated hot-wall melters typically employ simple metal crucible designs for containment, but that is generally not suitable for JHM systems; however, hot-wall containment is the method that is used in the basic JHM designs that were originated by PNNL. In these systems, the melt cavity is formed from a thick layer (typically several inches) of ceramic refractory brick that consists of a material that has superior glass corrosion-resistance, usually referred to as the contact refractory. The most corrosion-resistant materials are very dense and high in chromium (Xing et al., 1996) and tend to have rather high thermal and electrical conductivities (for refractories). Subsequent layers of refractory are increasingly good electrical and thermal insulators but also have poorer glass corrosion resistance. The final layers are typically standard ceramic fiberboard insulation before the melter shell. While the refractory blocks are cut and polished to provide relatively tight joints, that is not sufficient to seal the glass within the cavity and prevent seepage between the joints. Instead, the glass is sealed in by freezing it. The design challenge is then to manage the thermal profile through the melter wall such that the glass "freezes" (or becomes essentially immobile) before it can travel beyond the contact refractory. An extreme version of this approach is used in commercial glass melting where the contact refractories are simply held in place using a jack-bolt frame and are backed by open air. The steep temperature gradient prevents molten glass from seeping out of all but the widest gaps, and leaks that do occur are treated by forced cooling with air or water sprays to seal them by freezing. The advantages of the hot-wall approach are that heat losses are reduced and the entire melt pool can, in principle, be maintained at the operating temperature. The disadvantages include thick refractory walls, which result in increased unit size and disposal volume, and the need to actively manage thermal expansion in larger units.

Cold-wall containment is also employed in the commercial glass industry, particularly for smaller melters, and is referred to as "skull melting." The melt cavity is formed from a relatively thin layer of a material, typically a metal but sometimes a refractory, that need not have particularly good glass corrosion resistance. The outer surface of the material is actively cooled to such an extent that a layer of glass is frozen on the interior surface of the cavity. The molten glass is therefore contained within a layer (the "skull") of frozen glass. Obvious advantages of this approach are the much smaller amounts of material needed to form the walls, which results in smaller unit sizes and reduced disposal volume, and the greatly reduced rate of corrosion of the cavity wall. Disadvantages include much larger heat losses that place greater demands on the electrodes and may impact throughput due to large thermal gradients. Also, in waste glasses, the cold regions near the frozen glass skull may provide nucleation and growth sites for the formation of undesirable secondary phases.

Glass Discharge

The ability to safely and reliably start and stop the discharge of glass from the melter on demand is an important and sometimes underestimated area of melter design that is particularly important for hazardous and radioactive waste processing. Some of the discharge methods that have been employed are discussed in this subsection.

Perhaps the simplest type of discharge system is the "overflow discharge," but this offers the least control. A spout is taken from near the bottom of the melt cavity into a heated discharge chamber. As the glass level in the melter rises as a result of feed introduction, excess glass continuously spills over the end of the spout into the collection vessel. A variant of this approach, which offers more control, includes the ability to tip the entire melter to start and stop pouring.

In "vacuum discharge" systems, as with the overflow discharge, a spout carries glass from the main melter cavity into the discharge chamber. However, in this case, glass flow is initiated by drawing a vacuum on the discharge chamber, which is otherwise sealed by the collection container. This type of discharge is employed at the DWPF HLW vitrification facility.

In "air-lift discharge" systems, the spout is now oriented vertically (referred to as the discharge "riser") and opens into a trough that directs the glass into the discharge chamber, from which it empties into the container. A tube is installed from the top of the melter into the riser and terminates some distance from the bottom of the riser. When air is blown down this tube, the effective density of the fluid is reduced and therefore its height must increase to maintain hydrostatic equilibrium, which causes glass to flow into the discharge trough. This provides variable control of the glass flow rate simply by controlling the flow of air into the riser. The response is typically quite rapid with glass flow usually starting within a few seconds and stopping within a few minutes. This type of discharge is employed on the West Valley HLW melter, and on all of the DuraMelter™ systems.

"Bottom discharge" systems rely on gravity flow of molten glass through an orifice in the bottom of the melt cavity. The flow is stopped by cooling the discharge tube to form a glass freeze-plug that can be remelted to restart the flow. Many different designs for such discharge systems have been developed with varying levels of sophistication, some of which have been extensively tested. Methods of heating include induction heating, external resistance heating, and internal joule heating. The advantages of such systems include the ability to remove any accumulations of bottom phases (e.g., noble metal sludges). The disadvantages include potential weakening of the melt containment by the introduction of a hole in the bottom of the melter, the potential for unplanned discharge (especially with larger melters), the inability to remelt the freeze-plug, and the potential for introducing electrical shorts. Such systems are used on the French AVM process both in France and the United Kingdom, on the French cold-crucible melters, and on German and Japanese JHM systems in Japan, Belgium, and China. The German and Japanese systems appear to be the best developed and are reported to be able to stop and start the glass flow on demand. DWPF employs a bottom discharge that is intended for final emptying of the melter, but is also designed to be capable of use as the routine mode of discharge.

"Secondary phase discharge" systems are incorporated into some melter designs. It is possible, although generally undesirable, to form molten secondary phases that either float on top of the glass melt (e.g., sulfate salts) or sink to the bottom (e.g., metals, metal sulfides). One method of addressing this problem is to provide a means of tapping off the accumulated secondary phase through a separate discharge. A vacuum-assisted system for tapping off top phases has been demonstrated on small-scale melters at VSL. Some plasma and arc melting systems are reported to have the ability to tap off separate metal phases, but the methods that are typically employed (taken from the metal smelting industries) have to be modified and demonstrated for nuclear applications. A Russian "hybrid" melter system that uses a combination of a plasma torch and induction heating has an open bottom from which it is claimed to be able to continuously cast a metal ingot while discharging the glass slag from above.

Melt Pool Agitation

The rate of consumption of the feed pile into the glass melt depends on the temperature- and composition-dependent rates of reaction in the cold-cap region as well as the effectiveness with which heat is transported into that region and reaction products are transported away. Traditional JHMs, and many other types of melters that employ a melt pool, have relied on natural convective transport processes, which can be reasonably effective because the cold feed is introduced onto the top. Melters with more than two electrodes can also employ power skewing to increase convection by, for example, skewing the power dissipation toward the bottom of the melter. However, there clearly remains considerable margin for improvement in the effectiveness of these transport processes. Simple gas sparging tubes inserted into the melt have been used with varying degrees of effectiveness in several melter systems, including developmental systems at PNNL, West Valley, Sellafield WVP, and in the Japanese TVF system. The most direct stirring action is achieved in the Stir Melter systems, which employ mechanical stirring by means of an Inconel 690 paddle immersed in the melt. Unfortunately, mechanical strength issues result in further reduction of the operating temperature (1060°C is typical), which tends to offset the increased throughput achieved by stirring. DuraMelter™ systems employ melt pool agitation by distributed and organized gas sparging. Multiple gas outlets are deployed in such a way as to reinforce natural convection cells. Very significant increases in processing rates have been found with this system from the smallest to the largest DuraMelters™ that have been deployed, as illustrated in Figure 4.2.2. While perhaps not as energetic as the direct mechanical stirring, such a system has the distinct advantage of no moving parts. In most cases, the bubbler assemblies have been inserted from above and are designed to be replaceable, although bottom-entering systems have also been used.

Glass Chemistry Considerations

While there are many classes of glass forming systems, including chalcogenides, heavy metal fluorides, and oxynitrides, only two — silicates and phosphates — have found significant applications in waste treatment. However, silicates are by far the most commonly used, due mainly to the ubiquity, and therefore low cost, of silicon-bearing minerals in nature. Furthermore, the potential longevity of silicate glasses in the environment is substantiated by the geologic record, which is not the case for phosphate

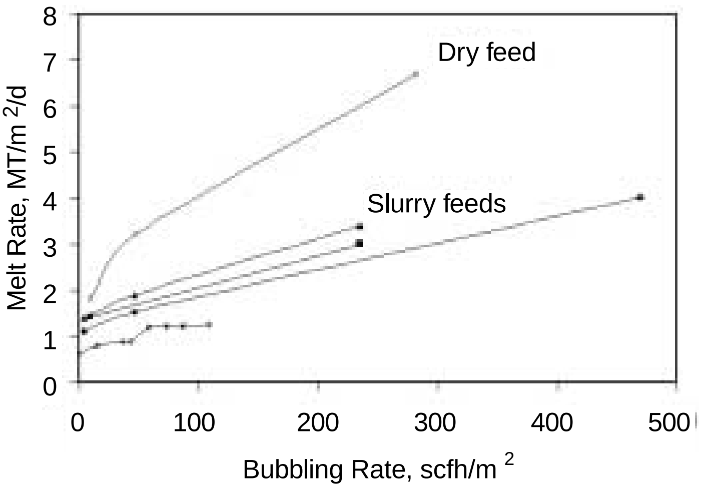

FIGURE 4.2.2 Effect of melt agitation (bubbling rate) on melting rate for joule-heated melters with melt surface areas from 0.02 to 3.3 m^2 using a variety of feed compositions. (From VSL/GTS Duratek, unpublished data.)

glasses. Silicate glasses can be formulated to incorporate a very wide range of concentrations of the majority of the elements of the periodic table.

Glass Formulation Development

Development of viable glass formulations for any given waste stream is basically a problem in constrained multivariate optimization and suitable formulations are the result of a reasonable compromise among a number of competing factors (Pegg, 1996). It is therefore essential to recognize and clearly state both the imposed constraints and the key variables in the problem. The specific constraints are determined by the waste stream characteristics, the requirements that the overall treatment process must meet, and the characteristics of the particular system under consideration and can usually be listed under three headings: economics, processability, and product performance, as illustrated in Figure 4.2.3. For the purpose of illustration, examples of such factors under each of these headings are discussed below; however, the specific factors that are relevant to the particular waste treatment problem under consideration must be determined.

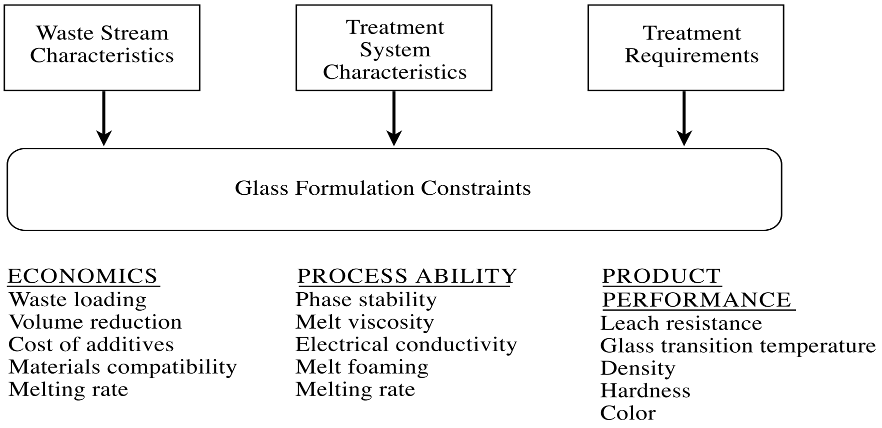

FIGURE 4.2.3 Influence of system factors on glass formulation. The selected range of glass formulations must then meet the imposed constraints.

Economics

A variety of factors that affect the overall economics of the process are impacted by the glass formulation (Pegg, 1994). These factors include waste loading (which determines the direct cost of additives, the fraction of operating capacity used to process the additives, and the fraction of the product that originates from additives, which contributes to disposal costs); volume reduction (which impacts disposal costs); and chemical compatibility with system materials of construction (which can impact system lifetime and maintenance requirements). In addition, the melting rate can be affected by the glass formulation and selection of glass forming additives, which also impact the process economics.

Processability

The particular factors that are important to processability depend on the melter type and design. The viscosity of the melt at the processing temperature is important for most types of melters, as is phase stability. Melt viscosity can affect the mixing and rate of waste incorporation into the melt, containment and discharge of the melt, and the rate of refractory corrosion. The melt viscosity is a strongly decreasing function of temperature that reasonably closely follows Arrhenius (or, more accurately, Vogel-Fulcher) behavior. Secondary phase formation is generally undesirable in most melter types but, as discussed above, some include features specifically designed for handling secondary phases (e.g., separate discharges for molten metals). Formation of insoluble crystalline phases during processing can lead to sedimentation and accumulation in the melt cavity and plugging of the discharge system. Thus, the liquidus temperature — the highest temperature at which crystals will form from the melt — is an important processing parameter. It is generally desirable to operate the process at a temperature above the liquidus temperature. The liquidus temperature is, in general, strongly composition dependent and is determined by different crystalline phases in different composition regions. Many electrically heated melters rely on electrical conduction through the glass melt, in which case the temperature- and composition-dependent electrical conductivity must be controlled within appropriate limits. Foaming of glass melts as a result of gas release (often triggered by temperature excursions) can lead to drastic expansion of the melt volume, which generally adversely affects processability.

Product Performance

In general, the final product is intended to perform some predetermined function. If the product is a waste form that is destined for disposal, the requirement may simply be based on the leach resistance as determined by one, or a suite, of test methods. If the product is intended for recycling or beneficial reuse, a range of additional properties may come into play, depending on the intended application. Examples might include the density, hardness, color, glass transition temperature, and mix of secondary phases. Secondary phases may form in the product to a greater or lesser extent during cooling and can affect many of the properties of the product; the formation of such phases may be incidental or may be deliberately induced (e.g., by heat treatment and formulation control) to impart particular characteristics (e.g., in decorative tiles).

An acceptable range must be specified for each of the relevant factors for the given problem. Then, because the glass composition affects all of these factors, the specification of an acceptable range for each of these factors essentially details a corresponding range of glass compositions that can meet these requirements (subject to other process controls). Operation of the process in such a way as to control the glass composition within that range is then a key element of the process control strategy to ensure that the system requirements are met. As an example, the (HLW JHM) constraint that the glass melt must have a viscosity between 20 and 100 P at 1150°C significantly restricts the range of suitable glass compositions (e.g., to a maximum silica content, minimum alkali content, etc.); consideration of other constraints serves to further bound the acceptable range. Note that, to the extent that a mathematical relationship can be obtained between each property of concern and the glass composition, the determination of the acceptable glass composition range reduces to the standard mathematical multivariate optimization problem, for which a number of methods, such as linear programming and extensions thereof, are available. The challenge, however, generally lies in the determination of property-composition models that are reliable over the range of interest for complex multicomponent waste glass systems. Such models, when appropriately developed and their specific limitations understood, play an important role in efficient glass formulation optimization. It should be noted, however, that the predictive capabilities and practical utility of supposedly "general" models are often exaggerated in the literature.

Frequently, the requisite property-composition models are too poorly known or insufficiently accurate to provide more than a guide for further, more definitive experiments. A likely range is defined on the basis of existing models and experience and discrete points in that range are then subjected to experimental testing. The results of these tests are compared with the constraints, a response formulated (i.e., new points to test are generated), and the process iterated until a suitably wide range of compositions is identified that satisfies the imposed constraints. Finally, the new data are used to augment the property-composition models over the specific composition range of interest, which can then be incorporated into the process control system.

Waste Loading and Solubility Limits

The waste loading that is achievable for a given waste stream has a direct bearing on the economic viability of vitrification as a potential treatment option. The waste loading limit can be determined by the solubility limit of a particular waste component (e.g., chloride) or the effect of the waste on a limiting glass property (e.g., leach resistance in the case of a high-sodium waste). The starting point in the evaluation of the suitability of vitrification as a treatment method for a particular waste stream is therefore characterization of the waste material. The characterization data are also essential in the development of optimum glass formulations. The primary data requirements are for chemical composition, with particular emphasis on the major components; it is often the case that detailed data on contaminant concentrations have been collected for regulatory purposes, but only very gross information is available on the bulk constituents. Waste stream compositional information should include all components present at greater than about the 1 wt% level on a dry basis for glass development purposes. Components with known low solubility limits, as discussed below, should be determined at correspondingly lower levels. This should include anions as well as cations. Total carbon content is important for assessment of potential redox effects, as is the content of metallic components.

In a broad sense, waste streams can be classified compositionally on a spectrum of "glass-former-rich" to "flux-rich," with these extremes having opposite effects on melting temperature and melt viscosity. The characteristics of the waste then determine the types and amounts of additives required to meet the design objectives discussed above. In general, flux-rich wastes (high in alkalis, alkaline earths, etc.) will not form acceptable glasses without glass-forming additives, due to either poor leach resistance or crystallization. Similarly, glass-former-rich wastes (high in silica, alumina, etc.) will form glasses only at high temperatures and typically require the addition of fluxing agents to reduce the processing temperature.

While silicate melts are capable of dissolving some amounts of most of the elements in the periodic table, for each waste stream component there will be a limit that depends on the other constituents present, as well as the processing temperature (and, in some cases, also the redox state). Specification of these limits is therefore a complex and inherently multidimensional problem. However, it is nevertheless useful to attempt to provide some general guidelines in terms of *single-component limits* that have been demonstrated, as shown in Table 4.2.1. In doing so, it must be emphasized that the level at which a given constituent can be incorporated will depend on what else is present in the particular waste stream under consideration and, therefore, *component interaction effects cannot be ignored.* Thus, while the general guidelines provided in Table 4.2.1 are useful for a "first-cut" analysis, each waste treatment problem should be considered on a case-by-case basis. These concerns are particularly acute with respect to limits based on secondary phase formation, where a small amount of one component can drastically reduce the solubility of another (e.g., the important and frequently waste-loading-limiting interactions between elements such as Fe, Mn, Ni, and Cr leading to the formation of spinel phases).

In the remainder of this subsection, noteworthy problematic constituents are discussed as well as the effects of common waste constituents that are processable but not significantly incorporated into the glass product.

TABLE 4.2.1 Approximate Oxide Solubility Limits in Silicate Glasses

>25 wt%	Al, B, Ca, Cs, K, Na, Pb, Rb, Si, U
15–25 wt%	Ba, Fe, La, Li, Mg, Nd, Sr, Zn
5–15 wt%	Be, Bi, Cu, F, Ga, Gd, Ge, Mn, P, Pr, Pu, Th, Ti, V, Zr
1–5 wt%	Am, As, C, Cd, Ce, Cl, Cm, Co, Cr, Dy, Eu, Hf, Mo, Ni, Np, Pm, Re, S, Sb, Se, Sm, Sn, Tc, Te, Tl, W, Y
<1 wt%	Ag, Au, Br, Hg, I, N, Pd, Pt, Rh, Ru

Note: Actual limits will depend on both temperature and glass composition.

Adapted from Volf (1984) and augmented with waste glass data from VSL and PNNL.

Water

Water is not incorporated into the glass to any appreciable extent (<1 wt%). Tolerance depends on the specifics of the melter and process design, but for many types of joule-heated melters, levels in the feed from 0 to 100% can be tolerated.

Nitrates

Nitrogen is not incorporated into silicate glasses to any appreciable extent except under extreme conditions (e.g., high-ammonia atmospheres as used to prepare nitride glasses) that are unlikely to occur in waste glass melters. Nitrates and nitrites are common in waste streams and increase gas evolution by thermal decomposition. Since NOx is a controlled air pollutant, the off-gas treatment system must be able to reduce NOx to below regulatory levels. It is possible to effect some level of NOx destruction in the melter by the addition of reductants to the feed. The addition of reductants also reduces melt foaming, as discussed below, which is especially prevalent under the highly oxidizing conditions associated with high-nitrate feeds.

Reducing Agents

Redox control is important in many waste glass vitrification systems due, in part, to the prevalence of multivalent species in most waste glasses. The analog of the electrochemical series for aqueous solutions in the case where molten glass is the solvent has been established for some waste glass compositions by the important work of Schreiber (1987). Reducing agents (oxalates, formates, organic acids, sugar, etc.) are used to control the oxidation state of the glass and to minimize melt foaming; formic acid is used at DWPF and sugar was used at WVDP and at M-Area. Without other actions, excess reductants can lead to the reduction of some oxides to metal or, in the presence of sulfur, to metal sulfides that have metal-like properties. Most melter designs are not compatible with such phases in the melt pool.

Excessive amounts of reducing agents can also cause foaming if the melt bath contains redox-sensitive species as a result of the reduction of higher oxides and liberation of oxygen. A common example is the reduction of Fe_2O_3 to FeO and ultimately Fe. Analysis of the feed is one method of control but direct measurement of the glass redox state, preferably *in situ*, would be desirable. Electrochemical *in situ* redox probes have been developed for the commercial glass industry; other methods include wet chemical or Mössbauer spectroscopic analysis of glass samples or even by inference from the oxygen fugacity in plenum gas.

The impact of organics in the feed on melt redox depends on the nature of the organic and the total carbon content (TOC) of the feed, as well as the type of process; in particular, combustion melters are generally more tolerant of organics. In JHMs, small amounts (<5 wt%) of TOC in the feed can generally be tolerated quite well if it is in the form of smaller molecules that will react predominantly in the cold-cap region. Larger molecules and pure carbon tend to pass incompletely reacted into the melt pool to some extent; entrained carbon in the glass melt can then create local, highly reducing regions and metal deposition. The tolerance to organics also depends on other constituents in the feed, such as nitrates, which can tend to offset the reducing effect, as well as the use of air- (or even oxygen-) sparging of the melt.

Sulfur

Sulfur has limited solubility in silicate melts and significant amounts of sulfates in the waste (i.e., such that SO_3 exceeds roughly 0.3 to 1 wt% in the glass, depending on the composition and operating parameters) can result in the formation of a liquid alkali sulfate phase that floats on top of the glass melt. This phase tends to readily incorporate chromium, as well as some cesium and strontium, among other elements. The formation of such a phase can be problematic because of its high electrical conductivity, high corrosivity, low melting temperature, high mobility, and its adverse impact on product quality. As with other constituents, the solubility limit for sulfur is dependent on the levels of all of the other constituents in the glass, as well as on the glass redox state. In general, glasses with high alkali contents tend to form sulfate phases at lower levels of SO_3, while those with higher alkaline earth contents tend to tolerate higher levels of SO_3. The solubility is, of course, also temperature dependent. One means of addressing high-sulfate wastes is to partition the excess sulfur into the off-gas stream. The addition of reductants to the feed is quite effective in this regard, but care must be exercised to ensure that the melt is not driven sufficiently reducing to produce molten sulfide phases. Increasing the processing temperature also drives more of the sulfur into the off-gas stream, with the result that higher-sulfur feeds can be tolerated. The practical limit of sulfur in the feed depends not only on the equilibrium solubility in the glass under the conditions in question, but also on important dynamic and transient effects present in an actual melter. In particular, sulfate phases can form in the cold-cap region and exist on top of the glass melt, even if the concentration in the glass melt is *below* the solubility limit under the prevailing conditions, as a result of its low rate of incorporation. Interestingly, there is evidence that the presence of a molten sulfate layer can increase processing rates by enhancing heat transfer, wetting, and spreading of the feed material over the melt surface, and it has been used in the glass industry for that purpose.

Halogens

With the exception of fluorine, which can be incorporated at up to about 10 wt%, the halogens have rather low solubilities in silicate melts; the value for chlorine is typically around 1 wt%. Significant amounts are lost from the melt by volatilization unless thick cold-caps are employed. Excess halogens can lead to the formation of molten salt phases, which present problems similar to the sulfate phases discussed above. Unlike sulfates, however, reductants are not effective in decomposing such phases.

Noble Metals

Noble metals (traditionally, ruthenium, rhodium, palladium, although silver behaves somewhat similarly) are only slightly soluble in glass and will remain in the metallic state or as an insoluble oxide. At the very low concentrations found in most waste streams, they do not pose a problem. However, at the still low but significant concentrations typical of most high-level nuclear wastes, they can lead to the formation of a conductive sludge layer on the melter floor. It is important to note that only a small fraction of the volume of this sludge is composed of the noble metals themselves; the bulk of the volume is composed of crystal phases (predominately spinels) that tend to nucleate on these metals (especially ruthenium) mixed with glass. Estimation of the potential magnitude of this problem is therefore not as simple as estimating the total volume of these metals in the waste, but also depends on the complex processes leading to the formation of the sludge, which in turn depends on the rest of the glass composition (e.g., high Fe, Cr, Mn, Ni, etc. tend to favor sludge formation). U.S. JHMs have adopted the approach of providing a sludge accumulation volume in the melter, whereas the German and Japanese systems have used bottom drains to remove them.

Phosphates

Phosphates also have limited solubility in conventional silicate glass systems. Most HLW process specifications generally restrict phosphate in the feed such that the concentration of P_2O_5 in the glass is less than about 1 to 3 wt%. However, somewhat higher levels are certainly possible, and up to 8 wt% has been successfully incorporated into Fernald Silo waste silicate glasses. Phosphates in combination with rare earths and/or high levels of calcium have been reported to lead, in some cases, to reduced melting rates due to the formation of a high-melting phosphate scum.

Applications

This subsection provides an overview of applications and commercial vendors of vitrification technologies around the world. Because many applications have been led by national initiatives to address the stabilization of high-level nuclear wastes, summaries of these national programs are also presented. To provide some initial perspective, Figure 4.2.4 shows a comparison between the total amounts of glass that have been produced to date by many of the nuclear waste vitrification systems that are discussed herein, while Figure 4.2.5 shows a similar comparison on a glass production rate basis.

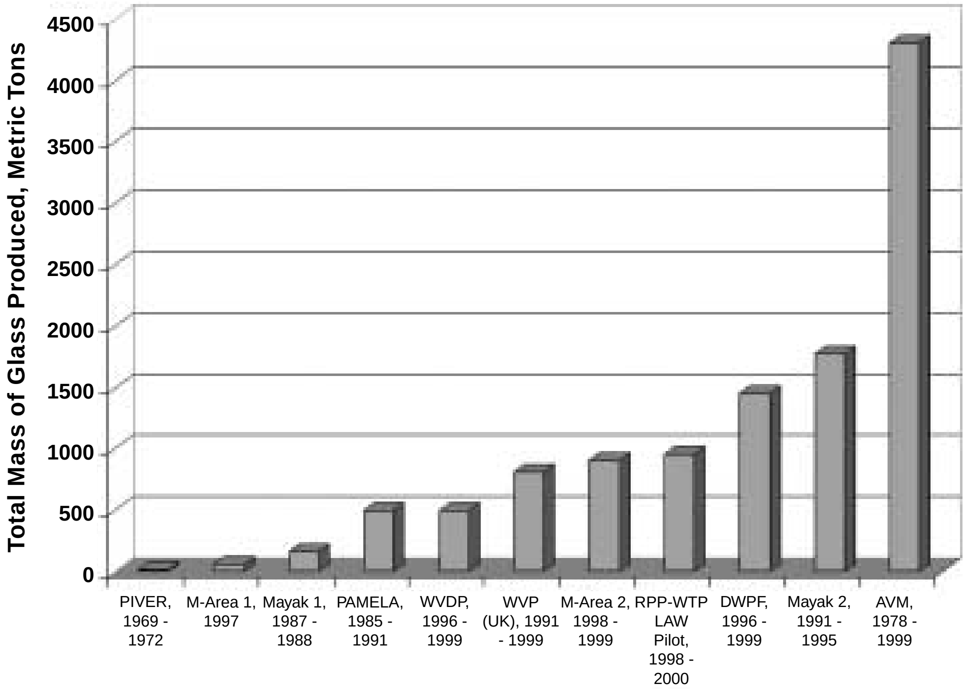

FIGURE 4.2.4 Comparison of the total amount of glass produced to date by various nuclear waste vitrification facilities.

Belgian-German Experience: PAMELA*

The PAMELA melter in Belgium, which started operations in 1985, was the earliest production application of slurry-fed JHM melter technology to HLW vitrification. The vitrification plant was designed by the German company DWK (Deutsche Gesellschaft fur Wiederaufarbeitung von Kembrennstoffen) and built at the Eurochemic site (now Belgoprocess) between 1981 and 1984. After a year of cold and hot testing with diluted waste, hot operation began in October 1985. By September 1991, some 900 m^3 of high level liquid waste from the reprocessing of spent fuel was successfully converted into 500 metric tons (MT) of glass product using two melters, each with a life of approximately 3 years. The first phase of the vitrification program, carried out under the responsibility of DWK, demonstrated the feasibility of the process. The second phase was performed on an industrial basis under the terms of a Belgo-German cooperation agreement.

In total, 1.51×10^{15} Bq of alpha and 4.44×10^{17} Bq of beta activity was vitrified to produce 2201 canisters of glass. After 6 years of vitrification operations, one ceramic melter and three other large components were dismantled and conditioned using a cement mortar as matrix. In total, 34.8 MT of solid waste containing 1.49×10^{12} Bq of alpha and 4.09×10^{14} Bq of beta activity were cemented in 187 200-L drums.

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*After M. Demonie, in NRC (1996).

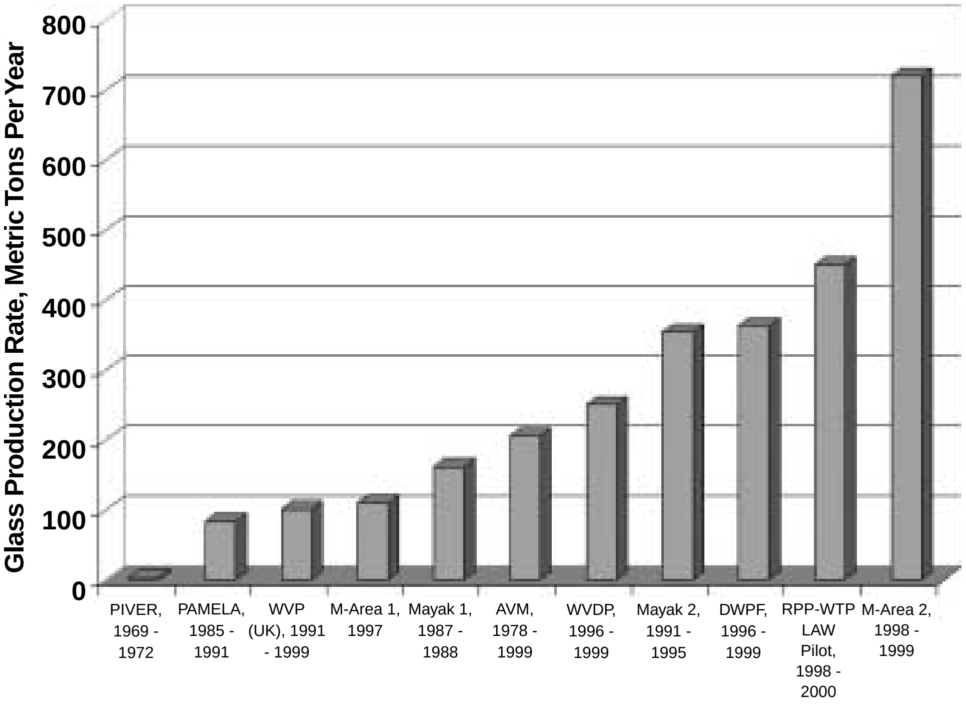

FIGURE 4.2.5 Comparison of the overall average glass production rates for various nuclear waste vitrification facilities.

Vitrification was effected in a single-step process using a JHM. Both the liquid waste concentrate and the glass frit were directly introduced into the melter, forming a process zone on top of the glass pool, where drying, calcination and melting reactions occur. The production melter had a melt surface area of 0.77 m^2, Inconel 690 plate electrodes, a Corhart ER 2161 contact refractory, and was equipped with both an air-lift and a bottom drain for glass discharge.

The performance of this system was generally good, with the principal difficulties being associated with noble metal sludges. The melter had four sets of electrodes, with the bottom set positioned ≈20 mm above the melter bottom to minimize deleterious effects of noble metals accumulation. However, the early melter feeds contained large quantities of noble metals, which within about a year accumulated to a depth of about 50 mm, causing electrical problems and difficulties with bottom-drain glass discharge. At this time, the primary discharge mode was changed from bottom drain to air-lift. Bubbling nitrogen gas in the melter bath was found to increase the processing rate but had very little effect on the removal of noble metals.

In total, two ceramic melters were used, each with a lifetime of approximately 3 years. Accumulation of noble metals was the major life-limiting factor for the first melter; the second melter experienced difficulties with a cracked riser block that led to leakage of air-lift bubbles. The change-out of a melter was performed in a period of 10 weeks using fully remote techniques. As a result of process variations, the target glass formulations had to be revised twice during operations.

French Experience[*]

Efforts toward the development of vitrification as a method for HLW treatment began in France as early as 1957. The world's first industrial vitrification facility, PIVER, began operations in Marcoule, France, in 1969. PIVER produced 164 glass blocks, weighing a total of 12 tons, from 24 m^3 of concentrated fission product solutions containing 6×10^6 Ci (6 MCi) before it was shut down in 1972. The facility resumed

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[*] After A. Jouan, NRC (1996).

operation a few years later to vitrify HLW solutions arising from the reprocessing of fast breeder reactor fuel, producing ten glass blocks of 90 kg each with very high specific activity. PIVER was a pot vitrification process in which glass frit and a gelling clay were fed into a melting pot while the pot was heated to effect calcination. After filling, the calcine was vitrified by further heating of the pot and finally discharged through a bottom freeze-valve.

During the 1970s, work was undertaken to develop a continuous vitrification process by first evaporating and calcining the feed solution in a rotary furnace, then melting the calcinate with glass frit in an induction-heated metal melter. The Marcoule Vitrification Facility (AVM) used this approach and was commissioned in 1978 to vitrify fission product solutions from French reprocessing activities. By the end of 1995, AVM had logged nearly 64,800 hr of operation and vitrified 1920 m^3 of solution containing 401 MCi, producing 857.5 tons glass in 2412 canisters, each containing 360 kg glass. The successful operating record and experience gained with AVM and the need for additional capacity led to the start-up of a commercial-scale HLW vitrification plant. Two similar facilities, R7 and T7, are now online at the La Hague reprocessing plant in France; R7 was commissioned in 1989 and T7 in 1992. By the end of 1995, 2434 and 1275 400 kg-canisters of glass had been produced at R7 and T7, respectively, from over 3000 m^3 liquid fission product solutions with 1490 MCi of activity. The R7 and T7 facilities produced 259 and 358 containers, respectively, during 1999, bringing the total amount of HLW glass produced by the AVM process to 4300 MT.

British Experience*

Vitrification process development in the United Kingdom began with initial work carried out at Harwell int the 1950s. The first process was based on a pot-melter approach (FINGAL) in which the melting pot was also the final container and a radioactive pilot plant was operated between 1962 and 1966 using this method. Process development was then temporarily halted due to lack of an economic incentive for treating the HLW and a high degree of confidence in the highly active waste storage tanks. Work on the modified and scaled-up version of FINGAL, known as HARVEST, was restarted in the 1970s and a new inactive pilot plant was operated between 1975 and 1980. The size of the HARVEST facility was full scale relative to what was then required in the United Kingdom, with glass batches of about 1000 kg compared to the 50 to 80 kg batches with FINGAL. In 1980 and 1981, British Nuclear Fuels, plc (BNFL) performed a comparison between HARVEST and the French AVM process and decided to adopt the latter, primarily on the basis of its demonstrated active operating experience and the potential for more rapid deployment and operation. From 1983, a full-scale inactive facility (FSIF) was constructed and operated by BNFL at Sellafield to develop the vitrification process for BNFL HLW, which culminated in the construction, commissioning, and active operation of the Waste Vitrification Plant (WVP) at Sellafield in 1991. The waste vitrification process consists of a high active liquor storage and distribution cell, two parallel vitrification lines consisting of vitrification and pouring cells, and container decontamination and monitoring/control cells. The process incorporates a rotary calciner through which HLW liquor is fed and partially denitrated. The calcine is mixed with glass frit and fed into a elliptical Inconel melter. After approximately 8 hr, the glass product is poured through a bottom freeze-valve into the container situated underneath. Through 1999, WVP had produced 2022 400-kg containers of glass from the treatment of HLW, including 328 during fiscal 1998/1999. As of May 2000, the facility had produced a total 810 MT of HLW glass. A third line is expected to be commissioned by the end of 2000 to increase plant capacity.

Japanese Experience: TVF**

The Tokai Vitrification Facility (TVF) was constructed as the first plant in Japan for conversion of high level liquid waste (HLLW) to borosilicate glass. Between April 1992 and December 1995, the TVF successfully completed test operations using both simulated waste and HLLW transferred from the Tokai Reprocessing Plant (TRP).

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[*] After G.A. Fairhall and C.R. Scales, NRC (1996) and Lutze and Ewing (1988).

[**] After M. Yoshioka and H. Igarashi, NRC (1996).

The TVF vitrification technology is based on the liquid-fed, joule-heated ceramic melter (LFCM) process developed by the Power Reactor and Nuclear Fuel Development Corporation (PNC) since 1977. This development work is a direct outgrowth of the U.S. DOE program in general and the West Valley program in particular. The melter has a melt surface area of 0.66 m^2, a 45° sloped bottom structure, and cold-bottom mode of operation intended to eliminate operational difficulties caused by conductive noble metal sludges. Inconel 690 plate electrodes are used with Monofrax K-3 as the contact refractory. Glass discharge is by means of a bottom freeze-valve with two-zone induction heating to allow smooth initiation and termination of glass draining; the nominal discharge frequency is once every 34 hr. The stated design life of the melter is 5 years. Although powdered and granular glass frits were tested, a novel glass fiber cartridge feed system was ultimately chosen on the basis of reduced particulate emissions into the off-gas stream. The cartridges are cylinders (70 mm dia. × 70 mm high), each of which absorbs about 200 mL HLLW before being fed into the melter.

Since 1992, 83 canisters of glass were produced in cold tests prior to beginning radioactive test operations in January 1995. However, glass accumulated in the coupling device between the melter and canister during the third glass draining to the canister. After carrying out improvements to the temperature control of the melter bottom and modification of the coupling device, the test operation was restarted and produced 20 canisters of glass. Radioactive test operations of TVF finished in October 1995 and the final operating license was obtained in December 1995.

Russian Experience*

Russian HLW vitrification activities have been concentrated on the production of phosphate vitreous materials in liquid-fed JHMs. The design of the melter units was developed and their operational suitability verified on the pilot-scale facility EP-100, which had a throughput of 100 L/hr of simulated waste solutions containing up to 400 g/L of solids and producing about 25 kg/hr of phosphate glass. On the basis of that experience, an industrial-scale facility EP-500 was built for the vitrification of actual HLW solutions at the Mayak radiochemical plant. The melters use molybdenum electrodes and an alumino-zirconium refractory (Bacor-30) as the glass contact material.

The vitrification complex occupies two connected buildings with the solution pretreatment area and off-gas system in the first building. The second building accommodates two ceramic melters, a unit for pouring glass into canisters, a remote welding system, and air-cooled storage. The first melter was put into operation in 1987 and operated for 1.5 years, including the period of cold tests. At this facility, 998 m^3 HLW with total activity of 3.97 MCi was vitrified, and 366 canisters with a total glass weight of 162 MT were produced.

The first melter was shut down in 1988 because of the failure of the power connection zone due to overheating. Following investigation of the melter failure, design changes were made and the second melter was built. That melter was put into operation in 1991 and by mid-1995, 9160 m^3 HLW (230 MCi) was vitrified to produce 1770 MT glass in 1372 containers.

Despite this experience base, recent efforts have been directed toward the development of borosilicate glass waste forms for Russian HLW.

Chinese Experience**

The Chinese vitrification development program was initiated in the mid-1970s. Research was then focused on a pot-melting process utilizing borosilicate glass as the product until 1985 when that program was discontinued. A liquid-fed JHM process was adopted in 1988 and the German technology was selected. The basic design of the mock-up facility was jointly carried out by Beijing Institute of Nuclear Engineering (BINE) and Institute für Nukleare Entsorgungstechnik (INE) in 1991. The full-scale melter was constructed at INE in 1992, tested in 1993, and delivered to China in 1994. Apparently, the Chinese HLW

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*After A.S. Aloy, V.A. Bel'tyukov, A.V. Demin, and Yu, A. Revenko, in NRC (1996).

**After Wang Xian De, in NRC (1996).

is rather low in noble metals but relatively high in sulfur, which ultimately limits the waste loading that is achievable (about 16%).

The melter has a stainless steel shell and a lining consisting of layers of high-temperature glass contact refractory, back-up bricks, and ceramic insulation material. Three pairs of Inconel 690 electrodes are installed on the wall of the melt pool opposite each other. The electrodes are cooled by air to keep them below 1050°C. The melter bottom has 75° sloped walls for collection and discharge of noble metals sludges via the bottom drain. The bottom drain valve is induction heated and the system is also fitted with an air-lift glass discharge system.

The waste solution and glass frit, in the form of beads 1 to 2 mm in diameter, are fed to the melter as separate streams. The feed to the melter is Ý65 L/hr of simulated waste solution with Ý5 L/hr of recycled waste solution from the off-gas treatment system. The glass product is discontinuously poured at a rate of 110 to 120 kg/hr into stainless steel canisters with a capacity of 400 kg glass.

The U.S. DOE Savannah River HLW Vitrification Facility (DWPF)

The DWPF is presently the largest U.S. HLW vitrification facility and includes a vitrification component that is now operating quite well. The entire facility, including the melter and all of its components, has been the subject of an extensive engineering effort. However, the protracted time scale over which the facility was designed and constructed has resulted in the melter's being of a rather early-generation JHM design. West Valley, on the other hand, being a much smaller project involving much simpler front-end processes (although the melter size is similar), benefited from later advances in JHM design.

The DWPF melter uses two pairs of Inconel 690 plate electrodes, a Monofrax K-3 contact refractory, a cylindrical glass cavity, and a vacuum-assisted overflow glass discharge system. The melter is also fitted with a bottom drain that is claimed to be capable of performing the service of routine discharge if the primary discharge should fail. The melt surface area is 2.6 m^2. The feed to the melter is nominally a slurry composed of HLW sludge plus cesium removed from the supernate stream combined with glass frit. However, the tributylphosphate (TBP) cesium precipitation pretreatment process has been shut down due to safety issues and the melter is therefore still being operated in "sludge-only" mode. For this reason, very little activity (for a HLW process) has been processed through this system at this time.

Approximately 80 canisters (Ý160 MT) of simulated waste glass were produced in tests prior to the commencement of hot operations in April 1996. The facility has produced over 1450 MT of HLW glass and needs to produce some 12,000 MT glass over a projected 25-year period to complete its mission.

The DWPF melter has limited capability to address issues associated with the formation of electrically conductive noble metal sludges. In particular, the timing was such that the design–construction process was unable to respond to the operational observations made on the PAMELA process. The bottom electrodes are only 3 inches above the *lowest* point on the dished floor of the melter; thus, there is little accumulation volume for noble metals. If the bottom set of electrodes were lost, processing could continue until the hole leading to the vacuum discharge riser, which is only a few inches higher, becomes occluded. The 51 tanks of HLW at the Savannah River site have been grouped into seven "megabatches" for processing families of waste types together. The first megabatch, which is currently being processed, has less than one third of the maximum concentration of noble metals found in the other megabatches. Because the feeds to date have been low in noble metals content, there is insufficient data to evaluate the effect of noble metals accumulation on the DWPF melter life.

The U.S. DOE West Valley HLW Vitrification Facility (WVDP)

The WVDP vitrification facility is based on a liquid-fed JHM. Unlike the DWPF, the WVDP melter design incorporates some level of noble metal mitigation, including a sloped bottom, a bottom electrode, and space for noble metal sludge accumulation. The melter has three air-cooled Inconel 690 plate electrodes, mounted on two opposing sides and on the bottom, and powered by a three-phase supply. The two side electrodes are positioned at a distance from the bottom of the melter to provide sufficient volume for noble metal accumulation without adversely affecting power supply to the glass pool. The contact refractory is Monofrax K-3 and two air-lift discharge chambers are installed for glass discharge;

the melter has no bottom drain. The melt surface area is 2.2 m^2. The feed to the melter is a slurried mixture of HLW sludge, cesium-loaded zeolite ion exchange media, and raw glass forming chemicals rather than glass frit.

From 1984 to 1989, the WVDP operated a full-scale glass production test facility. Conversion of that facility for radioactive processing (including the installation of a new but essentially identical melter) was completed in 1994 and functional testing was completed in mid-1995. Examination of the test melter showed very few signs of refractory or electrode corrosion. Radioactive operations commenced in June 1996 and have continued with minimal interruptions to the present time. The WVDP has processed in excess of 12 MCi and produced Ý500 MT of HLW glass in about 235 canisters. Although noble metal accumulation initially led to an increase (Ý40%) in the effective melt pool conductivity, it stabilized sufficiently over a period of time to allow steady-state operation of the melter. However, design modifications may be necessary if longer processing times with feeds containing higher levels of noble metals are required. Melter pressure fluctuations required modifications to the operations procedure to minimize positive pressure excursions leading to contamination of the hot-cell. A number of factors can lead to these pressure fluctuations, including introduction of the feed onto the hot glass-melt surface, pressure fluctuations associated with feed delivery to the melter using an air displacement slurry (ADS) pump, foaming events, and pressure fluctuations associated with the submerged bed scrubber (SBS).

GTS Duratek DuraMelter™ Technology

DuraMelter™ technology, developed and implemented by GTS Duratek and its partner the Vitreous State Laboratory (VSL) at The Catholic University of America, has been used in the vitrification of various radioactive, hazardous, and mixed wastes. Pilot systems capable of producing tens of kilograms to several tons of glass per day have been operating at VSL since 1985. These systems have performed process demonstrations on actual mixed wastes from most of the major DOE sites (Savannah River, Hanford, Idaho, Oak Ridge, Fernald, Los Alamos, Weldon Spring) as well as on numerous commercial wastes. Two of the larger applications of DuraMelter™ technology to waste vitrification are discussed below.

Mixed Waste Vitrification at the SRS M-Area

Between October 1996 and March 1999, GTS Duratek stabilized over 2500 m^3 mixed waste from an electroplating process, stored at the Savannah River Site's M-Area, using DuraMelter™ JHM technology. This project, one of the early "privatized"-style waste treatment procurements for the DOE, was the first commercial application of vitrification for mixed waste treatment and the largest-scale application of JHM technology in the United States (Bowan and Brandys, 1994). All of the supporting glass formulation and operating envelope development, as well as melter and process testing with actual M-Area wastes, was performed by the Vitreous State Laboratory of The Catholic University of America under private contract to GTS Duratek.

The initial DuraMelter™ 5000 deployed at M-Area had a melt surface area of 5.0 m^2, was rectangular in shape, and had a flat bottom because the waste contained no noble metals and therefore noble metals accumulation was not an issue. The melter had three Inconel 690 plate electrodes mounted parallel to each other and to the short walls of the melter and extending the entire width of the melter. Two of the electrodes were placed close to the walls and the third was placed at the center. The contact refractory was Monofrax K-3 with AZS back-up refractory and two air-lifts were installed for glass discharge. The melter employed agitation via air sparging to improve heat and mass transfer, and to enhance throughput. The feed to the melter was a slurried mixture of the waste and raw glass forming chemicals. The glass product was discharged into 70-gallon containers in the form of gems (flattened marbles). The DuraMelter™ 5000 was shut down in March 1997 when evidence of abnormally high rates of refractory corrosion were observed. The melter was used to produce Ý55 MT of mixed waste glass.

Between May and December of 1997, a new melter, the DuraMelter™ 5000A, with some design modifications, was installed and commissioned. The main design changes included (1) thickening of the contact refractory, (2) addition of active thermal expansion compensation system, and (3) addition of water cooling to the outside walls. The waste glass chemistry was also modified to reduce corrosion of contact refractory. Using the new melter, the waste treatment mission was successfully completed and the tanks were clean-closed by April 1999. During this campaign, the DuraMelter™ 5000A was used to produce over 900 MT glass at production rates as high as 5 MT glass per day, which is the highest throughput reported for a radioactive waste vitrification system, at an overall system availability exceeding 80%. At the end of the campaign, the melter was subjected to an autopsy to determine its condition and to identify any indications of potential problem areas. The melter was found to be in excellent condition with many more years of useful life, and no areas of concern were identified.

DuraMelter™ Technology for RPP-WTP

The DuraMelter™ JHCM is the current baseline technology for the vitrification of Ý200,000 m^3 of tank waste at the River Protection Project (RPP), Waste Treatment Plant (WTP) in Hanford, Washington. The tank wastes will be separated into HLW, which contains noble metals, and low-activity waste (LAW) which is composed primarily of sodium salts. The HLW melter design is similar to the WVDP design with three Inconel 690 plate electrodes, sloped melter bottom, space for noble metals accumulation, and two air-lift discharges. The glass melt surface area is 3.75 m^2, and the contact refractory is Monofrax K-3 with AZS backup. The LAW treatment facility is designed to have three production lines, each with a melter capable of producing 10 MT glass per day for a total of 30 MT glass production per day. The LAW melter is similar in design to the DuraMelter™ 5000A, with the major difference being in the number and locations of the electrodes. The RPP-WTP LAW melter is rectangular in shape with a flat melter bottom, and has a melt surface area of 10 m^2. The melter has three sets of electrodes, arranged opposite each other, along the length of the melter and placed close to the contact refractory. Glass discharge is with two air-lifts into steel drums.

The DuraMelter™ 3300, a Pilot Melter that represents a one-third section of the RPP-WTP LAW melter, financed by BNFL, Inc., was designed, built, and operated at GTS Duratek from October 1998 to the present. The melter has a melt surface area of 3.3 m^2, three Inconel 690 electrodes with one large electrode on one side and two smaller electrodes on the opposite side, and two glass discharge systems. One of the glass discharges operates by air-lift and the other has capabilities for air-lift and vacuum discharge. The contact refractory is Monofrax K-3. Over 1000 MT glass has been produced with melter feeds that are slurried mixtures of waste simulants and raw glass forming chemicals. An average production rate of Ý5 MT glass per day was achieved during a sustained throughput test of 45-day duration with overall system availability exceeding 90%.

The major difference between the DuraMelter™ melters and the DWPF and WVDP melters is the agitation system (air-sparging). For comparable feeds, the DuraMelter™ melters show throughputs two to four times higher than that for non-agitated melters (see Figure 4.2.2). Disadvantages of this system are slightly increased solids carry over to the off-gas and increased maintenance requirements for the air-sparging system. DuraMelter™ melters use Inconel air bubblers that are introduced from the top and require periodic replacement. Operational experience to date suggests that the increased throughput due to the DuraMelter™ agitation system more than offsets downtime associated with bubbler maintenance.

Envitco, Inc.

Envitco, Inc. began as an outgrowth of Toledo Glass, a designer and fabricator of large commercial glass melting systems. It was targeted at the waste treatment market and is now a part of the French Cogema group. Envitco, like Toledo Glass, provides fossil-fuel fired, propane/O_2 fired, and joule-heated glass melting systems. The JHM systems are based on water-cooled molybdenum rod electrodes that are standard in the commercial glass melting industry. An advantage of this system is its higher maximum operating temperature (stated as 1700°C) but, as discussed previously, molybdenum electrodes create some concerns for waste glass melting. The melters are of thin-walled, water-cooled refractory construction and have bottom and/or overflow glass draining systems. There has been relatively little consideration given to nuclearization of the system, which still most closely resembles commercial glass melting technology. The technology has been used in several small-scale DOE demonstration projects, although all but the recent TVS (Transportable Vitrification System) demonstration at Oak Ridge with very low activity waste sludge have been with surrogate wastes. The TVS program was conducted between 1993 and 1998 with the objective of demonstrating a transportable vitrification system with actual mixed waste, for which an Envitco JHM unit was selected. While the demonstration was started in October 1997, permitting issues and a glass leak incident in 1995 resulted in less than 10% of the intended 80,000 kg of waste being processed with production rates of less than 33% of the design basis.

Stir Melter

Stir Melter is a subsidiary of GlassTech, Inc., a company that produces machinery for forming automobile windshields. These melters employ vigorous mechanical mixing of the melt pool to increase production rates. The melter is formed from an Inconel can that forms one of the electrodes. The other electrode is a centrally located Inconel paddle that enters the melt from above and can be rotated. The units are fitted with overflow or bottom freeze drains. The challenge with this system lies in the high-temperature mechanical strength required of the paddle assembly; at least with Inconel, this necessitates reduced operating temperatures that tend to offset any increases in production rate. The Stir Melter was also investigated as a potential replacement for the DWPF melter because of its higher throughput potential. However, a Stir Melter system that was purchased and delivered to the Savannah River site has never been used.

Vectra

The "V-Skull" melter manufactured by Vectra, formerly a subsidiary of Pacific Nuclear Corp., is a water-cooled metal container with a bottom drain and top-entering molybdenum electrodes, which operates with a layer of frozen glass coating the melter walls. Considerable attention was paid to nuclear operation of the melter in its design and detailed engineering. A portable system was constructed that was intended for vitrification of spent organic ion exchange resins from nuclear power utilities but was never commercially operated.

Other Suppliers of JHMs for Waste Treatment

Several other companies, mostly commercial glass companies, have had some involvement in waste vitrification or have performed demonstrations and claim to supply such systems. Ferro Corporation is one such U.S. company. Ferro's waste vitrification experience appears to be limited to involvement in a few EPA-funded tests but is leveraged by their demonstrated ability to provide large-scale commercial glass systems. Sorg Gmbh & Co. is a German company with a similar background. It has built and commissioned more than 70 all-electric melters since 1969 and has supplied more than 200 joule boosters for conventional furnaces. Sorg has been involved in several asbestos vitrification test facilities and fabricated several of the test and production melters used in the German HLW program. The U.S. company Vitrifix has also used JHMs to treat asbestos wastes at a site in West Virginia and contaminated soils at a site in Faslane, England; again, Vitrifix does not appear to have any nuclear experience. A JHM was also operated at Oregon Steel for the vitrification of hazardous steel mill electric arc furnace dust. The process used commercial glass melting technology with top-entering molybdenum (and later graphite) electrodes and a refractory-lined melt cavity. The product was sold as grit blasting media.

In Situ Vitrification

In situ vitrification (ISV) of contaminated materials is attractive in that waste retrieval, transport, and disposal of the vitrified product are avoided. Geosafe Corporation, based in Richland, Washington, offers ISV services based on the joule-heated ISV technology developed by the DOE and Battelle Memorial Institute in the early 1980s. The traditional ISV technology offered by Geosafe Corp. involves in situ vitrification via joule-heating by passing electric current through electrodes installed into the contaminated material. Joule-heating is initiated by providing an electrically conductive path between the electrodes. Once melting starts, most soils are conductive enough to sustain electrical currents sufficient to continue the vitrification process. If the molten soils are not sufficiently conductive, the soil is preconditioned by addition of components that will impart the required electrical conductivity on melting. The process typically operates in the temperature range of 1600° to 1900°C. Geosafe Corp. offers both conventional top-down and planar melting methods. The conventional top-down melting produces melts typically wider than the depth processed, whereas planar melting is reported to produce tall and thin planar melts. Standard off-gas systems are used to contain and treat emissions. A variation of this process is the staged ISV, in which contaminated materials are consolidated at a preferred location for processing.

Geosafe Corp. has conducted over 80 demonstration projects at engineering scales of 0.1 to 1.0 MT, to large-scale demonstrations of 200 to 1200 MT glass. The company is currently in the process of completing the treatment of plutonium-contaminated soil in the Maralinga test range in South Australia.

One of the concerns in the application of this technology is the presence of undesirable materials in the treatment area. These may include sealed drums of flammable or explosive contaminants, large concentrations of organic contaminants, presence of large quantities of water, etc. Preconditioning of the treatment area, combined with detection and removal of undesirable materials, has been reported to be effective in the successful application of ISV.

Seiler Pollution Control Systems, Inc.

Seiler HT, based in Switzerland, and their U.S. subsidiary, Seiler Pollution Control Systems, Inc., market a combustion melter aimed at the hazardous, mixed, and low-level radioactive waste markets. The system consists of a feed make-up station, a gas-fired preheater that raises the feed temperature to Ý700°C, a gas-fired furnace that operates at 1500 to 1600°C, and off-gas equipment. Molten material is discharged from the bottom of the furnace. Modular units, 6 to 25 MT per day capacity, are reported to be available. Operation of the system in a radioactive environment has received relatively little attention in its design and engineering.

Marine Shale Processors

Beginning in 1985, Marine Shale Processors (MSP) operated a facility located in Amelia, Louisiana, that incinerated a variety of nonhazardous and hazardous wastes and vitrified the resulting ash. The incineration step was performed using modified rotary cement kilns, while vitrification was performed using a combustion-fired melter. The system is noteworthy for its demonstrated capacity of 300,000 tons of waste per year and vitrification capacity of 100 to 150 tons of glass product per day, with a maximum capacity of 400 tons per day. This may well make this facility the largest waste vitrification system to have operated in the United States. The glass product was sold as aggregate. Unfortunately, the MSP process became embroiled in regulatory issues related to its claimed status as a recycler vs. the EPA's final determination that it was, in fact, a hazardous waste incinerator. The issue was finally resolved in a 1997 federal consent decree under which MSP agreed to pay $10M to settle the allegations. GTX Inc. has since agreed to buy the facility for $25M and plans to spend an additional $60M in upgrades. At this time, there appears to be no intention to attempt to recycle the vitrified product, which will instead be destined for a landfill.

TRW, Babcock & Wilcox, and Vortec Combustion Melters

Combustion melters, based on technology developed for slagging combustion units for the coal and utility industries, have been proposed for vitrification of hazardous and radioactive wastes. Different versions of these melters have been developed by TRW Space & Technology Division, Babcock & Wilcox, and Vortec Corporation of Collegeville, Pennsylvania. The melters are compact units, mostly cylindrical in shape with water-cooled walls that operate in the temperature range of 1300 to 1600°C. Heat is supplied by gas- or oil-fired burners. These melters use either a very thin layer of refractory or no refractory. The forced cooling of the outside of the melter walls results in the formation of a cold layer of glass (skull) on the inside walls that prevents corrosion of the melter walls. These units are best suited for large-scale operations for which product quality and homogeneity are not major concerns. These melters can process various types of waste materials, including those that contain large quantities of organics and metals. Increased carryover to the off-gas, larger off-gas volume, and relatively inhomogeneous product quality due to short residence times are major concerns in the application of this technology to radioactive operations with stringent emissions and product quality requirements. Vortec Corp. has developed a melter system designed to treat hazardous, mixed, and low-level radioactive wastes. The system consists of a feed preparation stage, combustion preheater, cyclone melter, and off-gas components. The system is reported to be capable of operations using a variety of fuel sources, including pulverized coal, coal slurries, oil, natural gas, etc. Throughputs of these systems are reported to vary from a few metric tons per day to greater than 100 MT per day. The waste material, along with fuel and glass forming additives, are fed to the counter rotating vortex (CRV) preheater, where organics are destroyed by oxidation and inorganics are melted or heated close to their melting points. The CRV operating temperature varies from 1100°C to as high as 1900°C. The material from the CRV passes to the melter, from which it is discharged mainly in the form of a frit. One disadvantage of the system is that it cannot handle bulk feed materials and, in general, the feed materials must first be converted to a dry powder. Careful control of feed preparation and glass composition is necessary to produce homogeneous products of uniform compositions and properties.

Cold Crucible Vitrification

The principle of operation of cold crucible melters (CCMs) resembles that of the hot-wall induction systems, except that in this case the wall is segmented with dielectric materials to *prevent* the flow of current around the wall of the crucible. In addition, the wall is actively cooled to freeze a layer of glass on the interior surface, which provides containment of the glass melt and the ability to operate at much higher temperatures than is typically the case with hot-wall melters. In this case, it is the electrical conductivity of the glass melt that acts as the secondary of the transformer and the current is induced in the glass melt itself instead of the wall. Melters based on this approach have been developed in both Russia and France; the Russian systems are generally operated at higher frequencies than the French system. A nonradioactive prototype melter 0.55 m in diameter and 0.70 m high developed by the French CEA has been operating together with a calciner for several years at Marcoule. In Russia, a CCM pilot system has operated at Mayak with both phosphate and borosilicate glasses at rates of up to 18 kg glass per hour at processing temperatures of up to 1500°C. A similar radioactive pilot system with a melt surface area of 0.102 m^2 has been operated at the "Radon," with glass production rates of about 10 kg/hr at temperatures of about 1200°C. To date, the physical size, and hence capacities, of these systems are limited. This is because the power profile decays exponentially with distance from the wall into the glass and, therefore, most of the power is delivered to the glass that is closest to the (cold) wall, so the potential for scale-up is limited. Aqueous feeds can also present difficulties for these units as a result of the condensation of water on the cold wall above the melt line, which can lead to dielectric breakdown and shorting.

Framatome Vitrification Process (FVP)

The FVP system uses a metal melting pot that is indirectly heated by electrical resistance heaters to an operating temperature range of 1100 to 1200°C. The pot is fitted with a resistance-heated freeze-valve for discharge of the product. One of the unique features of this system is the injection of the waste feed *under* the glass melt which, it is claimed, minimizes the carryover of solids into the off-gas stream. Supplementary gas injectors are also included to provide redox control and to increase melting rates through improved agitation. The system also includes an integral secondary combustion chamber fitted over the melt to complete the combustion of organics. A pilot plant at Bollene, France, has been operated for more than 6 years at feed rates of up to 25 kg/hr with organic wastes including plastics and spent ion exchange resins.

Summary

Waste vitrification is now a relatively mature technology and, indeed, has become the preferred method of treatment for HLW, which presents one of the most challenging waste treatment problems. The sheer number of different types of vitrification systems that have been developed, demonstrated, and/or implemented at commercial scale underscores both the interest in this technology and its inherent flexibility. The development of waste glass compositions to meet a variety of requirements has itself become an active area of study, and systematic approaches have been established that enable this to be done efficiently. In addition, the diversity of waste types for which vitrification is considered a potential treatment option has steadily increased since the early focus on HLW streams. While, unlike the case for radioactive wastes, vitrification of hazardous wastes presents the possibility of offsetting the treatment costs by beneficial reuse of the product, there are still surprisingly few viable commercial examples of this approach in the United States.

Defining Terms

Calcining:	Heating a material (normally inorganic) to a high temperature to remove volatile materials and effect physical or chemical changes (e.g., oxidation) without melting.
Cold-cap:	Stratified layer of reacting feed on the glass melt surface where evaporation of water and volatiles, decomposition and calcination of feed materials, and initial melting of the feed materials occur.
Contact refractory:	High-temperature refractory that is in direct contact with the glass melt.
Cullet:	Broken glass collected for disposal or reuse. Reuse may include its addition to new melter feed to improve melting.
Gems:	Flattened glass marbles.
Glass forming chemicals:	Raw materials added to the waste to impart desired properties to the glass melt and the final glass product.
Liquidus temperature:	The highest temperature at which crystal can form from the glass melt.
High-level nuclear wastes:	Radioactive waste material resulting from the reprocessing of spent nuclear fuel up to the second cycle of reprocessing.
Waste form:	Material form in which to safely stabilize waste materials (e.g., radioactive waste in a borosilicate glass matrix).
Waste loading:	Mass fraction of the glass product that originates from the waste (weight%, wt%).

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4.3

Application of Steam-Reforming to Various Types of Radioactive Waste

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Introduction

Although incineration is the historical precedent for thermal waste destruction, incineration is no longer broadly applicable. New thermal alternatives are required to address applications for which incineration is not acceptable as a result of:

- Tighter regulatory controls
- Unacceptable risks of incineration (e.g., the generation of dioxins and furans)
- Negative public response to incineration of hazardous and mixed wastes during the permit phase of new projects[1-3]

As another example of incinerator regulatory and liability management issues, treating small-generator radioactive wastes via continuous operations (e.g., large throughput incinerators) commingles isotopes between customer batches, cross-contaminating the final ash residue and prohibiting process-and-return for clients that have limited or restricted access to disposal. Steam reforming offers a permittable, cost-effective alternative that meets the needs of process-and-return customers.

Similarly, many international applications feature waste streams that must be processed, with limited disposal options available and strong opposition to incineration. A key example is processing of mixed radioactive or PCB-contaminated wastes in Japan, where incineration is not an acceptable option. Steam reforming offers a technically superior solution, can potentially address the public's concerns during permitting, and offers a cost-effective approach to real-world problems. A key to the acceptance of steam reforming is to compare alternatives on a common basis for scale of operation, permit acceptability, and regulatory compliance. For example, one cannot compare, economically, a small steam reforming unit that might process one or two drums of waste per day to a production-scale incinerator that processes 450 to 680-kg/hr (1000 to 1500-lb/hr) of waste (particularly in areas such as Japan where steam reforming might be feasible and large-scale incineration is not). Comparing alternatives requires the following:

- Economics for both systems must be evaluated for the same throughput.

- At comparable scale, steam reforming capital and operating costs can be shown to approximate that of incineration.
- Safety performance and emissions for steam reforming are found to be superior.

The following subsections tour the reader through the steam reforming technology base, while covering the chemistry, hardware, and a range of experience that can solve radioactive and mixed waste problems for a variety of industries.

Process Overview

Steam reforming is a two-step process (shown in Figure 4.3.1) that reacts excess, superheated steam with organic constituents of waste streams.[4-7] Waste stream hydrocarbons are evaporated and partially reformed in a first-stage, waste feed evaporator (WFE) that can have a variety of configurations (DFE – as shown in Figure 4.3.1, HSE, etc.), depending on the type and form of the waste. This is the stage that is tailored most to integrate the technology with the end-use application based on the requirements for heat and mass transfer, waste segregation, and steam-waste contacting to ensure efficient destruction of the organic matrix.

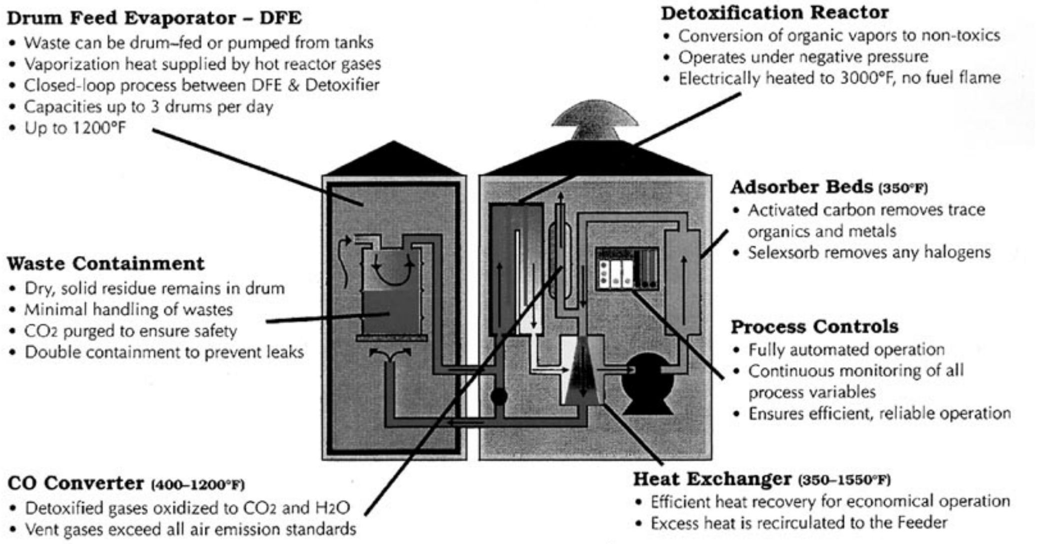

FIGURE 4.3.1 Schematic of operational features.

Within the WFE, hydrocarbon vapors begin to react with superheated steam between 350 and 600°C (600 to 1100°F). Steam reforming converts hydrocarbons to CO, CO_2, H_2O, H_2, and a small amount of CH_4; the mix depends on the atomic composition of elements in the waste, the amount of steam, and any residual free-oxygen present. Gases generated in the WFE are heated in a heat exchanger to 1000 to 1200°C (1800 to 2190°F) and mixed with excess superheated steam en route to the electrically heated main steam reforming reactor (SRR). In the SRR, the reactions proceed to completion to meet the Environmental Protection Agency (EPA) Resource Conservation and Recovery Act (RCRA) >99.99% or Toxic Substances Control Act (TSCA) >99.9999% DRE requirements.

Steam reforming advantages, relative to incineration, include:

1. Minimal entrainment and volatilization of radioactive species (particularly plutonium and actinides) due to low process gas flows, low first-stage temperatures, and operating under reducing conditions
2. WFE tailoring to specific process feeds with no impact on secondary stage design and operation
3. A compact mobile or fixed-base operation

4. Fail-safe operation during power failures due to the endothermic nature of the reforming chemistry
5. Outstanding safety and reliability through state-of-the-art process control

The following subsection covers the different WFE designs and discusses their advantages for processing different waste forms. Waste feeders discussed include the drum-feed evaporator, heated screw evaporator, and can-feed evaporator.

Drum Feed Evaporator: To Manage Waste Handling and Commingling Liabilities, Small Waste Volumes, and TRU Wastes:

The drum feed evaporator (DFE), schematically shown in Figure 4.3.2, is a specially designed, electrically heated evaporation chamber suitable for processing organic drummed waste where minimal material handling is desired. Hot recycled gases enter through the top of a standard drum equipped with a special process lid and evaporate the volatiles in the waste. In the vapor stream, steam and recycled gases start to react with the organics as they are pulled into the SRR under slight vacuum. After the SRR destroys the toxic organics by reaction at high temperature, the syngas product is recirculated to the DFE to further reform the waste. A small vent stream is released from the SRR effluent gas to an air pollution control system (APCS), which maintains system negative pressure. This hydrogen-rich vent stream is also available for potential applications in fuel cells as a co-generation step.

FIGURE 4.3.2 Drum feeder with door open and drum inside.

The system is fully automatic, ramping the flow rate and the waste temperature up to 600°C (1100°F) at the proper rate to produce a steady stream of volatiles and organics to the SRR. At the end of the cycle, when the H_2 or CO production decreases, the flow is steadily decreased to cool the drum and waste residue prior to drum removal. The automatic control system is designed for remote operation with minimal operator interaction, with safety interlocks to prevent premature opening. The SRR-DFE system has been designed to operate remotely, to be accessed by modem for updates on operating conditions, and the control system has been designed to call the operator by pager when the drum is cool and ready for removal. In this manner, one or multiple systems can be operated with minimal labor.

Heated Screw Feeder: To Reduce Cost Through Continuous Operation

The heated screw evaporator (HSE) (Figure 4.3.3) is particularly suited for continuous processing of slurries, sludges, and shredded solid wastes. Waste is fed continuously into one end of a slowly rotating single auger within an electrically heated trough. With heat input from the HSE and the countercurrent flow of steam and syngas, waste traveling through the screw is ramped from an initial reaction temperature of 150°C (300°F) to a final temperature around 510°C (950°F) at the discharge end. The waste is partially steam reformed along the screw, and the vapors generated proceed to the SRR to complete the reaction. SRR exit gases are recycled similar to DFE operation. At the discharge end of the HSE, a steady stream of processed residue is discharged.

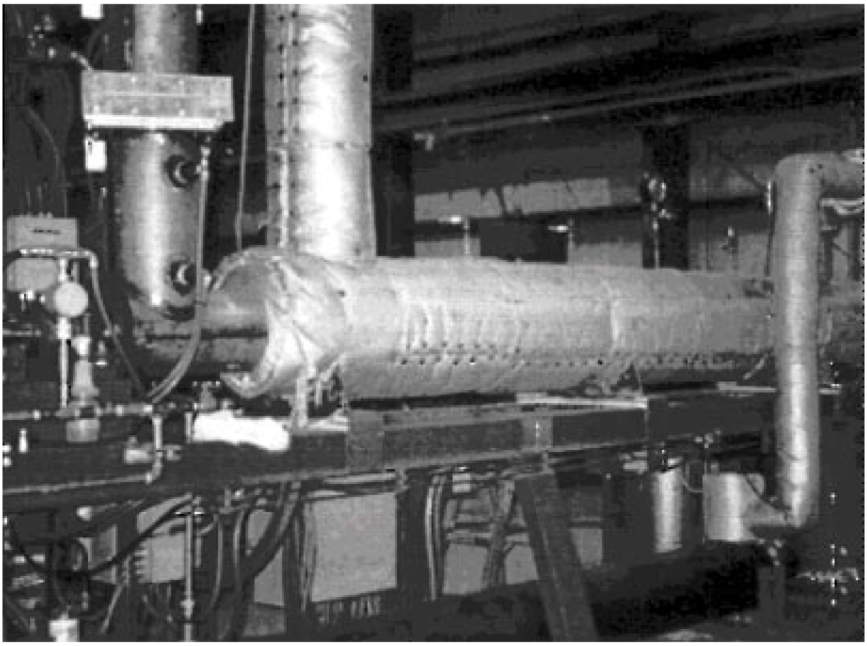

FIGURE 4.3.3 Photograph of heated screw and exit drum.

The important characteristics of the HSE are high volume and mass reduction, high heat and mass transfer for more rapid throughput, and a "gravel-like" finished product suitable for disposal or stabilization. A typical HSE uses a 23-cm (9-in.) diameter by 5-m (16-ft) long screw, which has ample capacity to deliver 1 ton/day (900-kg/day) of organics to the SRR.

Can Feed Evaporator: To Handle Utility Fuel Pools Waste

The can feed evaporator (CFE) (see Figure 4.3.4) was specially designed for processing fuel-pool, high-level, radioactive wastes. This CFE steam reforming design is the only NRC-approved thermal process

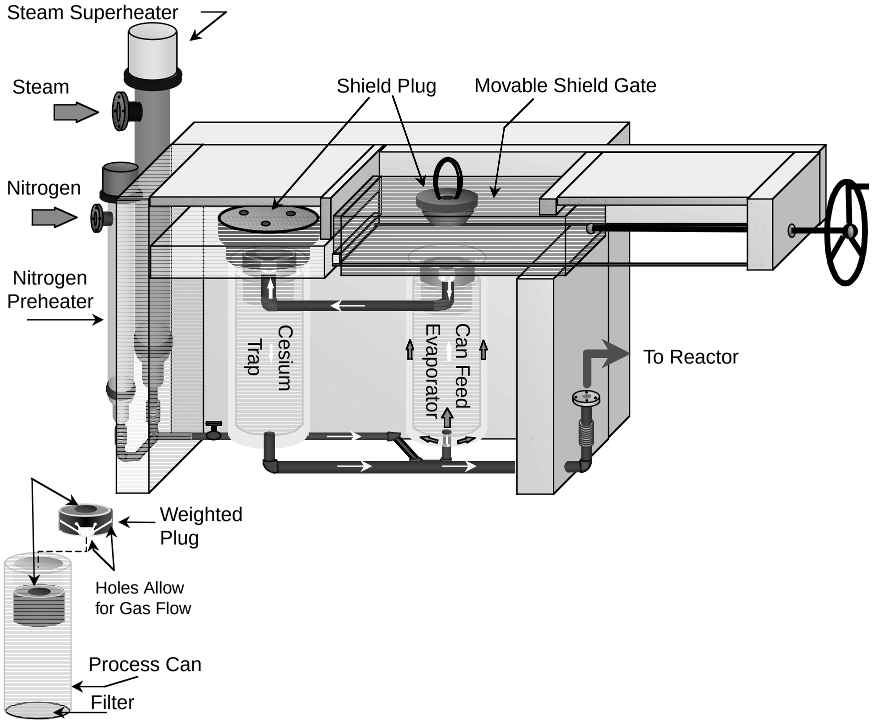

FIGURE 4.3.4 Schematic of can feed evaporator.

for operations within containment areas. This process was successfully used at the decommissioned Trojan nuclear power plant near Portland, Oregon, where organics and radiolytic hydrogen were removed from contaminated fuel pool wastes, and the residue was placed and sealed inside long-term storage canisters for eventual placement in a geologic repository.

The CFE uses a 20-cm (8-in.) diameter by 69-cm (27-in.) long process can that is loaded with high level waste submerged in the fuel-pool. Standard vacuum tools are used to retrieve the waste and filter it through a pleated or sock cartridge filter to recover the solids. The filter medium containing the high-level solids is removed under water and placed into the can, and the lid is attached by a simple rotating action. To transfer the can from the pool to the CFE, the can is remotely grappled and lifted into a heavily shielded transfer bell, and enclosed in the bell with a slide gate. The CFE is configured with a slide valve top entry port to mate and seal with the transfer bell so that the can is lowered from the transfer bell into the CFE processing chamber.

When the can is in place in the chamber, the waste is processed similar to DFE operation. The can is fitted with special high-temperature sintered metal screens at the top and bottom to ensure that the radioactive solids remain within the can. When processing is complete, the can is then extracted by the transfer bell and placed down into the final disposal canister, which is then helium back-filled and welded closed. This equipment and operation is fully certified by the NRC, and the final disposal canisters exceed the most severe repository requirements of no vented gases and internal hydrogen below the 5 vol% NRC limit.

Matrix of Waste Types

Steam reforming offers flexible feed systems to handle the following broad classes of waste types, both radioactive and nonradioactive, listed in Table 4.3.1.

TABLE 4.3.1 Processing Capabilities of Different Feeders

	FEEDER TYPES			
Waste Types	Loaded Drums in DFE	Pumped Liquid to HSE	Solids to HSE	Direct to SSR (no feeder)
Organic vapors				✓
Organic solvents	✓	✓		
Oily waste — rags, paper, sorbents	✓		✓	
Aqueous + Organics	✓	✓		
Heavy organic slurry	✓	✓		
Halogenated wastes	✓	✓	✓	
Spent paint waste (part cans)	✓			
Paper pulp waste slurry	✓	✓		
Organic laden sorbents	✓		✓	
Activated carbon beds (loaded)	✓			
Spent ion exchange resin	✓		✓	
Spent sand blast media	✓		✓	
Spent bead blast media	✓		✓	
Wood waste (pallets, flooring)	✓			
Lab. paper, cloth, glove waste	✓		✓	
Contaminated protective suits/gloves	✓		✓	
Contaminated soil and sawdust waste	✓		✓	
Tank/pond bottoms sludge		✓		
Contaminated cartridge filters	✓			
Contaminated loaded HEPA filters	✓			
Pharmaceutical drug waste	✓			
Hallucinogenic drug and paraphernalia	✓			
Bio-test animal carcasses	✓			
Red bag hospital medwaste	✓		✓	
Dental/oral surgeon waste	✓		✓	
Pesticide, fungicide, etc. waste	✓	✓		
Napalm bombs	✓			
Chemical weapon agents	✓			
Biological weapon agents	✓			
Spent rocket propellant	✓	✓		
Spent military energetics	✓	✓		
TNT contaminated groundwater		✓		
Spent autothermal epoxies		✓		
Spent Kevlar® military waste	✓		✓	
Spent classified waste	✓		✓	
Spent printed circuit boards	✓			
Nitrate liquid waste		✓		
Tritium and C-14 waste	✓	✓		

Basic Reaction Chemistry

Steam reforming detoxification chemistry does not involve combustion, with its attendant risks of self-sustaining exothermic reaction and generation of dioxins. Steam reforming is an endothermic reaction; the chemical reduction reactions initiate in the WFE and complete in the SRR as follows:

$$C_{3X}H_{6Y} + 5X\ H_2O \underset{\text{Elect. heat input}}{\rightarrow\rightarrow\rightarrow\rightarrow} 2X\ CO + (4X+3Y)\ H_2 + X\ CO_2 + X\ H_2O \qquad (4.3.1)$$

$$C + H_2O \leftrightarrow CO + H_2 \qquad (4.3.2)$$

$$C + CO_2 \leftrightarrow 2\ CO + Heat \qquad (4.3.3)$$

$$H_2 + CO_2 \leftrightarrow H_2O + CO \tag{4.3.4}$$

$$C + 2H_2 \leftrightarrow CH_4 \tag{4.3.5}$$

etc.

The molar ratio of steam:hydrocarbon in Equation (4.3.1) is significantly greater than the common stoichiometry practiced in refinery steam-cracking operations or in natural gas-to-hydrogen reforming operations.[4-7] This excess stoichiometric steam (i.e., about 31 vol% excess or about 2.5 mass ratio) is required to drive organic compound conversion to H_2 and CO preferentially. This excess steam ensures a >99.99% destruction and removal efficiencies of organic wastes that have volatilized into the gas phase. The SRR then produces a clean syngas that can be safely and environmentally discharged to the atmosphere through an APCS or processed through a catalytic converter or fuel cell.

SRR Conditions to Achieve High DREs

The critical process conditions of excess superheated steam, high temperature, and residence time in the SRR ensure that the process DRE (>99.99% under RCRA law and >99.9999% under TSCA law) is achieved for regulated compounds. SRR residence time is adjustable from 1 to 2 seconds at the elevated, nearly isothermal conditions in the electrically heated reactor. This is superior to the nonuniform exposure to high temperatures typical of an incinerator flame region. Although SRR details are proprietary, the specially designed reactor produces a high level of micro-mixing to ensure intimate molecular contact between the waste and steam. Because the syngas is recycled to the WFE for partial organic destruction of the waste prior to the SRR, the total system DRE is even greater than that achieved by the SRR alone.

The DRE obtained is a direct function of the SRR residence time and operating temperature. For example, core temperatures between 870 and 1040°C (1600 to 1900°F) will achieve DREs >99.99% for RCRA waste, and temperatures between 1150 and 1200°C (2100 and 2200°F) will achieve DREs over 99.9999% for TSCA waste. Figure 4.3.5 illustrates the relationship between temperature and DRE for a wide range of RCRA organic tracer compounds. More details are available from the California State Department of Health Services Grant Program Final Report.[7]

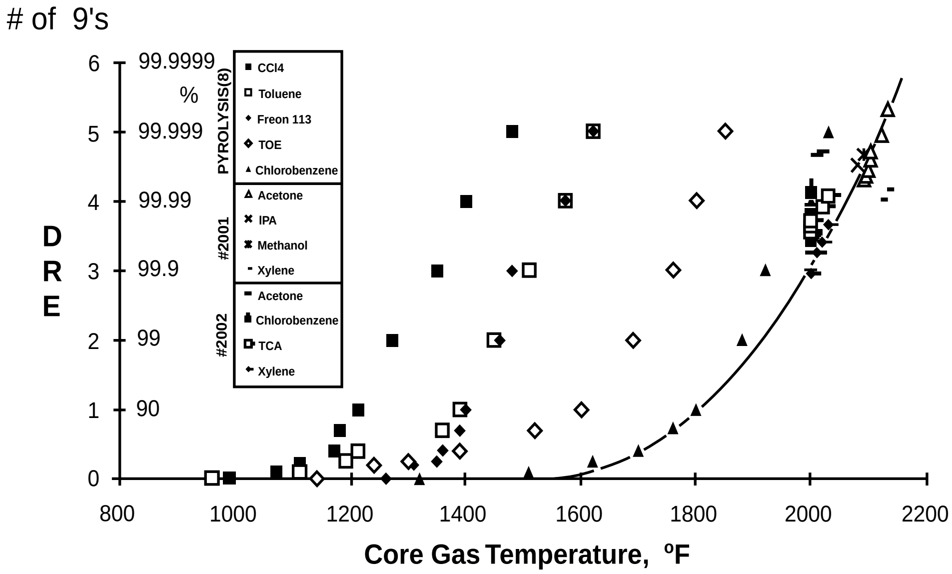

FIGURE 4.3.5 Temperature dependence on destruction efficiency.

The electrical heat input to the SRR is controlled so that the required SRR temperature, typically between 870°C (1600°F) and 1135°C (2150°F), is maintained to achieve the desired DRE for a particular waste (RCRA, TSCA, etc.) with minimum operating cost. In addition to the >99.99% DRE of each principal organic hazardous constituent (POHC), the measured air emissions have low-risk levels (discussed in more detail in References 7 to 9). The steam reforming control system then offers four redundant layers of safety in the design to ensure that the process chemistry is controlled, avoiding the "puffs" characteristic of incinerators, and the risks of achieving a lower than required DRE.

Also, because steam reforming uses neither fuel air nor flame (as required for combustion of the hydrocarbon liquid hazardous waste), the SRR avoids production of troublesome SO_x, NO_x, and incinerator products of incomplete combustion (PICs).[3] The SRR produces a clean gas product sufficient to meet the tough federal and state air emission requirements of the California Air Resources Board.

Thermodynamics, PICS, and Dioxins

Any high-temperature process that achieves near-thermodynamic equilibrium, including incineration combustion and steam reforming, generates "thermodynamically reformed compounds" (TRCs) from the recombination of the reactive molecular fragments. Incineration tends to form toxic dioxins or furans, whereas the steam reforming chemistry forms light olefins and aromatics, typified by benzene. Using high-resolution GC/MS for volatile/semi-volatile aromatic analyses, benzene, toluene, xylenes, naphthalene, styrene, etc. are found at levels just above detection limits. Reforming tests of simulated hospital waste including biological material, showed that benzo-a-pyrenes were not formed.[10]

The EPA has recently had serious concerns over dioxin emissions resulting from the incineration of municipal and medical wastes containing chlorinated plastics (i.e., PVC).[9] Steam reforming tests run on high-level chlorinated organic feeds produced vent gases with dioxins (specifically 2,3,7,8-TCDD) below the detection level of 3.7 picograms (i.e., 0.3 pg/m^3). This ability to avoid forming environmentally significant levels of dioxins or furans is attributed to superheated steam stripping of halogens from the aromatic organics, the lack of oxygen, and low particulate levels hindering their surface-initiated *de novo* synthesis. Aromatic levels are well below the EPA lifetime *deminimis* risk level of 1×10^{-6} for air toxics; in fact, the emissions from experimental testing produced a calculated risk level of only 1.6×10^{-8}.[9]

Table 4.3.2 provides a summary of steam reforming product gases from a waste mixture of 670mL/L acetone, 150 mL/L methanol, 100 mL/L isopropanol, 50 mL/L butanol, 50 mL/L xylene, 50 mL/L trichloroethylene, and 50 mL/L dichlorobenzene. These results were obtained after 10 hr of steady-state operation. Only two effluent gas components in Table 4.3.2 are regulated emissions: carbon monoxide and benzene. The Federal Clean Air Act set limits of CO releases to 45 metric-ton/yr (50 tons/yr) for a non-complying urban area and 180 metric-ton/yr (200 tons/yr) for all other urban areas. A steam reforming unit at 1-ton/day organics throughput is well below these limits at around 27 metric-ton/yr (30 tons/yr).

Benzene is shown with the range of 4000 ppm to 35 ppm in response to increasing the superheated steam from 35 to 55% stoichiometric excess, respectively. This reduction was observed real-time with online gas chromatography with a flame ionization detector. There were smaller but similar changes found for toluene. Additionally, the remaining aromatics were near or at the level of detection. It should be noted that the results in Table 4.3.2 are the outlet of the emissions of the SRR; the APCS will further lower the emissions to meet any specific local air district emission requirements, such as for HCl or benzene. For example, in California, with residences one block away, the air permit required two beds of granulated activated carbon (GAC) in series on the effluent, with a continuous emission monitor to record benzene levels before, between, and after the GAC beds. The permit required that the downstream bed replace the upstream GAC bed when the isotherm tail approached 20 ppm. Thus, the nearly fresh downstream bed provided redundancy to cover any process upsets or first bed failures in operation. During operation, benzene in vent exhaust was continually at or near the detection limit of 1 ppm. The spent beds of GAC were reactivated monthly by processing in the DFEs.

TABLE 4.3.2 SSR Gas Product Composition

Carbon dioxide	14%	Water	12%
Hydrogen	49%	Light hydrocarbons	3 %
Carbon monoxide	22%	Hydrogen chloride	1%
Particulate matter	<Background	NO_x	0.3 ppm
2,3,7,8-TCDD	<0.3 ppt	1,2-Dichlorobenzene	4 ppm
Benzene	<4000 ppm	Xylene	3 ppm
Ethylbenzene	<4 ppm	Toluene	<30 ppm
Naphthalene	4 ppm	Styrene	4 ppm

Note: % = mole %; ppm and ppt are on volume basis.

Chlorohydrocarbon Destruction Chemistry

Chlorohydrocarbons, widely used as solvents and in plastics, have become a serious hazardous and mixed waste problem because of their high volatility and high-density stratification in groundwater aquifers. Their disposal as hazardous waste is expensive and problematic, and when contaminated with radioactive waste, their treatment and disposal have been nearly impossible because of the difficulty of permitting mixed waste incinerators.

Yildirim and Senken,[11] Granada et.al.,[12] and Senkan et.al.,[13] studied the pyrolysis and steam reforming of chloroform. Their results, addressing the optimal role of steam in minimizing problematic decomposition products, have been confirmed by a California State/EPA study by Synthetica.[8] (See Figure 4.3.6.)

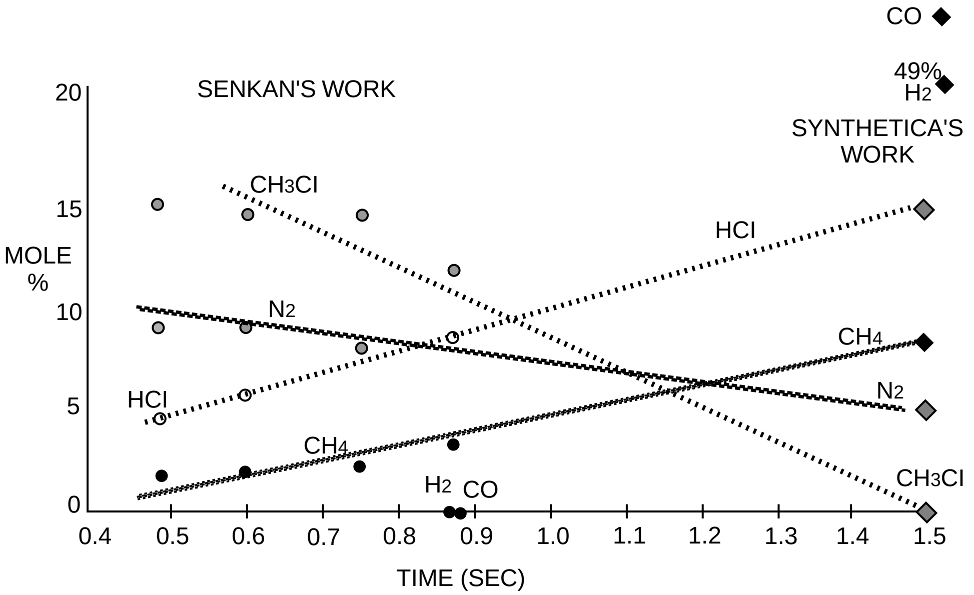

FIGURE 4.3.6 Chlorohydrocarbon destruction chemistry.

Figure 4.3.6 shows a comparison of Senkan's experimental plug flow results at short residence times from 0.4 to 0.9 seconds (on the abscissa) with Synthetica's results at residence times of 1.5 seconds sufficient to reach thermodynamic equilibrium compositions. Both sets of data were obtained by conventional ASTM Method 1946 light gas chromatography, and cover the same temperature range of 350 to 750°C (600 to 1100°F). The importance of residence time is shown in the differences between Senkan's gas product composition at short residence times and the gas products observed by Synthetica over the last decade of waste processing at longer residence times.

Processing fluorine-containing organics requires a slightly higher dehalogenation temperature. There are only slight effects depending upon the molecular structure involved, because the carbon-halogen bond strength depends weakly on the electronic environment surrounding this portion of the molecule. The largest difference is found between the halogen species. For example, the fluorine-carbon bond is stronger than the chlorine-carbon bond. Thus, a slightly higher dehalogenation temperature is expected for fluorohydrocarbon destruction.

Steam Dehalogenation

The term "steam dehalogenation" is used when:

- Steam reforming chemistry is applied to react a halogen substituent in an organic compound to form a halogen-based acid gas.
- Acid gas is neutralized immediately upon generation, so that the salt can be removed from the gas stream.

GTS Duratek[14] developed dry sorbent injection equipment as part of its extensive Steam Reforming patent portfolio that centers on a standard porous ceramic or metal filter where the filter surface is precoated with an alkali-neutralizing dry powder agent. In steam dehalogenation, as shown in Figure 4.3.7, volatilized halogenated hydrocarbons, generated by desorption in the WFE, proceed to a filter-housing chamber flooded with superheated steam. The filter surfaces in the chamber are radiantly and indirectly heated by surrounding electrical heaters. An automatic feed system provides dry sorbent injection by continuously adding fresh alkali powder upstream of the chamber housing; even into the WFE headspace, depending on the halogenated hydrocarbon. The volatile halogenated hydrocarbons react with the superheated steam to produce halogen acid gas that is instantly neutralized by the alkali either in the gas stream or on the filter coat. The salt product from the neutralization reaction is then captured by the filter, while other steam reforming product gases, such as H_2, CO, CO_2, and H_2O, pass through.

When the pressure drop across the filter system reaches a predetermined set-point, the filters are pulsed with an inert gas to remove solid deposits, which fall downward through the conical exit section and into a disposal drum located below the filter housing. These filter units have proven highly reliable, with more than 24,000 combined operating hours in a commercial unit at Palo Verde Nuclear Generating Station and at the GTS Duratek Oak Ridge, Tennessee, site.

Individual Case Studies

System Application Guide

This subsection is designed to assist in tailoring the system to the specific needs of various applications. General recommendations are given in Table 4.3.3 to help select particular waste feeder options for a particular class of waste type.

One flexible configuration that handles a wide variety of waste types combines an SRR with multiple DFEs and an HSE. Using multiple DFEs optimizes throughput, because while one DFE is being loaded or unloaded, the other DFEs are processing waste. Simultaneous operation of the DFEs with the HSE ensures that the SRR is continuously and fully loaded to capacity.

Figure 4.3.8 shows two DFEs into which drums are placed alternately for processing and then cooling and removal. Both units shown are designed for explosion-proof operation for solvent waste, which can be fed to the DFE by pumping the liquid into an empty drum. With the drum inside the DFE, the temperature is first ramped up to 700°C (1300°F) or less, depending on the final properties of the residue desired; then pumping starts. For processing full drums containing liquid solvents, the temperature ramping is performed slowly through component boiling ranges.

The DFE or CFE (similar in operation to the DFE) is an optimum selection when processing high level radioactive waste, where minimal material handling is required to achieve adequate contacting with the steam in the WFE. This application was successfully demonstrated at the Trojan Nuclear Power Plant,

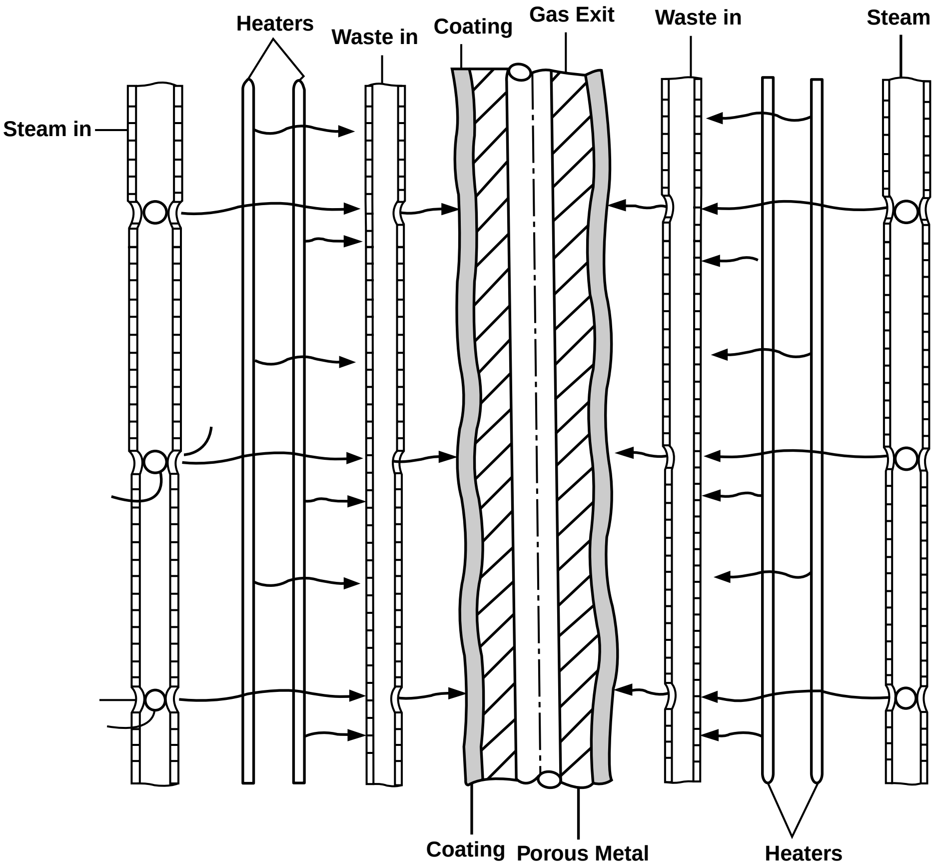

FIGURE 4.3.7 Steam dehalogenation destruction mechanism.

Table 4.3.3 Application Guidance To System Configurationn

Desire to keep waste in drums ==================	DFE
Slurry feed (pumpable)======================	HSE
Fuel pool waste ===========================	CFE
High level TRU waste =======================	DFE or CFE

where CFE operation permitted remote handling and processing of high level fuel-pool wastes. Another advantage of processing waste in drums or cans is that it allows for detailed surveillance, characterization, and criticality control for TRU radioactive wastes. Thus, the individual isotopic-specific customer wastes can be isolated and segregated, avoiding the problematic commingling of isotopes and waste holdup that occurs in large incinerators.

The heated screw evaporator (HSE), shown in Figure 4.3.9, is where dry active waste (DAW) is fed in bulk into the lockhopper feeder and shredder that feeds the heated screw. Typical volume reduction is between 20:1 and 50:1. The residue can be compacted, solidified, and/or vitrified for disposal.

Figure 4.3.10 is a photograph of an SRR on the right and a 1-micron candle filter on the left. The filter protects the SRR from possible fines carry-over from the HSE or DFE. The SRR enclosure area is maintained under negative pressure as a preventive measure in the unlikely event that fugitive emissions are released from the process. The unit is controlled either by remote computer consoles from a control room or locally by the maintenance console, shown here at the left of the enclosure.

FIGURE 4.3.8 Pair of drum feeders.

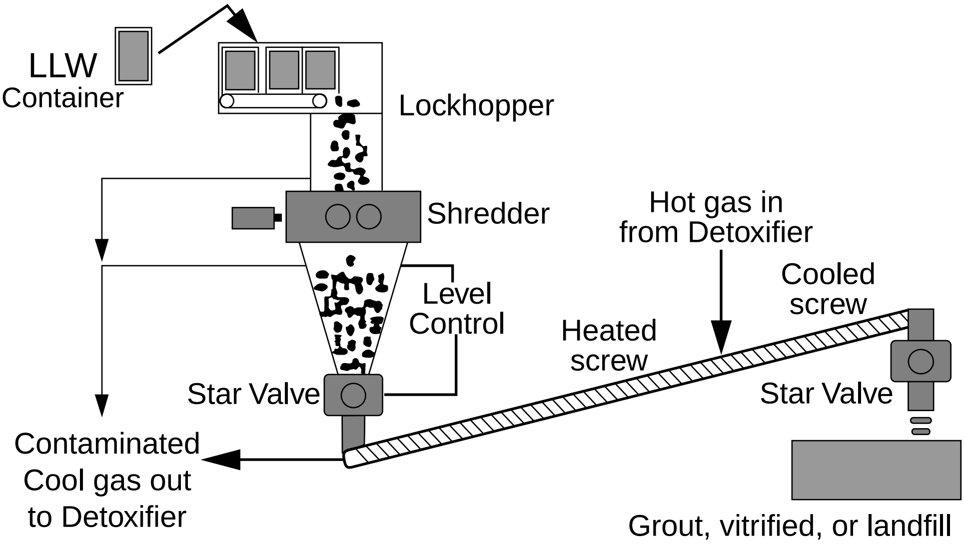

FIGURE 4.3.9 Heated screw feeder.

Pharmaceutical Waste: Case Study #1

Steam reforming has processed various biohazard-radioactive wastes, as generated by nearly every major pharmaceutical company. The base waste matrix for volume reduction ranges from DAW to laboratory animal carcasses. This waste is typically under 2 mR/hr, containing primarily radioactive isotopes of carbon-14, tritium, and typical medical isotopes of sulfur, phosphorous, barium, and potassium. In routine operations at GTS Duratek's Oak Ridge site, refrigerated trucks transport frozen drummed waste from across the country for steam reforming.[15] The drums are stored at the site in large commercial refrigeration rooms prior to processing. To protect operating personnel against bio-infectious agents, the

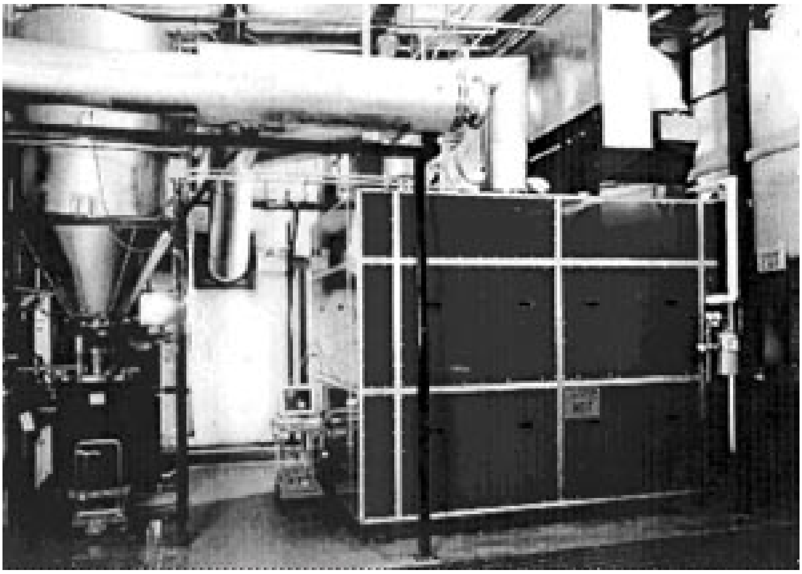

FIGURE 4.3.10 Steam reforming reactor.

drums are placed into the DFE while still frozen. Once the frozen drum is placed inside the DFE, the door is closed and locked, and the processing is started.

After processing, the spent drum is usually nearly empty, with only a small quantity of grayish-white residue remaining. The residue is analyzed for carbon-14 and tritium, which are normally not detectable because the isotope-tagged organics are steam reformed and oxidized to $^{14}CO_2$, HTO, and T_2O. The carbon-14 and tritium isotopes can be captured from the scrubbed vent gases using a chilled alkali scrubber operation, or they can be vented with the scrubber operating at saturated conditions. In most cases, the concentrated residue is consolidated into the minimum number of 55-gal drums and disposed at the appropriate repository or returned to the customer for their "store and decay program." Volume and mass reduction ratios range between 20:1 and 50:1. The used drums are painted and reused within the plant as containers or are recycled in the site's metal melt furnace for reuse as shield blocks.

Nuclear Power Plant EDTA Mixed Waste: Case Study #2

The mobile SRR/twin HSE system was deployed for 8 months at the Palo Verde Nuclear Generating Station (PVNGS) near Phoenix, Arizona to process spent EDTA steam-generator cleaning solution. Throughputs of 608 kg/day (1340 lb/day) were achieved, just short of the system capacity, with an 85% availability factor. Chromium (Cr^{6+} mixed with Cr^{3+}) was the constituent of regulatory concern, with concentrations ranging from 7 to 15 ppm. The reductive chemistry of the steam reforming process produced an inorganic residue with a high volume reduction and reduced the highly soluble Cr^{6+} to the more insoluble Cr^{3+}, such that the residue was below the EPA Toxicity Characteristic Leaching Procedure (TCLP) limits. The project successfully demonstrated that steam reforming is a practical and viable alternative for EDTA processing compared with incineration, which produces a hazardous Cr^{6+} residue.

Nuclear Power Plant Fuel-Pool Waste: Case Study #3

The purpose of these projects is to clean up the contaminated spent fuel canisters located in the nuclear power plant fuel-pool racks to produce a concentrated residue with very low hydrogen content. The Nuclear Regulatory Commission (NRC) requires that any formation of radiolytic hydrogen in long-term storage casks be below 5-vol% of the contained void space.[16-18] Note that this is very restrictive, and equivalent to only about 250 mg H_2 in a typical final sealed/welded storage cask.

At the Portland General Electric (PGE) Trojan Nuclear Power Plant, near Portland, Oregon, fuel pool canisters contained deteriorated waste, cylindrical sock filter cartridges loaded with clay sediment, metallic electrodialytic machining (EDM) waste, and other organics all contaminated with failed fuel element fines and several fuel pellets. Fuel-pool clean-out operations involved remote handling procedures for the recovery of this waste and the loading of 20-cm (8-in.) diameter × 76-cm (27-in.) tall process cans fitted with a porous sintered plate bottom and closed by a similar top, once filled. These process cans were inserted into the electrically heated CFE that was surrounded by 23-cm (9-in) thick shielding. The waste was processed at about 600°C (1100°F) in the CFE, with the organic off-gases being further processed in the SRR to produce a clean, dry-vent stream that passed through the plant's high-efficiency particulate air (HEPA) filter ventilation system.

Prior to operation at the PGE Trojan Nuclear Plant, Proof-of-Principle tests were successfully completed using GTS Duratek's Oak Ridge Steam Reforming facility in late summer 1996. Integrated system tests, using actual full-scale equipment, were successfully completed at the Washington Public Power Supply System inactive nuclear plant, WNP-1, in June 1997. The full-scale system was transported to the Trojan Nuclear Plant, tested on surrogate waste, and commissioned while remote retrieval of fuel-pool waste was underway. All residues produced during the project met the NRC requirement for hydrogen content. The process cans containing the residue product were stacked into the disposal canisters, which were filled with helium and seal-welded closed. These canisters are presently being stored, awaiting a future repository site. Only the PVC flange gaskets on the pleated filters presented a processing challenge, because they contained materials (i.e., a heavy oil extender) high in hydrogen content. To address this challenge, these gaskets were sorted and size-reduced prior to steam reforming to enable the waste form to meet the NRC specification.

Contaminated Soil Clean-Up: Case Study #4

Another steam reforming demonstration was performed for an Australian customer on DDT pesticide contaminated soil that contained EPA-listed waste codes U060 and U061, and was above the toxicity characteristic limit for 2,4,5-trichlorophenol (D041). The tests, which were conducted with DFE treatability equipment, concluded that a temperature of 650°C (1200°F) is required to remove both the light organic components and the heavy polychlorophenolic (creosote) compounds. The finished soil was odor-free through removal of aromatic hydrocarbons and all other organics down to 6 mg/L, and contained very low levels of any heavy metals, with arsenic at 2.5 mg/L as indicated by the TCLP analysis as shown in Table 4.3.6 below.

TABLE 4.3.6 Soil Cleanup Analytical Results

Element/Species	Initial Meas. Level	Initial TCLP Equiv. (mg/L)	Final TCLP Result (mg/L)	U.S. Reg TCLP Limit
TOC	0.5%*	250	6	—
Arsenic	10%	5000	2.5	5.0
Barium	NA	NA	NA	100.0
Cadmium	NA	NA	NA	1.0
Chromium	NA	NA	NA	5.0
Lead	NA	NA	NA	5.0
Mercury	NA	NA	NA	0.2
Selenium	NA	NA	NA	1.0
Silver	NA	NA	NA	5.0
4,4′-DDD	0.5%	250	0.037	—
4,4′-DDT	5%	2500	0.210	—
Chlorophenol	15%	7500	ND	400.0

Note: 10,000 mg/L = 1%.

Steam Reforming achieved 99.9998% DRE of the DDT and its degradation product, DDD. Thus, these results showed that under local Australian environmental laws, this soil could be free-released.

Reactivation of Granular Activated Carbon and Other Adsorbents: Case Study #5

Granular activated carbon (GAC) is used in radioactive waste processing to capture lower level organics, such as benzene, before release to the environment. Steam reforming is ideally suited to reactivate GAC beds used with APCSs or other processes. Reactivation using syngas and steam outperforms standard regeneration and allows the GAC to be reused up to 20 times.[19-22] For Steam Reforming GAC reactivation, the GAC canister bed is placed within the DFE, where the recycled gas from the SRR and electric heat gradually raise the GAC inlet temperature to allow vaporization of the organics adsorbed on the GAC. As the thermal front moves upward through the GAC bed (i.e., opposite to bed loading), the adsorbed organics are removed and carried along with the syngas as it moves out of the top of the bed and to the SRR. Superheated steam is then added within the SRR unit, the temperature is increased, and the organics are steam-reformed to >99.99% destruction.

Reactivation of carbon loaded with a broad range of molecular weight organics is performed more efficiently, with minimum coking within the activated pores, by ramping the temperature gradually through the range of boiling points. Commercial regeneration furnaces quickly subject the carbon to very high temperatures, resulting in coking of the heavy organics within the pores. The steam reforming process uses real-time process control of key operating parameters such as exit temperature and carbon monoxide to ensure efficient reactivation. Standard procedures for typical regeneration measure the carbon after regeneration by either the iodine test or the molasses test. Because testing is done after regeneration, optimum operating parameters cannot be established during regeneration.

Activated carbon releases the adsorbed organics at temperatures about 150°F above their boiling point. However, the environment produced by the steam-reforming chemistry greatly accelerates the H_2 and CO reactions down into the deepest pores of the loaded GAC. In the demonstration discussed below, GAC was contaminated with a range of organics, from light hydrocarbons up through C_{8+}, and was then reactivated in the DFE.

Temperature history and CO data taken during the reactivation process are shown in Figure 4.3.11 in the upper and lower half, respectively. The monitoring locations in the legend at the center left are shown in the order of gas flow inlet to outlet, from bottom to top. The hot syngas, used to reactivate the GAC, is generated within the SRR and is sent out to the DFE inlet, where it fills the DFE chamber. From the chamber, this hot gas is pulled upward through the GAC in the opposite direction in which the GAC was loaded. This countercurrent reactivation speeds up the reactivation process by ensuring that the higher concentration organics in the GAC bed are removed without passing through the cleaner portions of the bed. No change in the weight between the fresh GAC drum and the reactivated drum was observed during the many cycles of the GAC, which indicates that no carbon coking occurred due to steam reforming chemistry.

As the hot gas passes upward through the GAC from axial positions labeled "Drum 4" to "Drum 1" and then for the GAC outlet gas temperature, "DFE Outlet," it can be seen that the reactivation temperature fronts also sequentially pass upward and out of the GAC. For example, the first temperature in the bed to rise to the DFE chamber gas inlet temperature is "Drum 4" at the bottom of the GAC, and the last is the "DFE Outlet" at the top of the GAC.

Note that it took about 2 h to raise a single 113-kg (250-lb) GAC bed from room temperature to about 100°C (212°F), at which point the interstitial water in the GAC vaporized as the syngas passed upward through the bed. This "steaming" of the GAC as the thermal front travels through the bed drives most of the volatile organics off the GAC. This reactivation step from 100°C (212°F) to 270°C (520°F) takes just over 2 h. At 270°C (520°F), heavy organics no longer appear to remain on the bed, based upon relatively uniform temperature in all GAC zones. To ensure complete reactivation past the completed isothermal bed condition, the GAC was increased in temperature from 270°C (520°F) to almost 315°C (600°F). The total cycle time required to reactivate the GAC drum was about 10 h.

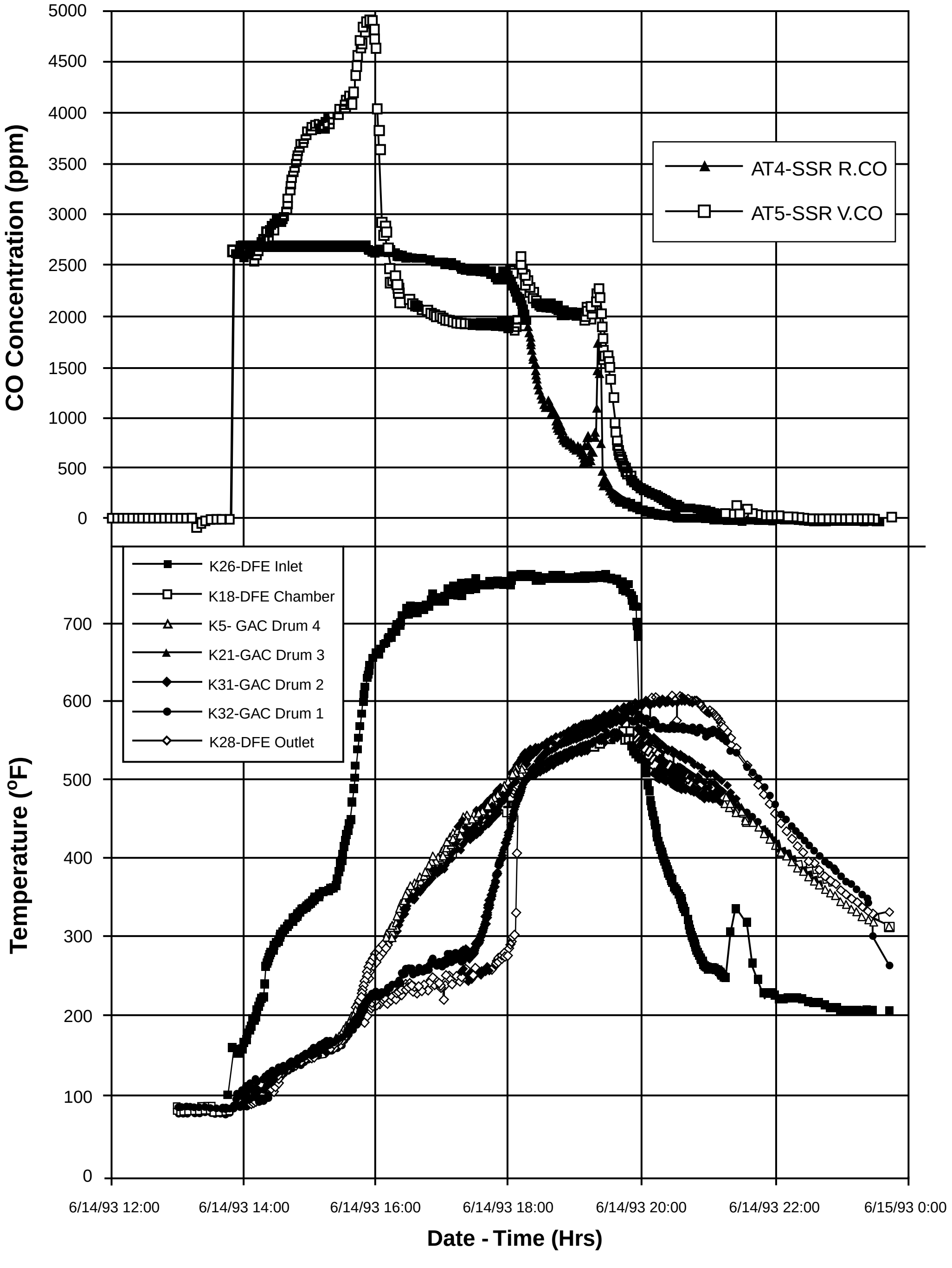

FIGURE 4.4.11 Temperature trends: steam reforming reactivation of GAC.

Additional reactivation tests were performed using a GAC bed that removed organics from air. The organics contained 99% toluene, 0.5% trichloroethane, and 0.5% dichlorobenzene. This GAC bed was loaded and reactivated in eight cycles and the capacity showed small losses of 3 to 5% per cycle as validated by measured iodine number.

Typically, the GAC can be loaded and reactivated for up to 20 cycles with this loss in capacity, which is superior with commercial regeneration at 10 to 20% loss per cycle. Experience has shown that steam reforming can also be used to regenerate special sorbents, such as special zeolites, with similar results.

New Waste Stream Applications

The range of waste streams covered in the case studies above is wide and representative of waste streams that the environmental or waste processing engineer will likely encounter. For particular waste streams that involve peculiar combinations of components for which little or no experience is available, treatability testing can be readily performed using actual or surrogate waste. The treatability test is very simple, involving a bench-top quartz tube furnace followed by a glass condenser or scrubber. To perform the test, the sample is placed onto a quartz boat that is slipped into the quartz tube. The weight loss of the sample and the off-gas composition are continuously monitored by GC and are used to calculate the destruction level. The residue remaining in the quartz boat can be further analyzed for leachable metals, reactive components, and other problem constituents that may be of concern. If a gas scrubber is to be used, the scrubber liquid must also be analyzed for the waste component of concern. The analytical information characterizing any material captured in the condenser or scrubber will be helpful to the process design engineer in laying out the off-gas processing train needed to meet the environmental air emission requirements. All of this analytical characterization information will be very welcome by the environmental control agencies.

Acknowledgments

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4.4

Wet Air Oxidation

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Introduction

Wet air oxidation (WAO), as practiced commercially, is described as the oxidation of organic and oxidizable inorganic compounds in aqueous solution or suspension using oxygen or air at elevated temperatures and pressures either in the presence or absence of catalysts. This process, when taken to completion, oxidizes organics to carbon dioxide, hydrogen to water, sulfur to sulfates, phosphorus to phosphates, nitrogen to ammonia or nitrogen and halogens to the corresponding acid or halogen salt.

Initially, WAO was most commonly used to oxidize those streams containing a substantial amount of water that could not be easily concentrated to increase their fuel value to a level adequate to sustain combustion under conventional burning conditions. Such streams include sewage sludges of all types, pulp and paper mill wastes, and waste organic sludges. All of these streams oxidize very easily. Since then, WAO has been used to treat spent caustic waste streams in petroleum refineries and petrochemical plants, scrubbing liquors from coke oven gas clean-up processes, streams containing cyanide wastes, sulfide wastes, phenolic wastes, nonhalogenated pesticide wastes, solvent still bottoms, waste streams from dyestuff, fine chemicals and bulk drugs manufacture, electroplating wastewaters, wastewaters from acrylonitrile manufacture, and, in general, for treatment of wastewaters containing toxic compounds and/or nonbiodegradable compounds. Many other hazardous pollutants are amenable to treatment via WAO (Dietrich et al., 1985). Studies have shown the potential of WAO for combustion of coal slurries (Engleman, 1983) and soil detoxification (Unterberg et al., 1998). Several hazardous wastes listed under F, K, P, and U classification of the EPA, as well as some under the SIC Code Numbers, are good candidates for WAO treatment (Reactor, 1989). The oxidation reaction takes place regardless of the state of the oxidizable substances in the wastewater. It does not seem to matter whether the impurities are dissolved in the wastewater or they are in fine or coarse dispersion. It is, however, important that the chemical oxygen demand (COD) of the wastewater fall within the range of 8000 to 200,000 mg/L. Wastewaters are normally concentrated or diluted to ensure that the value of the COD is within the applicable range (Copa and Gitchel, 1989).

In typical industrial applications, the operating parameters of the process leads to the oxidation of the organics to low-molecular-weight carboxylic acids, especially acetic acid (Shende and Mahajani, 1997). These low-molecular-weight carboxylic acids are often refractory to WAO, especially under the conditions used for oxidation, but are biodegradable (Lin et al., 1996). In the majority of cases, the extent of oxidation is controlled to produce a liquid effluent that is free of toxic compounds and is amenable to subsequent biological treatment. Thus, a WAO system is normally part of an integrated wastewater treatment plant.

An example of another integrated application is a biophysical treatment process for wastewaters that employs the addition of powdered activated carbon to the aeration basin of a conventional activated sludge process. This process (also called the PACT® process) provides numerous treatment advantages, including improved organics removal, improved treatment stability, excellent mixed liquor settling rates and flocculation, increased adsorption of toxic organics, reduction in odor, and increased oxygen consumption (Randall, 1983). This process is now widely practiced for treatment of municipal and industrial wastes. WAO can be used to regenerate the carbon for reuse in the process to improve the economics of the process. A two-step process, combining WAO with either a biological or a biophysical process, has been reported (Wilhelmi and Ely, 1976). In biological wastewater treatment plants employing the PACT® process, it has been found advantageous to install a WAO system because it can be used to treat, recover, and recycle not only the powdered activated carbon but also oxidize the biological solids, thereby finding an effective solution to the secondary handling and disposal problem (Wilhelmi and Ely, 1976).

Under conditions used in commercial operations, WAO is autothermal and does not require energy to carry out the oxidation. Calculations show that a well-designed WAO system with a feed having a COD above 8000 mg/L can be a net generator of energy (Chou and Verhoff, 1981).

Example Industrial Applications

WAO is a proven technology, with almost 250 plants operating worldwide. The operating temperatures and pressures used in the WAO process depend on the nature of the feed and the process objectives. A recent summary of various industrial applications of WAO has been published (Mishra et al., 1995).

Municipal Sewage Sludge

WAO is reported, as early as 1981, to have been used successfully by more than 125 municipalities around the world (Perkow et al., 1981). The treatment objective in these plants is to oxidize the sludge to a sterile and biologically stable form that cannot be identified as sewage and possesses good settling and dewatering (compacting) characteristics. Data on the operation of several WAO plants for sewage sludge is available (Teletzke, 1965).

The WAO of sewage sludge results in removal of the insoluble organics by oxidation and solubilization. The reduction in insoluble organics has been reported to exceed the COD reduction by 10 to 30%. With 30% reduction in COD, insoluble organics decreased by about 50%. A 30% reduction in COD resulted in a 50% reduction in volume of the settled solids, and the volume occupied by the drained solids was 8% of the original. These substantial reductions in volume provide corresponding savings in the overall treatment and disposal costs. The reported operating conditions for these plants were a temperature range of 220 to 276°C (428 to 529°F) and pressures ranging from 3000 to 12,000 kPa (435 to 1740 psi).

It was observed (Teletzke, 1965) that during low-pressure WAO of sewage sludge, most of the sulfur was oxidized to sulfate and remained dissolved in the filtrate, thereby eliminating the problem of odor. Phosphorus was retained in the cake as a precipitate, resulting in an effluent free of phosphate. Organic nitrogen was converted to soluble amino acids and to ammonia and primarily was present in the filtrate. By operating at lower temperatures such that the level of oxidation was just enough to get a filterable residue, it was possible to retain a substantial part of the nitrogen in the solids. The residue could be separated by any of the conventional techniques, and the resulting effluent was readily treatable by aerobic biological processes. In one instance, a low-pressure WAO system has been installed to thermally condition municipal sewage sludge so that it can be dewatered to a self-burning cake and incinerated for energy production (Reactor, 1991).

Pulp and Paper Mill Wastes

WAO has been used for the oxidation of black liquor generated during the manufacture of pulp by the sulfate method. WAO also permits the recovery of soda lye suitable for reuse. At 300°C and 22,000 kPa pressure, with a COD of 130,000 mg/L, a reduction in COD of 98% was achieved (Perkow et el., 1981).

Effluents from sulfite pulping mills can also be purified by WAO. An 85% reduction in COD is obtained at 230°C. Chemical recovery methods have also been developed for some of the mill liquors (Zimmerman and Diddams, 1960). Teletzke (1964) has described flowsheets and material balances for the recovery of sodium and sulfur from a pulping wastewater and for steam production from calcium-base spent sulfite liquor. The first full-scale commercial application was at a eucalyptus mill in Australia in 1966. WAO has also been used to successfully treat paper mill sludge to recover filler clay, thereby virtually eliminating landfilling, as well as to generate a large quantity of low-pressure steam.

Activated Carbon Regeneration

Activated carbon is commonly used in adsorptive separation processes to purify gases and liquids. The gases are stripped of their odors by adsorption of odorous substances by activated carbon. It is fairly common to find activated carbon adsorbers in effluent treatment plants. These are usually polishing units and are used to improve the quality of wastewater before discharge or recycle. Powdered activated carbon is also used for wastewater treatment, as in the PACT® process. Activated carbon treatment is widely used in the chemical industry to improve product quality. The regeneration of activated carbon assumes importance for improving the economics of this adsorption process. Thermal and WAO techniques regenerate the spent carbon with the simultaneous destruction of the adsorbed substances.

Traditionally, the regeneration of activated carbon is carried out by heating the carbon to between 700 and 900°C, resulting in considerable energy costs and large loss of carbon due to oxidation. Regeneration of activated carbon by WAO can overcome the disadvantages of thermal regeneration. At regeneration temperatures of approximately 250°C, carbon losses are lower than 7% and the processing costs are lower by 20%. In thermal regeneration processes, the energy supplied must take care of the sensible heat of the liquid, heat of vaporization of the liquid, and sensible heat of the vapor and air.

In WAO, however, the maximum energy requirement is the enthalpy difference between the effluent and influent streams. At a feed COD of 15,000 mg/L, WAO becomes authothermal. In carbon regeneration, gravity thickening of the spent carbon slurry permits this value to be reached. For thermal regeneration, a COD of 400,000 mg/L is required for the autogenous point to be reached, which means a feed slurry containing 50% solids (Knopp et al., 1978). When using the PACT® process, WAO plants have been installed to permit carbon recovery and recycle (Copa and Gitchel, 1989).

Scrubbing Liquors from Coke Ovens

The off-gases from coke ovens containing sulfur- and cyanide-based compounds are scrubbed before being burnt for its fuel value. The resulting scrubbing liquors contain hydrogen cyanide, phenols, and other toxic substances that are not biodegradable. These liquors can also not be discharged without treatment in order to reduce, if not eliminate, the toxicity. WAO has been used successfully to treat these liquors. WAO of these liquors converts ammonium thiocyanate to ammonium sulfate and carbon dioxide; ammonium thiosulfate to ammonium sulfate and sulfuric acid; suspended sulfur to sulfuric acid; and sulfide and polysulfide ions to sulfate ion. The liquid stream from the WAO reactor contains 35% ammonium sulfate, 1.6 to 2.4% sulfuric acid, and water, and is sent to the scrubber where it is used to scrub the WAO vapors prior to their release. The sulfuric acid in the liquid reacts with the ammonia in the off-gas to form additional ammonium sulfate. The ammonium sulfate can be recovered for sale and the sulfuric acid can be recycled to the plant (Reactor, 1990).

Refinery Spent Caustic

The characteristics of the spent caustic effluent in refineries depend on various factors such as the characteristics of the crude oil being refined and the refining processes used. These streams typically contain mercaptans, sulfides, and cresylic and naphthenic compounds (Ellis, 1998). The COD content of the spent caustic ranges from 50,000 to 400,000 mg/L, with the bulk of the COD being organic in nature. WAO has been used to successfully treat these streams. The influent COD is restricted to between 80,000 and 100,000 mg/L by dilution with other low COD streams or water if necessary. The oxidation requires a temperature of 260°C and WAO at that temperature, with a residence time of 1 hr, results in a 70 to 80% reduction in COD and greater than 99% removal of specific components. The residual COD primarily consists of short-chain aliphatic acids that are easily biodegradable.

Ethylene Plant Spent Caustic

Spent caustic scrubbing liquors from olefin plants typically contain emulsified hydrocarbons, mercaptans, phenols; and sodium sulfide. WAO has been successfully used to treat these streams, achieving COD reduction of 97.4%, destruction of all the sulfide, reduction of more than 99.99% of mercaptans, and the conversion of phenols and hydrocarbons to low-molecular-weight carboxylic acids that are easily biodegradable. A low-pressure wet air oxidation (LPWAO) process has been developed for treating these streams (Matthews, 1997) and has been successfully operating since 1993. The LPWAO process operates at 120°C and pressure of approximately 600 kPa. This process requires prior removal of the hydrocarbons by means of a gasoline wash. Due to the lower temperature used in the oxidation reactor, the residence time is significantly higher than in a conventional WAO system. It has, however, been claimed that this is compensated for by significantly lower costs of equipment, both in terms of using cheaper materials of construction, such as stress-relieved carbon steel for the reactors and lower wall thickness. Lower operating costs are achieved using normally available plant air and medium-pressure steam from the plant mains.

Oxydesulfurization of Coal

The production of fuel by the gasification of coal generates a fuel gas that needs to be scrubbed with water to get rid of contaminants liberated during the gasification operation. The water used for scrubbing liquor contains tars, various organic substances, and dissolved gas. The COD of this scrubbing liquor can be as high as 80,000 mg/L. It has been found that this liquor can be effectively treated using WAO (Chou and Verhoff, 1981), and a process has been described to generate power from WAO of this stream. It has been reported that a COD of 8000 mg/L is required to sustain the operation without any input of external energy. In addition, it has been claimed that operation at higher pressures improves the efficiency of the WAO process.

Cyanides in Electroplating Wastewaters

Spent cyanide solutions from electroplating baths are commonly treated by alkaline chlorination, followed by precipitation, clarification, and dewatering of the sludge generated. The concentrations of total cyanide in the dewatered sludge are normally in the range of 200 to 1000 mg/L. The sludge also contains varying concentrations of a range of metals. The cyanide concentration of these sludges can be high enough to restrict land disposal of the dewatered sludge without additional treatment. WAO treatment of spent cyanide bath solutions has been found to be successful in converting cyanides in electroplating wastes to carbonate and ammonium ions. WAO of the dewatered sludge mixed with water to convert it into a slurry was carried out at 232°C (450°F) and 11,720 kPa (1700 psi). The treatment was successful in removing 99.9% of the cyanide (Warner,1989)

Wastewater from Acrylonitrile Manufacture

Wastewaters from the manufacture of acrylonitrile exhibit a COD in the range of 30,000 to 60,000 mg/L and cyanide concentrations (in the form of hydrogen cyanide and organic nitriles) ranging from 500 to 3000 mg/L (Wilhelmi and Ely, 1976). Because these wastes also contain ammonium sulfate, incineration poses serious air pollution problems due to the decomposition of the ammonium sulfate into ammonia and sulfur dioxide. A two-step treatment incorporating WAO followed by biological oxidation has been used to treat these wastewaters. WAO is reported to remove more than 99% of the cyanide and show a reduction in COD of 97%.

Effluents from Pharmaceutical Manufacture and Organic Chemical Synthesis

WAO has been used to completely remove *para*-amino phenol from the effluent generated in the manufacture of the well-known analgesic paracetamol (Reactor, 1991). Wastewaters from the manufacture of pharmaceutical intermediates and organic synthesis have also been successfully treated by WAO (Foussard et al., 1989).

Wastewaters from Manufacture of Dyestuff Intermediates and Dyestuffs and from Dyehouses

The dyestuffs industry uses a variety of intermediates having very poor biodegradibility. Some examples are naphthalene-based dyestuff intermediates and nitroaromatic compounds. The wastewaters generated in the manufacture of many of these intermediates are colored, virtually non-biodegradable, and high in inorganic salts. These wastes can be concentrated by thermal means and sometimes by ultrafiltration. However, the concentrated wastes are difficult to dispose except by incineration. The corrosive nature of the constituents of these wastewaters, especially at the high temperatures achieved in incineration, leads to severe problems with incinerator corrosion with resulting downtime. WAO has been found to be suitable for the treatment of these wastes. The organics are oxidized to lower molecular weight acids that are easily biodegradable. The treated liquor from the WAO plant is usually sent to the biological treatment plant for further reduction in COD. Wastewaters from intermediates manufacture have been subjected to WAO in Germany (Perkow et al., 1981).

As already mentioned, wastewaters from dyestuffs manufacturing are often highly colored and contain a high percentage of inorganic compounds, particularly sodium chloride. Dyeing and printing operations also generate wastewaters having similar characteristics. Ultrafiltration has been successful in treating these streams but the process generates a very polluted concentrate (TOD was measured to be 12,000,000 mg/m^3) for which no treatment is known. WAO of the concentrate at 573K resulted in a TOD reduction of 94% (Foussard et al., 1989).

A catalytic WAO process called LOPROX® has been developed by Bayer and used for the treatment of wastewaters from dyestuff manufacture (Holzer et al., 1992). This process operates at temperatures below 200°C (392°F) and pressures between 500 and 2000 kPa (73 and 290 psi). The LOPROX® process uses pure oxygen as the oxidation agent and the reaction is carried out in a bubble column reactor in the presence of a catalyst system consisting of ferrous ions and organic quinone-forming substances. This process is claimed to be especially suitable for treating effluent streams prior to entering a biological treatment plant. Apart from effluents from dyestuffs manufacturing, the LOPROX® process has also been used for treatment of wastewaters from pulp manufacture.

WAO for Mixed Radioactive and Toxic Wastes

The WAO process that uses air or oxygen requires relatively severe operating conditions (pressures up to 25,000 kPa and temperatures greater than 300°C) and this has limited its large-scale industrial application. The process, however, can be carried out at relatively low pressures and temperatures (up to 1600 kPa and 200°C) using hydrogen peroxide and catalysts. Reaction conditions for the mineralization of an organic mixture, simulating the radioactive organic solvent wastes produced at an Italian nuclear fuel reprocessing plant, have been optimized (Nardi, 1989; Nardi et al., 1991). The laboratory tests were carried out using a concentrated hydrogen peroxide-iron (II) salt (Fenton reagent) at boiling temperature (100°C) with vigorous stirring. Pilot plant studies were carried out in 50-L glass reactors, the composition of solvent waste being long-chain tertiary aliphatic amines (TAA) 293 g/kg, alkylaromatic hydrocarbons (Solvesso 100) 85 g/kg, tributyl phosphate (TBP) 383 g/kg, mesitylene (1,3,5 trimethyl benzene) 118 g/kg, and kerosene 121 g/kg. The catalyst was $FeSO_4 \cdot 7H_2O$ (100 g/cycle); the oxidizing mixture was 36% H_2O_2 plus concentrated H_2SO_4. The process was complete after three cycles, with an oxidant consumption of about 55 L. The reaction final products were: 60 L aqueous wastes with an average COD of about 1000 mg/L, and 450 mL organic wastes, essentially kerosene components.

Process Setup

The WAO process may take several variations, depending on the application. The basic flowsheet for a WAO process is shown in Figure 4.4.1. The wastewater is pumped into the system using a positive displacement, high-pressure pump. The feed is preheated by heat exchange with the hot oxidized liquid effluent before flowing into the reactor. Air is either introduced directly into the reactor or mixed with the feed liquor prior to the preheater, whereby a gas-liquid mixture is fed to the reactor. The oxidation

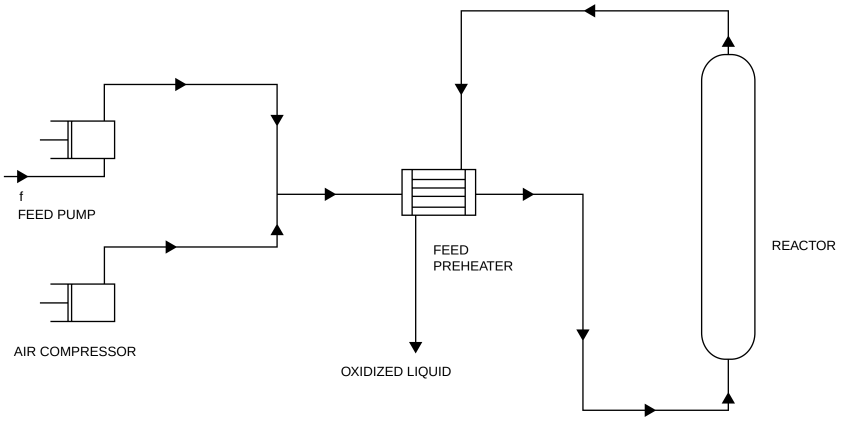

FIGURE 4.4.1 Basic wet air oxidation (WAO) process.

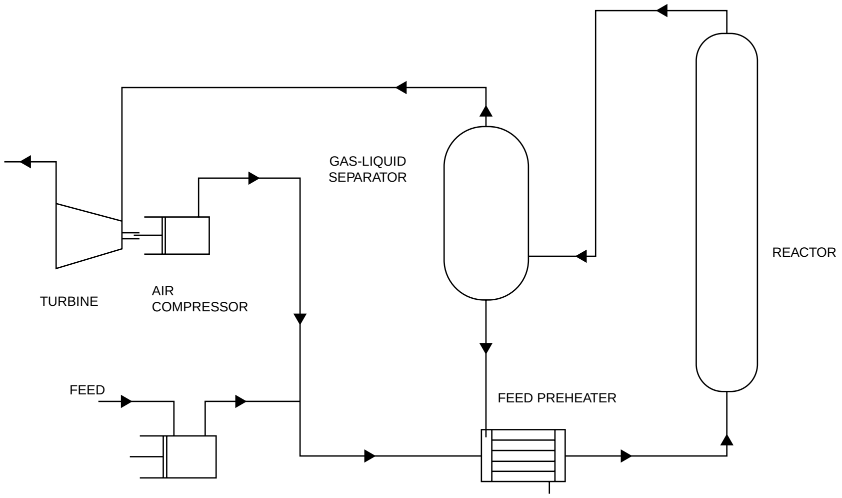

FIGURE 4.4.2 WAO process with heat recovery and power generation.

reaction is exothermic and is accompanied by a rise in temperature. The oxidized effluent stream is used to preheat the feed (Pradt, 1972). Figure 4.4.2 shows a variation of the process in which the effluent from the reactor is sent to a gas-liquid separator. The liquid stream is used to preheat the feed and the hot gases are expanded through a turbine that runs the air compressor. In Figure 4.4.3, the hot gases are first cooled to generate steam, then led into another gas-liquid separator where any liquid formed is separated and then finally expanded through a turbine to generate power, which is now used to run the air compressor. The liquid stream separated is recycled to the reactor. The nature of the effluent feed along with the degree of oxidation usually determines which of the variation(s) to the basic flowsheet can be used. An elegant flow diagram for this scheme has been presented (Chou and Verhoff, 1981) that shows that the process can be self-sustaining even with a feed COD of 8000 mg/L.

Chemistry and Kinetics

The wet oxidation of organic compounds is reported to be a combination of various free radical mechanisms (Day et al., 1973; Tufano et al., 1993):

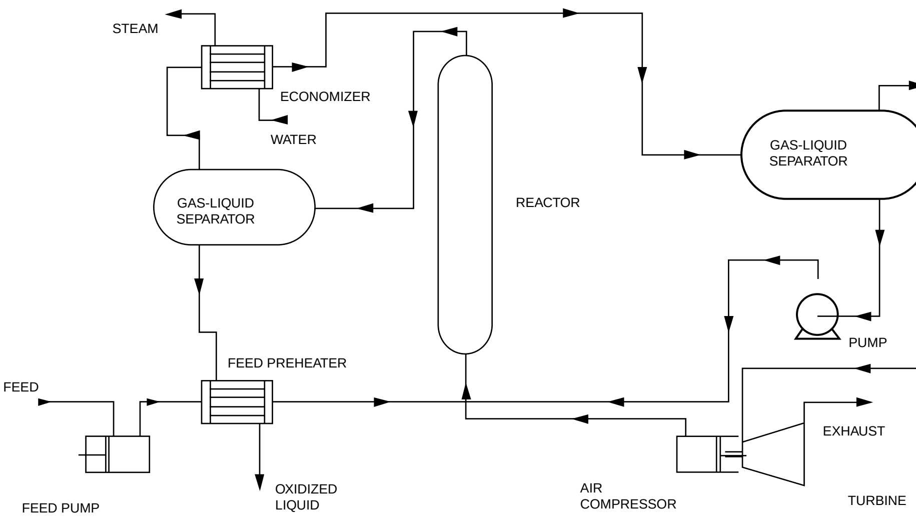

FIGURE 4.4.3 WAO process with steam generation, heat recovery and power generation.

$$O_2 \rightarrow O\cdot + O\cdot \tag{4.4.1}$$

$$O\cdot + H_2O \rightarrow HO\cdot + HO\cdot \tag{4.4.2}$$

$$RH + HO\cdot \rightarrow R\cdot + ROOH \tag{4.4.3}$$

$$R\cdot + O_2 \rightarrow ROO\cdot \tag{4.4.4}$$

$$ROO\cdot + RH \rightarrow R\cdot + ROOH \tag{4.4.5}$$

$$RH + O_2 \rightarrow R\cdot + HOO\cdot \tag{4.4.6}$$

$$RH + HOO\cdot \rightarrow RO\cdot + H_2O \tag{4.4.7}$$

where RH = organic mixture resulting in COD.

It has been found that WAO of organics results in the formation of low-molecular-weight carboxylic acids and alcohols (typically acetic and formic acids and ethanol and methanol) that, under the conditions used in the oxidation, are stable and resistant to further oxidation. These substances are referred to as refractory intermediates and are the cause of most of the COD in the effluent stream of a WAO reactor. In a typical WAO reactor, some organics are oxidized to the final oxidation products (i.e., CO_2 and H_2O), while others are converted to refractory intermediates. The reaction pathway can be represented as:

$$\begin{tikzcd}
\text{Organic compounds} + O_2 \arrow[rr] \arrow[dr] & & CO_2 + H_2O \\
& \text{Low mol. wt. organic acids} \arrow[ur] &
\end{tikzcd} \tag{4.4.8}$$

Because the wastewater is usually a complex mixture of various organics, a global reaction rate model is used (Li et al., 1991). The general form of the global rate equation can be represented as:

$$-(dC/dt)= k[C]^n[O]^a \tag{4.4.9}$$

$$\text{and } k = k^\circ \exp(-E/RT) \tag{4.4.10}$$

where

k = Global rate constant
k° = Pre-exponential factor
E = Activation energy (kJ/mol)
R = Gas constant (8.314 J/mol.K)
T = Temperature (K)
C = Concentration of organic contaminants (mol/L)
O = Concentration of oxygen (mol/L)
n = Order of reaction with respect to organic contaminants
a = Order of reaction with respect to oxygen
t = Time (s)

Based on kinetic data (Li et al., 1991) for WAO, the value of n is usually taken as 1. The value of exponent 'a' varies from 0 to 1. In many cases, the value of 'a' is zero or near zero.

The development of a generalized kinetic model (Li et al., 1991) is based on the assumption that part of the organic contaminants is oxidized to carbon dioxide and water while the balance is oxidized to acetic acid. Acetic acid is further oxidized to carbon dioxide and water:

$$A + O_2 \rightarrow CO_2 + H_2O \qquad (4.4.11)$$

$$A + O_2 \rightarrow B \qquad (4.4.12)$$

$$B + O_2 \rightarrow CO_2 + H_2O \qquad (4.4.13)$$

where A represents organic contaminants in the wastewater and B represents acetic acid. Development of the kinetic expression has been described in detail (Li et al., 1991) and leads to the following expression:

$$[A + B]/[A + B]_0 = [A]_0/[(A) + (B)][\{k_2/(k_1 + k_2 - k_3)\exp(-k_2t)\} + \{(k_1 - k_2)/(k_1 + k_2 - k_3\}\exp\{(k_2 - k_1)t\}] \qquad (4.4.14)$$

where

[A] = [Concentration of all initial and intermediate organic contaminants – acetic acid]
[B] = [Concentration of acetic acid]
k_1 = Rate constant for reaction (4.4.11)
k_2 = Rate constant for reaction (4.4.12)
k_3 = Rate constant for reaction (4.4.13)

The concentrations of group A and B can be expressed in forms other than mol/L, such as COD, total oxygen demand (TOD), or total organic carbon (TOC). The ratio of the average formation rate coefficient of acetic acid (k_2) to that of the end products (k_1) has been defined as the point selectivity (E):

$$E = k_2/k_1 \qquad (4.4.15)$$

The oxidation of organic compounds in the feed can be expressed as a series of scission reactions, one carbon atom at a time. For every scission reaction, 1 mole of carbon dioxide is formed. This would continue until the number of carbon atoms in the compound is reduced to 3, when acetic acid is formed. It can reasonably be assumed that the rate constants for each reaction step are approximately equal and can be represented by a single value of k, the reaction rate constant. If n is the average number of carbon atoms in the feed, (n – 2) moles of carbon dioxide are formed for every mole of acetic acid. In this manner, the wet oxidation of organic substrates results in the formation of both acetic acid and carbon dioxide. The average point selectivity $\hat{E}$ can then be defined as the ratio of the average formation rate of acetic acid to the average formation rate of carbon dioxide:

$$\hat{E} = 1/(n - 2) \tag{4.4.16}$$

where n is the average number of carbon atoms in the feed.

The adoption of the first-order reaction kinetics model is based on the finding that the WAO of the original organic substrate proceeds in two steps. In the first step, the organic compounds are oxidized to low-molecular-weight intermediates. These intermediates are subsequently oxidized to carbon dioxide and water in the second step. The kinetic data shows that the rate coefficient for the first step is significantly larger than that of the second step, (i.e., $k_2 \gg k_3$), reflecting the much slower oxidation of acetic acid:

$$k_1 = k_1^o \exp(-E_1/RT) \tag{4.4.17}$$

$$k_2 = k_2^o \exp(-E_2/RT) \tag{4.4.18}$$

$$k_3 = k_3^o \exp(-E_3/RT) \tag{4.4.19}$$

For most organic wastes, the values of E_1 and E_2 are nearly equal because groups B and C represent the series degradation products from similar reactions. The value of E_1 is found to be larger than either E_2 or E_3 indicating that the energy barrier for oxidation of acetic acid is higher than that for other organics and acetic acid is a stable intermediate.

Design

The design of a WAO plant depends on the following factors:

1. Temperature
2. Total pressure
3. Oxygen partial pressure
4. Gas-liquid mixing
5. Inlet contaminant concentration (inlet COD)
6. Extent of oxidation (% reduction in COD)
7. Reactor
8. Other

Temperature

It has been found that temperature is the most important variable in carrying out WAO (Lin et al., 1996). The temperatures used in wet air oxidation range from 120 to 320°C (248 to 608°F). Low-temperature processes are often, although not always, carried out in the presence of catalysts. The reaction rate constants follow the Arrhenius law with respect to temperature, as shown in Equations 4.4.17–4.4.19. It has been found that the operating temperature can determine whether the reaction is controlled by mass transfer in the liquid phase or by kinetics.

Total Pressure

Pressures used in WAO range from 490 kPa (70 psi) to 21,000 kPa (3047 psi) and are a direct function of the temperature used for oxidation because the major role played by the pressure is to ensure that a liquid phase is maintained and that the oxidation takes place in this phase. It has been reported (Perkow et al., 1981 that for the reaction to proceed at an acceptable rate, at least part of the water in the reactor must be present as liquid. The operating pressure is therefore adjusted to a value above the saturated water vapor pressure at the operating temperature. The influence of pressure on the progress of the reaction is not considered to be significant (Lin et al., 1996).

Oxygen Partial Pressure

Oxygen partial pressure is a function of the operating pressure and the composition of the gas. Because the operating pressure is determined independently, the oxygen partial pressure is therefore determined by the composition of the oxygen source. The two common oxidants used in wet oxidation are air and oxygen, with the former being more predominant in industrial installations based on safety and cost considerations. Explosions have been reported when using pure oxygen at elevated temperatures in titanium or titanium-lined steel vessels.

Gas-Liquid Mixing

The WAO reaction involves mass transfer with simultaneous chemical reaction. The reaction is subject to a number of resistances that affect the overall rate expression. The total resistance is the sum of:

1. Mass transfer of oxygen in the gas phase from the bulk to the gas-liquid interface
2. Mass transfer of oxygen from the interface to the bulk liquid
3. Chemical reaction

In wet oxidation reactors, the mass transfer resistance in the gas phase is negligible and therefore can be neglected. The liquid-phase mass transfer resistance depends on the design and configuration of the oxidation reactor as well as on the reaction temperature. Although for a well-mixed reactor this resistance can be ignored, it is necessary to estimate the value of the liquid-phase mass transfer coefficient as well as the interfacial area to determine whether the reactor is operating in the mass transfer or kinetic control regime. The oxidation reaction is an example of mass transfer with slow chemical reaction. This implies that almost all the oxidation takes place in the bulk fluid and almost none in the liquid film.

Extent of Oxidation

It is not always necessary or desirable to effect complete oxidation of all the organic substrate in the feed. Once the necessary extent of oxidation has been determined, the gas flow rate is fixed. A 2 to 10% excess flow rate of air is usually used. The reaction kinetics can then be determined at different temperatures and the desired inlet temperature for reactor operation chosen.

Reactor

The oxidation reactor is the most critical piece of equipment in the WAO plant. The design of the reactor is therefore critical for achieving the desired performance. The reactor must be designed for carrying out gas-liquid reactions and operating in the kinetic control regime. This condition requires that the reactor must be designed to eliminate gas-phase and liquid-phase mass transfer resistances. Although the oxidation reaction is exothermic, WAO reactors operate adiabatically, allowing the temperature in the reactor to rise. Therefore, heat transfer to the outside can be ignored.

The types of reactors that meet the required criteria include:

- Vertical bubble column (also known as a tubular reactor)
- Vertical bubble column with sieve plates (also known as a sectionalized bubble column)
- Vertical bubble column with radial baffles (also known as a sectionalized bubble column)
- Cascade of stirred tanks
- Tall compartmentalized stirred tank

A deep well reactor using oxygen has been used for the treatment of sewage sludge (Bowers et al., 1991). This, however, is an unusual design and will not be discussed further.

With the exception of the tall compartmentalized stirred tank, all the other reactor types have reportedly been used for WAO. Considering the high pressures and temperatures required for carrying out WAO, the cost of building such a reactor, designed and fabricated to ensure low downtime, would be uneconomical. Further discussion is therefore restricted to the simple and sectionalized bubble column reactors and the stirred tank cascade reactor. Most of the reactors used in commercial installations fall into these categories.

Bubble Column Reactors

These reactors have high aspect ratios and the design of the gas distribution system is important to their proper functioning. One publication (Kastanek et al., 1991) is devoted to the design of gas-liquid reactors and covers both types of bubble column reactors as well as stirred tank gas-liquid reactors. Another treatise (Deckwer, 1992) discusses both types of bubble column reactors.

A simple bubble column reactor can be described as a series of N completely mixed reactors in which both the gas and liquid phases are completely mixed, coupled with an exchange of flow between compartments (Heijnen and van't Riet, 1982). The value of N can be computed from:

$$N = 1.25 \times [H/T] \tag{4.4.20}$$

where

H = Liquid height in the reactor
T = Diameter of the reactor

Bubble column WAO reactors have high aspect ratios and, typically, N » 1. Under these conditions, the effective liquid dispersion coefficient can be calculated from the following equation (Heijnen and van't Riet, 1982):

$$D(e) = 0.38 \times [gT^4v]^{1/3} \tag{4.4.21}$$

where

v = Superficial gas velocity (m/s)

In simple bubble columns, gas sparging causes intense liquid circulation to develop although the net liquid flow is very small. The liquid flows upward near the center and downward near the column wall, thereby giving rise to backmixing. This liquid-phase backmixing also causes gas-phase backmixing due to the gas holdup. One way to reduce this backmixing in bubble column reactors is to divide the column into sections. Such reactors are referred to as sectionalized bubble column reactors. The sections can be plates (e.g., sieve plates with or without downcomers), or baffles (e.g., disc and doughnut baffles, or even simple radial baffles).

An optimum design for radial baffles has been proposed (Joshi and Sharma, 1979). It has been recommended that the ratio of the central hole to the column diameter should be 0.71 and that the ratio of the baffle spacing to the column diameter should be 0.81. It is claimed (Pandit and Joshi, 1983) that this configuration reduces the extent of backmixing by 2 to 3 times that in a simple column. Design methods for plate-type sectionalized bubble column reactors have been provided (Deckwer, 1992; Kastanek et al., 1991). Reduction in the extent of backmixing causes the gas flow to approach plug flow. Most of these reactors operate in co-current mode.

Mathematical models for design of co-current and countercurrent bubble column reactors for WAO of sewage sludge have been described (Ploos van Amstel and Rietemas, 1973). Correlations for estimation of mass transfer coefficients, interfacial area, gas holdup in bubble column reactors have been provided (Heijnen and van't Riet, 1982).

Cascade Stirred Tank Reactor

This reactor is essentially a compartmentalized horizontal vessel with an agitator provided in each compartment. The liquid levels in each of the compartments are maintained such that liquid flows from the first compartment to the second, from the second to the third, etc. Such a reactor has been described (Baillod et al., 1979). In an agitated tank, the mass transfer resistance lies entirely within the liquid-phase. Correlations for liquid phase mass transfer coefficient, interfacial area, gas holdup, and agitator power requirements are available (Treybal, 1980). A more recent and detailed review of correlations for these parameters has been published (Tatterson, 1991). It must be noted that under the high temperatures and pressures prevalent in WAO reactors, significant attention needs to be paid during the mechanical design phase to address the likely problems in agitator shaft sealing.

Regardless of the type of reactor chosen, data on the solubility of oxygen in water at the elevated temperatures and pressures used in WAO is required. Equations for Henry's law constant in water (Himmelblau, 1960) and in brines (Cramer, 1980) have been published. Methods for computing the water content and thermodynamic properties of saturated combustion gases have been published (Heidemann and Prausnitz, 1977). These properties are required for power recovery from the WAO systems.

Other major components of a basic WAO plant are the feed pump, air compressor, feed-air mixer, feed preheater, and residue cooler, construction materials. If additional energy recovery schemes are implemented, then additional heat exchangers will be required.

Other Components

Feed Pump

For the flow rates typically used in WAO installations, a high-pressure plunger type pump should be suitable. In cases where the feed contains solids (e.g., for regeneration of powdered activated carbon), use of replaceable liners in these pumps or use of multistage centrifugal pumps should be evaluated.

Feed-Air Mixer

It is not strictly necessary to mix the feed and air outside the reactor. It appears, however, to be advantageous to premix the feed with the air and preheat this mixture before feeding it to the reactor. In such cases, use of a static mixer before the preheater may prove beneficial.

Air Compressor

A reciprocating air compressor should probably be used due to the high pressures required.

Feed Preheater

The purpose of this heat exchanger is to preheat the feed to reaction temperature, or close to the reaction temperature, using the reactor effluent as the heating medium. In this way, no additional thermal energy is required to sustain the reaction. A conventional shell- and-tube heat exchanger is used with the feed in the tubes and the heating medium in the shell.

Residue Cooler

This is a heat exchanger used to cool the oxidized liquid stream before discharge. Here too, a conventional heat exchanger is used.

Materials of Construction

The high temperatures and pressures used in a WAO system accelerate corrosion processes so that even nonaggressive fluids start causing corrosion. In addition, the composition of the hazardous waste can also cause corrosion. This is especially true when the waste to be treated contains dissolved ions such as halides or sulfates. A recent paper (Kane, 1999) has reviewed the literature on suitable materials for hydrothermal oxidation processes. The findings indicate that, in general, the most suitable materials of construction for use in components and parts exposed to high temperatures and pressures in WAO systems are the advanced nickel-based alloys such as Alloy C-276, Alloy 625, and Titanium Grade 7. However for certain wastes, SS316 may also be suitable although it is recommended that the materials proposed for use be tested in a laboratory autoclave under operating conditions. Heat treatment of the welds and fittings after fabrication is recommended.

Economics

The capital cost of a basic WAO system is proportional to the waste stream flow rate, the reactor operating pressure, and the reduction in the oxygen demand. The reduction in oxygen demand determines the air feed rate as well as the reactor operating temperature, and this in turn determines the operating pressure. WAO uses a significant amount of power for pumping wastewater and in air compression. The energy utilized in compressing the air is present in the reactor off-gases in the form of thermal and pressure energy. Power can be recovered from the off-gases by expanding them through a turbine, thus reducing the net power requirements. If the oxygen demand in the waste is sufficiently large, both steam and power can be generated. In smaller WAO plants, the additional capital cost and the resulting complexity in recovering both power and steam cannot possibly be justified. The capital investment for steam generation can probably be justified in smaller WAO plants. To make WAO economically viable for treatment of a waste stream, the COD of the stream should be above 20,000 mg/L. It may therefore be necessary to concentrate the waste stream to increase the COD to the minimum value. The increase in concentration can be achieved using membrane separation processes, thermal evaporation processes, or a combination of the two. Higher COD values of the waste stream could permit economical steam generation. A relationship between the COD of the waste stream and the energy available for recovery as process steam has been presented (Flynn, 1979). The capital cost of a WAO installation is a strong function of the feed rate, COD reduction, reactor operating pressure, and the material of construction of the reactor, as well as the installed associated equipment. It has been estimated (Copa and Gitchel, 1989) that for an operating pressure of 13.8 MPa (2000 psi) and a 50 g/L COD reduction, the capital cost of a WAO installation would vary between \$2.5 and 3.6 million for a feed rate of 1 m^3/hr, to \$6.5 to 9.0 million for a feed rate of 14 m^3/hr. Estimates of operating and maintenance costs (Copa and Gitchel, 1989) show total operating costs ranging from \$32/m^3 for a feed rate of 1 m^3/hr to \$8/m^3 for a feed rate of 14 m^3/hr. For the LOPROX™ process cited previously, an investment cost of \$3.5 million is suggested, based on the following parameters: 6 m^3/hr capacity, 8300 hr/yr. operation, input COD at 40 g/L with 70% removal, 20 bar, 200°C and Ti-clad reactor (Hertrampf and Shadiakhy, 1999).

Supercritical Wet Air Oxidation

Supercritical wet air oxidation (SWAO) is an extension of WAO and is performed in water at temperatures in excess of 374°C and 22.1 MPa, that is, above the critical point of water. Under supercritical conditions, in general, organics are completely miscible with water, while inorganics such as sodium chloride are practically insoluble. Oxygen is also completely miscible in all proportions in supercritical water. At these conditions, organic compounds and oxygen form a single homogenous phase and there is no mass transfer resistance. At 400 to 500°C, the destruction efficiencies reach 99 to 99.9%, and reaction times are of the order of 1 to 5 min (Wightman, 1981). The oxidation end products are CO_2 and simple acids, and the final effluent is sufficiently innocuous that it can be discharged without further treatment. SWAO is an excellent technique for the destruction of toxic and hazardous wastes, and molecules resistant to WAO can be effectively destroyed by this technique. Mathematical models for calculating detailed thermal hydraulics and chemical component distribution in SWAO reactors have been published (Oh et al., 1997). There are, however, practical difficulties in the use of SWAO, as for example, the use of very high pressures and temperatures, costly materials of construction, and the plugging of the reactor system due to the precipitation of salts present (Mishra et al., 1995), although it has been reported (Oh et al., 1997) that the MODAR design addresses the plugging problem.

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4.5

Supercritical Water Oxidation

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Introduction

Supercritical water oxidation (SCWO) is a chemical process technology that can be used for treating hazardous and mixed wastes. It is applied most economically to aqueous wastes with between 1 and 20 wt% organic carbon. Such wastes are too concentrated to treat economically by adsorption or some other separation process, and they are too dilute to treat economically by incineration. Of course, economics does not always dictate the choice of treatment technology. SCWO possesses other attractive features, as delineated in subsequent paragraphs, that make it a candidate treatment technology for high-risk wastes.

SCWO technology was patented in the early 1980s, and it has been further developed and refined as time has passed. The concept behind SCWO is that water above its thermodynamic critical point (T_c = 374°C, P_c = 218 atm) serves as the reaction medium for the conversion of organic carbon and hydrogen to CO_2 and H_2O via reactions with O_2. Typical reaction conditions are 450 to 600°C and about 250 atm, and typical treatment times are on the order of tens to hundreds of seconds. The goal is complete oxidation and mineralization of organic wastes. Sulfur and phosphorus atoms are oxidized to sulfate and phosphate, respectively, and organo-nitrogen atoms generally appear in the SCWO products as N_2 or N_2O.

SCWO takes advantage of the unique and adjustable properties of water above its critical point. These properties make supercritical water (SCW) a very different solvent and reaction medium than ambient liquid water. For example, in ambient liquid water, NaCl is very soluble (>30 wt%); but in SCW at 500 to 600°C, the solubility drops to about 100 ppm. Organic compounds and permanent gases, on the other hand, show the opposite behavior. These become completely soluble in SCW, whereas they are only sparingly soluble in ambient liquid water. The experimental data in Figure 4.5.1 for *n*-heptane provides a representative example. Thus, an advantage of conducting complete oxidation reactions above the critical temperature of water is that organic compounds, oxygen, and water exist in a single homogeneous fluid phase at the reaction conditions. This single-phase environment ensures intimate contact of the reactants and guarantees the absence of inter-phase mass transport limitations for SCWO. The elevated temperatures and the absence of transport limitations in SCWO lead to rapid destruction of organic compounds. Indeed, SCWO of organics goes essentially to completion with a treatment time of only a few minutes. Of course, if the reaction is complete, there is no need to treat the reactor off-gases or liquid effluent. Another advantage of SCWO is that the temperatures used in

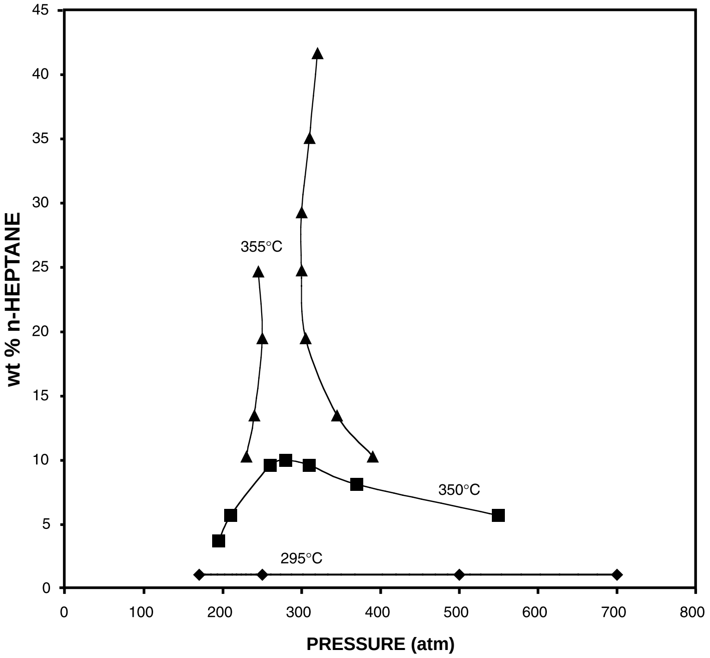

FIGURE 4.5.1 Solubility of *n*-heptane in water. (From Connolly, J.F. 1966. Solubility of hydrocarbons in water near the critical solution temperature, *J. Chem. Eng. Data*, 11, 13–16. © 1966 American Chemical Society.)

SCWO are lower than those encountered in incineration and, consequently, the generation of NO_x is much less of a problem. Furthermore, one can use the heat liberated during the exothermic oxidation of wastes with sufficiently high organic content to maintain the elevated reactor temperature and preheat the feed. Thus, after start-up, the process would not require an external energy source. A final attractive feature of this technology is that it can qualify as a totally enclosed treatment facility. That is, the treated effluent can be held in reserve and analyzed prior to release to the environment. If the effluent does not meet the specifications of the relevant regulations, it can be recycled to the reactor and treated again. This feature guarantees that no uncontrolled emissions of environmentally damaging compounds will occur during SCWO treatment. Note that this feature stands in contrast to incineration, in which the effluent is emitted continuously.

SCWO can be thought of as an extension of wet-air oxidation, which is discussed elsewhere in this Handbook, to more severe processing conditions. Wet-air oxidation involves oxidation reactions in an aqueous phase, but at lower subcritical temperatures and pressures. It does not typically lead to complete mineralization. Thus, wet-air oxidation is often used as one unit operation in a multi-step waste treatment process, whereas SCWO is capable of providing complete mineralization in a single-unit operation. SCWO can also be thought of as an alternative to incineration. The same types of overall reactions occur (complete oxidation) in both technologies, but the reaction conditions are very different. Incineration is a gas-phase, high-temperature, ambient-pressure process, whereas SCWO involves lower temperatures, higher pressures, and reaction in a supercritical water phase.

Previous research and development work has shown that SCWO is an effective treatment technology for a wide variety of wastes. Moreover, commercial viability is evidenced by a commercial-scale SCWO unit going into operation in 1994 at a facility owned by Huntsman Chemical near Austin, Texas.

The main reservations regarding SCWO technology center on solids management and corrosion. Solids can form during SCWO processing. The solids can be inorganic materials present in the reactor feed, oxides of metals leached from metal surfaces in the process, or salts that form during processing and then precipitate because of their low solubility in SCW. Some of the solids, especially several different salts, strongly adhere to the reactor surface and build up appreciable deposits that can eventually plug a conventional tubular reactor.

Corrosion is an issue, especially for the processing of halogen-containing wastes. The high temperatures and high chloride ion content in such SCW mixtures lead to rapid corrosion. Interestingly, corrosion tends to be more rapid at temperatures below the critical point where the water density and dielectric constant are still somewhat liquid-like. At higher supercritical temperatures, water does not support ionic chemical processes as well.

Thus, it is clear that the SCWO process involves high pressures and quite possibly the need for clever reactor designs to handle the solids and corrosion problems. One option is to use special corrosion-resistant alloys for the reactor, which increases the costs for the equipment. Economic analyses show, however, that SCWO appears to be cost competitive with existing treatment methods (Modell, 1989) for several applications. Both Modell (1989) and Tester et al. (1993) provide more general information about SCWO technology.

SCWO Process Description

A typical commercial-scale SCWO process flowsheet has multiple feed streams, as shown in the schematic in Figure 4.5.2. There is always an organics-containing waste stream and an oxidant stream (typically compressed air or liquid oxygen), but there may also be an auxiliary fuel stream, a neutralizing agent, and an additional water stream if the organic content of the waste stream is too high. These streams are mixed together and fed to the SCWO reactor.

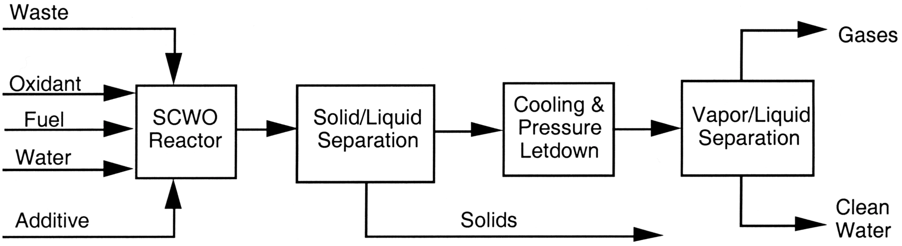

FIGURE 4.5.2 Block diagram for generic SCWO process.

Many different reactor designs have been proposed and used in laboratory and pilot plant tests. These include conventional tubular flow reactors, lined tubular flow reactors, transpiring wall tubular reactors, and vessel-type tank reactors. A conventional tubular flow reactor would be operated at a high fluid velocity to minimize the deposition of solid particles on the reactor wall. Mechanical devices have also been proposed for removing particles from the wall and resuspending them in the fluid phase. A lined tubular flow reactor separates the tasks of corrosion resistance and pressure containment. The liner, which comes in contact with the reaction medium, would be made of some corrosion-resistant material (ceramics, titanium). The pressure vessel can then be constructed from less-expensive material. The transpiring wall reactor is a type of lined reactor. It handles the solids deposition issue by having jets of water enter the reactor along its entire length. This zone of fluid near the wall hinders the deposition of particulates. Transpiring wall reactors are discussed in more length later in this section. A vessel-type tank reactor for SCWO is typically designed to operate with two distinct zones in the reactor. The feed streams enter through a nozzle at the top of the reactor and the oxidation reactions proceed quickly in this upper SCW reaction zone. The bottom part of the reactor contains a subcritical aqueous brine solution wherein the solids (salts) will accumulate as they fall down the reactor. Regardless of the reactor type, downstream processing includes cooling and depressurizing the effluent and separating the products into gas, liquid, and at times, solid phases. The hot reactor effluent can be used to provide some of the heat required for the reactor feed stream, so SCWO processes often strive for autothermal operation.

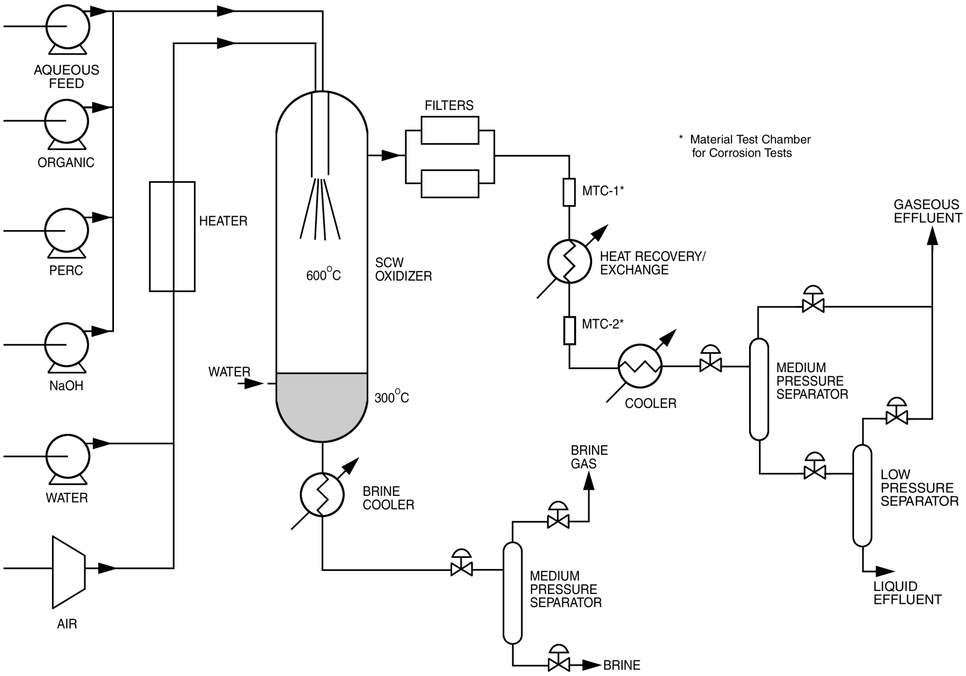

FIGURE 4.5.3 Schematic of General Atomics SCWO pilot system.

Figure 4.5.3 shows a more detailed schematic of a General Atomics flowsheet (previously MODAR's flowsheet) for a supercritical water oxidation pilot plant. Organic wastes are fed into a vessel-type reactor along with preheated air. A neutralizing chemical component of NaOH is added, and the mixture is sprayed through a nozzle. The oxidation reaction takes place downstream of the nozzle, forming CO_2 and H_2O as the primary products.

The vessel reactor can be thought of as a continuously stirred tank reactor (CSTR) with a nozzle jet providing the mixing force. In the upper portion of the vessel, shown in more detail in Figure 4.5.4, the temperature is maintained near 600°C by the heat generated during the reaction. At this temperature, inorganic chemical components such as metal oxides and salts separate from the supercritical mixture due to their low solubilities and precipitate into the brine pool by gravity. The lower region of the reactor vessel is cooled to approximately 300°C by the injection of cold water. Returning to Figure 4.5.3, one sees that the brine and brine gas exiting the reactor are separated through a medium-pressure separator. At the upper exit of the reactor, filters remove residual sticky solids from the main overhead effluent. The effluent is cooled to ambient temperature before it enters the first of two pressure letdown stages to separate the effluent gas and liquid.

Status of SCWO Commercial Development

Supercritical water oxidation (SCWO) was patented in the early 1980s, and a few companies formed to commercialize the technology. Some of the processes designed were for subsurface installations where the hydrostatic head would provide most of the high pressure required to reach near-critical or supercritical conditions. Vertech, GeneSyst International, and Oxidyne were three companies with research and development activities directed toward subsurface, deep-well wet oxidation systems. Oxidyne had a contract with the city of Houston, Texas to construct a deep-well (5000 ft.) sludge treatment system, but funding constraints caused the project to be aborted. City Management Corporation obtained the Oxidyne patents, but apparently had no immediate plans for further SCWO development.

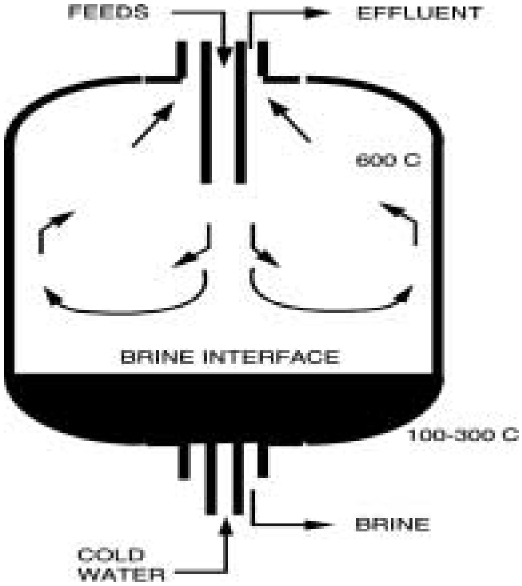

FIGURE 4.5.4 Typical SCWO vessel-type tank reactor.

Modar, Inc., was one of the pioneering companies in this field for above-ground SCWO process technology, and ABB Lummus Crest was a licensee. General Atomics recently acquired Modar and has been continuing research and development work regarding SCWO technology. Modell Development Corporation (MODEC) was another of the pioneering firms. Eco Waste Technologies has also been involved in demonstrating, developing, and marketing SCWO process technology. The Eco Waste process is unique in that it has been implemented commercially at a Huntsman Corporation site near Austin, Texas. The waste treated there contains long-chain alcohols, glycols, and amines. The total organic carbon concentration typically exceeds 50,000 mg/L. This implementation of SCWO technology won the 1996 Texas Governor's Award for Environmental Excellence in the Innovative Technology category. In early 1999, Chematur Engineering AB of Sweden acquired Eco Waste and is now actively marketing SCWO technology under the name of Aqua Critox. Organo Corp., in Japan, is also active in the SCWO technology field. It has a pilot plant facility and plans exist for a commercial installation.

SCWO for Treating Hazardous and High-Risk Waste

There have been innumerable demonstrations of the efficacy of SCWO for treating hazardous wastes. Some of the demonstrations involved SCWO treatment of actual hazardous wastes (e.g., PCB-containing transformer fluids, wastes from the microelectronics industry) and others involved treatment of individual hazardous chemical compounds. Modell (1989) has summarized some of the early technology demonstrations for individual compounds. High destruction efficiencies were reported for aliphatic compounds, aromatic hydrocarbons, halogenated aliphatics, halogenated aromatics, oxygenated compounds, and organic nitrogen-containing compounds. The summary indicated that destruction efficiencies of about 99.9% could typically be obtained from treatment at 400 to 500°C for 1 to 5 minutes. A 99.99% destruction efficiency typically required 500 to 550°C and about 1 minute of treatment, whereas 99.999% destruction required 550 to 600°C and less than 1 minute of treatment.

SCWO can also be used to treat high-risk military wastes such as propellants, explosives, and other energetic materials. For example, SCWO treatment with excess H_2O_2 (as oxidant) for 11 seconds at 600°C and 370 atm led to destruction efficiencies exceeding "three nines" (99.9%) for RDX (cyclotrimethylene trinitramine), TNT (2,4,6-trinitrotoluene), and NQ (nitroguanidine). Destruction efficiencies for HMX (cyclotetramethylene tetranitramine) and PETN (pentaerythritol tetranitrate) were closer to 99% under these processing conditions.

An alternative to direct oxidation of the energetic materials, which have a low solubility in ambient liquid water, is a two-step treatment process. This process uses base-catalyzed hydrolysis around 100°C in the first step and then SCWO treatment of the hydrolysate as the second step. This method also provides very high destruction efficiencies, but it also offers higher waste processing rates than direct SCWO treatment.

SCWO has also been demonstrated to be effective in destroying chemical warfare agents such as GB, VX, and mustard gas. For example, destruction and removal efficiencies exceeding six nines (99.9999%) have been achieved from SCWO treatment of these materials at 450°C and 4000 psig.

SCWO for Treating Mixed Waste

Mixed wastes are those that contain both radioactive and hazardous organic components. There is a need for alternatives to incineration of mixed wastes. Indeed, there is considerable difficulty in permitting the incineration of radioactive and organic-containing waste. The two approaches taken most frequently for treating mixed wastes are separating the radioactive elements from the organic components or destroying the organic components so the waste is only radioactive and no longer classified as mixed. SCWO is a process technology that can be used for the latter approach to treat mixed wastes. The combustible portion of a mixed waste can be converted to CO_2 and water, and any nitrate can be reduced to N_2 or N_2O. The radioactive components will concentrate in the inorganic, noncombustible solids that remain. Thus, SCWO treatment eliminates the organic part of the waste and the radioactive portion is greatly concentrated. This concentration is advantageous because the volume of radioactive waste that needs to be vitrified and held for long-term storage has been greatly reduced. SCWO also offers the advantage of treating the waste in a totally enclosed process or vessel. Finally, SCWO facilitates the separation of metals and actinides. Figure 4.5.5 shows a potential process flowsheet for SCWO treatment of mixed waste. This flowsheet is adapted from work at Los Alamos National Laboratory (Worl et al., 1999), which has demonstrated the feasibility of SCWO for treating mixed waste.

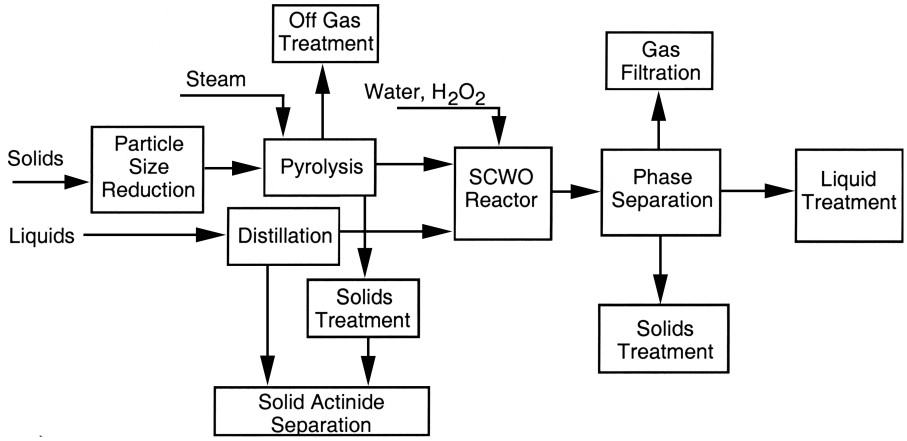

FIGURE 4.5.5 Conceptual process flowsheet schematic for SCWO treatment of mixed waste. (From Worl, L.A. et al., 1999. Demonstration of Hydrothermal Plutonium Combustible Waste Treatment Process, LA-UR-99-2967, report from Los Alamos National Lab).

The block diagram in Figure 4.5.5 is similar to that given earlier in Figure 4.5.2. The chief differences are in the additional processing steps required upstream of the reactor and in the additional treatment required for the off-gases and solids because these may contain radioactive elements. The process in Figure 4.5.5 can handle both solid and liquid mixed wastes. Solid materials would first undergo particle size reduction and/or pyrolytic treatment to convert most of the solids to a pumpable material. The small fraction of gases produced and the remaining solids would be treated appropriately. The liquids are then mixed with an oxidant and water in the SCWO reactor. Phase separation follows complete oxidation. After SCWO processing, the waste is no longer mixed, and the volume of the radioactive waste has been greatly reduced.

SCWO has been evaluated as a potential means of treating tank wastes from the Hanford, Washington, DOE site (e.g., Dell'orco et al., 1993). The site houses numerous underground storage tanks that contain a variety of mixed and hazardous wastes generated from the recovery or enrichment of nuclear materials. These tanks contain radioactive (e.g., uranium), toxic (e.g., ferrocyanides, heavy metals), and organic (e.g., EDTA) components. The main component is sodium nitrate. The nitrates, ferrocyanides, some heavy metals, and all organic compounds need to be removed from these wastes if they are to be treated by vitrification and eventual long-term storage in a geological formation. SCWO may be able to accomplish these requirements. The nitrate present in the waste can serve as an oxidant to destroy the organic compounds and ferrocyanides. The excess nitrate can then be converted to N_2 or N_2O via reactions with added ammonium. The applicability of SCWO technology in concept was demonstrated using simpler model systems to mimic some of the components in Hanford tank wastes. Much research remains to be done, however, to determine how well SCWO will work for the actual wastes.

An important part of the SCWO process for managing mixed waste in general is the feed pretreatment portion. Mixed wastes can include large pieces of solid materials that need to be pretreated before entering the SCWO reactor. Pretreatment options may include size reduction or pyrolysis. The Los Alamos team examined both options, but paid particular attention to pyrolysis. Different solid materials were decomposed thermally in a 9 to 20-g sample, with the goal of producing pumpable liquids that could be fed to the SCWO reactor. Representative results of these pyrolytic pretreatment tests appear in Table 4.5.1. The results of these tests revealed that about 85 wt% of the solids could be converted to a partially pyrolyzed liquid form for subsequent complete destruction with SCWO.

TABLE 4.5.1 Results from the Pyrolytic Pretreatment of Solids for SCWO

Description	% Solids Conversion to Liquids	Initiation Temp. (°C)
Latex rubber gloves	95.3	320
TRIonic® rubber gloves	98.3	320
Glovebox gloves (white)	67.0	276
Yellow chamois	99.7	423
Kimwipes®	86.1	316
Cheesecloth	91.3	336
Yellow paper coveralls	88.9	380
White coveralls, hoods, & sleeves	97.9	425
Acid suits	63.8	270
Pipette tips	100.0	400
Sample vials	99.5	470
Funnel	100.0	440
RELLEX HPQ (resin)	77.3	235
Yellow tape	76.0	270
Masking tape	84.1	160
Tygon® tubing	94.3	255

From Worl, L.A. et al., 1999. Demonstration of Hydrothermal Plutonium Combustible Waste Treatment Process, LA-UR-99-2967, report from Los Alamos National Lab.

The Los Alamos team also used SCWO to treat actinide-containing combustible materials. The wastes contained 5000 to 23,000 ppm total organic carbon. The actinide was either plutonium or americium. The types of materials treated and the organic destruction efficiency obtained from treatment for 60

TABLE 4.5.2 SCWO Treatment of Actinide-Containing Combustible Material

Waste Type	Organic Composition	Actinide	Effluent pH	Organic Destruction
Vacuum pump oil	Petroleum distillate; $(CH_2)_n$	Pu	4.0	99.99%
Analytical solution	Ultima Gold-AB diisopropylnaphthalene	Pu(IV) nitrate or $AmCl_3$	4.0–2.5	99.99%
Solvent extraction solution	70% Dodecane, 10% decanol, 20% tributylphosphate	Pu(IV) nitrate or $AmCl_3$	2.5	99.95%
Dense liquid	Bromobenzene	$AmCl_3$	2.0	99.96%
Cl heteroatoms	1.5 M Trichloroacetic acid	Pu	1.0	99.94%
Pyrolysis liquids	Partially pyrolyzed polypropylene rags	Pu	4.0	99.98%
Water-soluble polymer	Methylpolyvinyl-pyridine $(C_7H_3N)_9(NO_3)$	Pu	2.5	99.92%
Reillex HPQ ion exchange resin	$(C_8H_{10}N)+_n$ 36:62:2 ratio of resin, water, CMC	Pu	1.0	99.97%

From Worl, L.A. et al., 1999. Demonstration of Hydrothermal Plutonium Combustible Waste Treatment Process,” LA-UR-99-2967, report from Los Alamos National Lab.

seconds at 540°C and 46.2 MPa are listed in Table 4.5.2. Roughly 100% excess oxidant was used in these tests.

As can be seen, the types of materials treated include conventional organic liquids (vacuum pump oil), liquids produced by pyrolytic treatment of solids, and solids (ion exchange resin). The ion exchange resin was mixed with water and a viscosity-enhancing agent (carboxymethyl cellulose [CMC] sodium salt) to generate a pumpable mixture. The viscosity of the mixture is high, and the resin beads did not settle out. The pH of the reactor effluent in these tests was between 1.0 and 4.0, depending on the concentrations of heteroatoms in the organic waste. It is clear from the results in Table 4.5.2 that organic destruction efficiencies of greater than 99.9% can be achieved by SCWO treatment.

In addition to destroying the organic component of a mixed waste, it is advantageous to concentrate the radioactive elements into a smaller volume. SCWO can also provide this advantage because the actinides selectively partition into the solid phase during SCWO treatment. The Los Alamos team varied the plutonium concentration in the organic waste entering the reactor from 0.01 to 1046 μCi/L and the americium concentration from 0.23 to 203 μCi/L. They found that the activity of soluble species in the reactor effluent reached a plateau at about 1 to 2 μCi/L, which corresponds to the solubility limit. Thus, the data indicates that most of the actinide that enters the reactor appears in insoluble species after the solubility limit is reached. The solid plutonium species (likely oxide or carbonate forms) are then easily removed from the effluent by filtration. The activity in the filtered SCWO effluent was close to that acceptable for discharge of industrial waste (0.5 μCi/L). Thus, SCWO leads to formation of easily separable solids that contain most of the radionuclides.

The research performed to date has demonstrated the application of SCWO for treating radioactive combustible waste. Organic carbon can be converted to CO_2 with high destruction efficiency. The actinides can be converted to insoluble products, and only a small amount remains in solution. Simple filtration can produce an effluent activity nearly low enough to be acceptable for industrial waste discharge, and additional filtration or ion exchange could reduce the effluent activity even further for some elements.

Additional, and much more detailed information on metal speciation during treatment with supercritical water was obtained from a hydrothermal crystallization study of simulated high-level liquid waste (Smith et al., 1997). The goal of the study was to use hydrothermal crystallization (reduced solubility of metal salts in near- and supercritical water) to recover metals from high-level liquid waste. Table 4.5.3 summarizes the metal recoveries obtained at different temperatures (and solution densities). The simulated waste mixture was prepared by dissolving metals in 1.6 *M* nitric acid. The experiments were performed sequentially; that is, the mildest conditions were used first. Any solids that formed were recovered and analyzed. The remaining solution was then exposed to the next set of conditions, again with solids recovery and analysis. This procedure continued until the most severe conditions were encountered.

Table 4.5.3 also reveals that Zr, Mo, Fe, and Cr become insoluble at modest temperatures. They precipitate and can be recovered in high yields from near-critical water treatment at temperatures below 300°C. At 400°C, which is slightly higher than the critical temperature of water, Ce and Pd also precipitate out. At 450°C, Mn becomes largely insoluble. At least 75% of these seven elements were recovered by hydrothermal crystallization. The recovery of Pr was 52%. All other elements tested were recovered in less than 10% yields, which indicates that they remained soluble in the supercritical water-nitric acid solution.

TABLE 4.5.3 Recovery (%) of Elements from Hydrothermal Treatment at Conditions Specified

Element	200°C 0.88 g/cm$_3$	250°C 0.83 g/cm$_3$	300°C 0.75 g/cm$_3$	350°C 0.64 g/cm$_3$	400°C 0.36 g/cm$_3$	450°C 0.15 g/cm$_3$	Total Recovery
Gd	—	—	—	—	—	6.5	6.5
Na	—	—	—	—	—	—	—
Fe	—	92.4	7.1	—	—	—	99.5
Nd	—	—	—	—	—	5.8	5.8
Ce	—	—	—	1.6	95.9	—	97.5
Zr	93.5	6.1	—	—	—	—	99.6
Cs	—	—	—	—	—	—	—
Pr	—	—	—	1.0	37.4	14.0	52.4
Ba	—	—	—	—	—	1.5	1.5
La	—	—	—	—	—	4.0	4.0
Sm	—	—	—	—	—	6.6	6.6
Cr	—	34.4	26.6	—	11.6	2.6	75.2
Ni	—	—	—	—	—	8.3	8.3
Sr	—	—	—	—	—	—	—
Y	—	—	—	—	—	8.2	8.2
Mn	—	—	—	—	—	77.0	77.0
Mo	95.6	3.6	—	—	—	—	99.2
Pd	—	—	—	27.9	71.8	—	99.7
Eu	—	—	—	—	—	8.0	8.0
Cd	—	—	—	—	—	5.3	5.3
Ag	—	—	—	—	3.1	5.5	8.6

From Smith, R.L. et al., 1997. Recovery of metals from simulated high-level liquid waste with hydrothermal crystallization, *J. Supercritical Fluids,* 11, 103–114. With permission.

This subsection has briefly reviewed a portion of the process development work that has been done to assess the efficacy and applicability of SCWO for treating wastes with both radioactive and organic components. The results have been encouraging. It appears that SCWO can completely destroy the organic components and greatly reduce the volume of the remaining radioactive waste.

SCWO Research

The information provided to this point has dealt primarily with SCWO process technology and technology demonstrations. That is, the focus was on previous work that demonstrated the performance of SCWO for treating hazardous and mixed wastes. It is clear that the technology can be useful, and this realization has motivated numerous, more fundamental research programs. Indeed, there is a relatively large body of literature devoted to SCWO research. Issues such as heat and mass transfer in SCW, phase behavior, salt solubility, corrosion, reactor modeling, and reaction rates and mechanisms are all important and have received attention. This subsection discusses some of the major research areas and summarizes the work performed to date. Readers who desire more extensive information are referred to additional resources (Tester et al., 1993; Tester and Cline, 1999).

Corrosion and Reactor Engineering

As previously noted, corrosion is a very real issue for SCWO treatment, but primarily for wastes containing heteroatoms such as halogens, sulfur, and phosphorus. Wastes containing only hydrocarbons (C, H, O-containing compounds) are relatively easy to treat by SCWO because corrosion rates are significantly lower. This recognition of the importance of corrosion for developing SCWO as a general waste treatment technology has prompted several investigations into corrosion mechanisms and materials testing for SCWO conditions, as has been recently summarized (Tester and Cline, 1999).

Corrosion tends to be most problematic at subcritical temperatures where the water density remains liquid-like. The problems are typically manifested in the heat exchangers in an SCWO process. Corrosion of the actual SCWO reactor, if it is operating at temperatures well above the critical temperature, tends to be less of a problem. Both simplified theoretical analysis and carefully designed experiments have confirmed and provided an explanation for these processing observations. At a fixed system pressure, corrosion rates tend to first increase with temperature, reach a maximum, and then decrease with further increases in temperature. These maxima typically occur around the critical temperature of water. The initial increase has been attributed to the effect of temperature on the rate constants of the reactions responsible for the corrosion. The decrease at higher temperatures occurs because, at a fixed pressure, the water density decreases with increasing temperature. This density decrease is accompanied by a sharp reduction in the dielectric constant; thus, water becomes a poorer medium for ionic reactions. As a result, there is less dissociation into ions at the higher temperatures. This reduction in the ability of SCW to host ion formation overwhelms the increase in the rate constant and thus the observed corrosion rate decreases. Therefore, solutions of heteroatom-containing compounds in subcritical water tend to be more corrosive than solutions of the same compounds in supercritical water at the same pressure.

Corrosion rates of many different materials have been measured in different SCW solutions. When exposed to solutions containing halogens, sulfur, or phosphorus, corrosion of stainless steel and nickel alloys such as Inconel and Hastelloy tends to be rapid. Corrosion of metals such as Nb, Ti, Ta, Zr, and Pt tends to be much slower, however. Selection of the appropriate materials of construction for an SCWO process must be done on a case-by-case basis. There does not appear to be a single unique material that is suitable for all applications. It does appear, however, that materials can be identified for all applications so that SCWO technology can be technically feasible. See Chapter 21 in *Innovations in Supercritical Fluids. Science and Technology* (Hutchenson and Foster, 1995) for a summary of corrosion tests performed on more than 20 different materials, at three different temperatures and in three different aggressive aqueous solutions.

In addition to studies of corrosion rates (kinetics), there have been investigations into the thermodynamics of corrosion. The relevant thermodynamics can be summarized as potential vs. pH diagrams, which are also known as Pourbaix diagrams. These diagrams provide information about the regions of possible corrosion and regions of possible protection by passivation. One must keep in mind, however, that Pourbaix diagrams simply show which reactions are possible or prohibited. They give no information regarding the rates of those reactions. Additionally, Pourbaix diagrams constructed for a bulk metal cannot account for localized corrosion phenomena within a crevice unless the local conditions are known. Thus, the metal might be immune from corrosion under the bulk conditions, but nevertheless experience rapid local corrosion if the local conditions differ from those in the bulk.

One of the ways explored to handle the corrosion and solids management problems associated with SCWO treatment of Cl-containing wastes is to develop novel reactors. An example of this approach is the transpiring wall reactor (Mueggenburg et al., 1995). The key idea here is that a permeable reactor liner be used such that water passes through the liner wall to form a boundary layer along the interior. This action can prevent salt deposition and prevent contact between the corrosive SCWO phase and the liner wall. Two different materials are used in the transpiring-wall SCWO tubular reactor. The role of the outer material is to serve as a pressure vessel and maintain the structural integrity of the reactor. The outer material will come in contact only with pure water; thus, an alloy such as Inconel can serve this purpose. The inner material is the one through which the corrosive SCW mixture will flow, but it can be made of a stainless steel because there will be no direct contact between the liner and the SCW mixture. Because this liner has a large number of small holes along its surface, pure water, which is flowing between the liner and the metal tube, will pass through the liner along its length. These water jets can inhibit the deposition of solid salt particles on the reactor surface. Transpiring-wall reactors of this type have been constructed and used to treat different hazardous and high-risk military wastes by SCWO.

There have been other variations on this theme of separating the tasks of pressure containment and corrosion resistance for SCWO reactors. Liners made of ceramics, titanium, and other materials have been investigated and found to offer good corrosion resistance.

SCWO Reactor Modeling

The work discussed heretofore dealt with the development of novel reactor concepts for SCWO treatment. After showing proof of concept, reactor modeling can be done to improve the reactor design and to understand reactor performance. Ideally, a reactor modeling study would reveal the flow fields and mixing patterns established as the fluid flows through the reactor and also provide the fluid composition and temperature at any point within the reactor. Such insight into the detailed behavior of SCWO reactors can be obtained by developing mathematical models of the governing physical and chemical phenomena. Models for "ideal" chemical reactors, which have simple flow fields and mixing patterns, are readily available in textbooks. SCWO reactors, such as the one in Figure 4.5.4, however, are rarely ideal. Thus, to model these reactors, one needs to describe the complex flow field and mixing that occurs simultaneously with the chemical reactions. The subsection that follows provides an illustrative example (Oh et al., 1997), and it focuses on the vessel-type reactor in Figure 4.5.4.

The flow field in the vertical vessel-type reactor can be described by the set of governing differential mass, momentum, and energy equations. These equations account for the occurrence of a single overall chemical reaction along with all of the participating physical processes. The numerical solution of the governing partial differential equations begins with discretization of the field into a collection of control volumes. The differential equations can be approximated by a set of algebraic equations on this collection, which can then be solved to produce a set of discrete values that approximate the solution of the partial differential system over the field. In this particular study, the algebraic equation system was solved by a semi-implicit iterative scheme that starts from an initial guess and converges to a solution after performing a sufficient number of iterations. The numerical techniques described thus far are available from several commercial computational fluid dynamics software packages (e.g., Fluent, Inc., 1998).

Turbulence affects the flow calculations via the effective viscosity. The turbulent viscosity was calculated in this study using the renormalization group turbulence model.

Calculations were performed using a single-step chemical reaction model that was either diffusion controlled or kinetically controlled. For the kinetically controlled model, an Arrhenius expression was used to calculate the reaction rate, and for the diffusion-controlled model, the turbulence levels were used. It was assumed that the lesser of the two rates controls the reaction.

Having outlined the mathematics involved in simulating the physical and chemical phenomena in a vessel-type SCWO reactor, we now present some representative results. The feed fluids are introduced vertically downward into the reactor. The reaction products, (CO_2 and water), exit the upper portion of the reactor. This flow configuration gives the recirculation flow pattern shown in Figure 4.5.6. The top of the vessel is at the left of the figure and the bottom is at the right.

The results from the numerical calculations show a large recirculation pattern caused by jet entrainment from the fluid exiting the nozzle and the reaction products exiting at the top portion of the reactor. The feed fluids are oxidized downstream of the nozzle as heat is released by the exothermic chemical reaction initiated by the preheated air in the flow domain. The reaction products do not penetrate toward the bottom portion of the reactor because of buoyancy effects; the density of the reaction products is much less than that of the cold water injected at the bottom to maintain the brine pool. The recirculation flow pattern is important to reactor performance. This flow has added heat from the reaction, and its entrainment serves to preheat the incoming feeds. The volume occupied by the recirculation causes a significant reduction in the minimum flow residence time. Also, this circu-

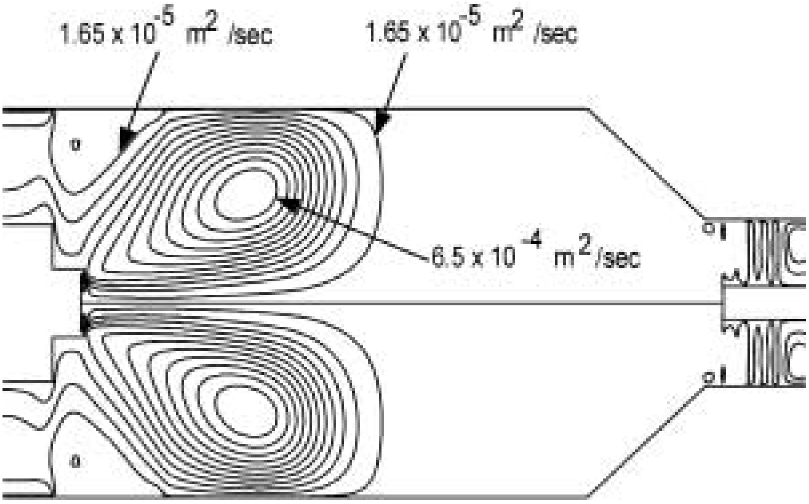

FIGURE 4.5.6 Predicted stream functions in the vertical vessel reactor. (From Oh, C.H., 1997. Numerical analysis and data comparison of a supercritical water oxidation reactor, *AIChE J.*, 43, 1627–1636. Reproduced with permission of the American Institute of Chemical Engineers. Copyright © 1997 AIChE. All rights reserved.)

lation flow entrains small salt particles and directs them toward the nozzle tip where they can be deposited due to low temperatures on the nozzle tip. The existence of this salt deposit was verified by General Atomics during its tests.

Because of the strong thermal coupling with the fluid properties and chemical kinetics, accurate temperature calculations are very important. Strong thermal gradients are found near the nozzle where the two inlet streams mix and react. The sharp temperature increase leads to significant changes in fluid properties. Due to the complexity of the SCWO reactor and limited instrumentation in the high-pressure system, General Atomics fluid-temperature measurements are confined to temperatures near the wall. Figure 4.5.7 shows the predicted fluid-temperature distribution along the reactor vessel wall and General Atomics measured fluid temperatures at those locations.

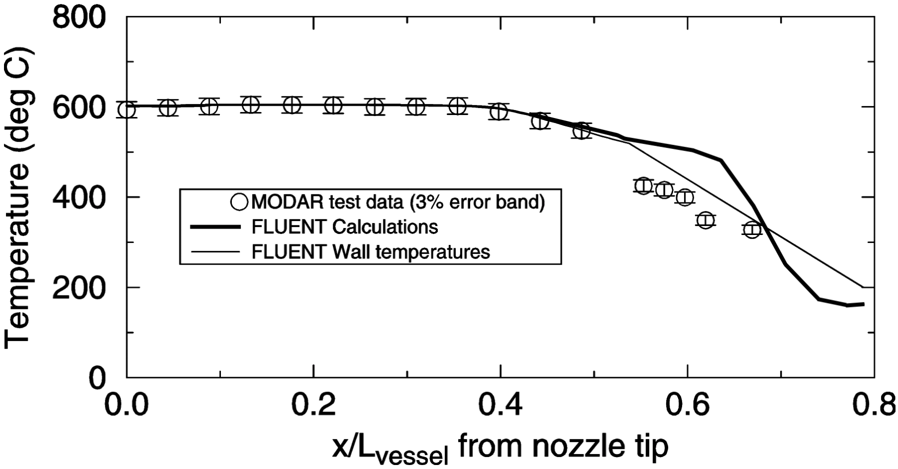

FIGURE 4.5.7 Comparison of experimental fluid temperatures with predicted ones. (From Oh, C.H., 1997. Numerical analysis and data comparison of a supercritical water oxidation reactor, *AIChE J.*, 43, 1627–1636. Reproduced with permission of the American Institute of Chemical Engineers. Copyright © 1997 AIChE. All rights reserved.)

As noted, fluid temperatures are uniform in the upper half of the reactor outside the reaction zone at a value of 605°C. The temperatures decrease relatively linearly as the brine pool is approached. As shown in Figure 4.5.7, there is good agreement in the region of the insulated upper region; this is partially due to the fact that the core water flow and inlet temperatures were adjusted to match the calculated fluid temperatures with measured temperatures.

To summarize, the current SCWO vessel-type reactor model (Oh et al., 1997) has been validated by comparison with experimental measurements. This validated computational fluid dynamics model shows great promise in calculating the detailed temperatures and flow patterns, including particle trajectory to help understand the salt deposit distribution. Therefore, it is clear that computational fluid dynamics can be useful to design the SCWO reactor and scale-up from a pilot system to a commercial one.

Reaction Kinetics and Mechanisms

Previous research into the reactions and kinetics associated with supercritical water oxidation has been reviewed (Tester et al., 1993; Savage et al., 1995; Savage, 1999). The work generally fits into one of three main areas. The first reports were feasibility studies that demonstrated the efficacy of the technology for diverse applications. Studies of this type typically reported the destruction efficiencies achieved for specific wastes or specific compounds under a specific set of reaction conditions. As such, the information is very specific to the compounds and conditions used. A second class of studies on the kinetics of supercritical oxidation has focused on the oxidation kinetics and mechanisms of very simple compounds such as CO, CH_4, and H_2. These studies are of little value from an environmental engineering perspective because such simple compounds are not important components of a real waste stream. Such studies are of great value from a more fundamental perspective, however, because they provide a means to test and validate kinetics models based on the governing mechanism. To focus on the reaction mechanism is an attractive approach because a model based on this fundamental chemistry can be used with confidence even for reaction conditions much different from those explored experimentally. Unfortunately, the mechanistic models developed thus far have been for simple compounds, and they have rarely been capable of quantitatively predicting all of the experimental observations. The final class of studies on the kinetics of supercritical oxidation are those that reported empirical global rate laws and reaction pathways for the oxidation of model pollutants. These rate laws and reaction pathway models are useful for engineering purposes, provided one remains within the experimental parameter space originally investigated. The information available for supercritical oxidation of organic pollutants includes global rate laws for the kinetics of reactant disappearance and for CO_2 evolution, quantitative models of the reaction network that give the yields of the by-products and intermediates formed from supercritical oxidation, and postulated reaction mechanisms for supercritical oxidation of phenol.

In addition to the work on homogeneous supercritical water oxidation outlined above, there is a growing literature on the complete oxidation of organic compounds via heterogeneously catalyzed reactions in supercritical water. Transition metal oxides are popular catalysts, as are noble metals. The economics of catalytic supercritical water oxidation have also been assessed (although not in detail) and found to be superior to conventional homogeneous SCWO for the specific cases considered. More engineering work and more detailed economic analysis are required, however, before definitive statements can be made regarding the process economics.

SCWO Kinetics of Individual Compounds

Essentially all of the reports of SCWO kinetics research with individual compounds often present in real wastes give either destruction efficiencies at a specific set of conditions or empirical global rate laws and global reaction pathways under a specific range of operating conditions. Model pollutants for which complete global rate laws (i.e., reaction orders, Arrhenius parameters) have been experimentally established are limited to a small number of compounds that include acetic acid, phenol, chlorophenols, 2-methylphenol, pyridine, acetamide, and ammonia. Experimental data has been reported for other compounds and analyzed using assumed reaction orders, but complete rate laws were not firmly established.

Additionally, complete rate laws are available for methane, methanol, hydrogen, and carbon monoxide, but these are not model pollutants that represent those likely to be found in aqueous waste streams to be treated by SCWO.

Power-law rate expressions are typically used, and the Arrhenius parameters and reaction orders are determined by fitting the proposed rate equation to experimental data. These rate laws, being empirical, have limited predictive ability outside the range of operating conditions used to determine their parameters. For example, a global rate law developed for SCWO of methane at 550 to 600°C and an initial concentration of about 10^{-3} *M* failed to predict the kinetics measured for methane SCWO around 400°C and at about 10^{-1} *M*. Clearly, kinetics models with predictive ability would be desirable, and this fact has motivated work with mechanism-based models, which have predictive capabilities. It is also noteworthy, however, that combining the two data sets for methane SCWO led to an empirical global rate equation that did describe the SCWO kinetics over the wide range of temperatures and concentrations covered in the two sets of experiments. Therefore, the utility of global rate laws increases as the range of experimental conditions used to determine the rate law parameters broadens.

The information available from most global rate laws is limited in that the rate laws give only the kinetics of reactant disappearance and CO_2 evolution for a few real pollutants. Aside from reports on phenol oxidation, there are no phenomenological models with experimentally determined Arrhenius parameters and reaction orders that give the yields of the by-products and intermediates formed from SCWO of real pollutants over a range of operating conditions. This is an important gap in the literature because the identities of by-products and their formation and destruction rates are essential pieces of information for the evaluation of a waste treatment technology. One must be certain that hazardous by-products of incomplete oxidation are not emitted to the environment in such concentrations that they pose an environmental risk.

Mechanism-Based Models for SCWO

None of the published research work with actual pollutants has yet included an accurate, predictive, mechanism-based kinetics model. Some predictive mechanistic models have been reported for the SCWO of very simple compounds such as CO, CH_4, and H_2. These models were developed by adapting gas-phase combustion mechanisms and kinetics to describe SCWO conditions. These models are predictive because no data from SCWO experiments is required for their development. Although the early models were rarely capable of quantitatively predicting the experimental observations, the most recent and more chemically sound models for CH_4, CO, and H_2 oxidation are very promising.

A philosophically different mechanism-based modeling approach has been reported for the oxidation of alcohols and acetic acid in high-temperature (300 to 400°C) water. Rather than using rate constants for the elementary steps measured in independent experiments, experimental SCWO data was used along with the postulated mechanism to regress values for the Evans-Polanyi parameters for the kinetics of each reaction family. This approach is not predictive because it uses the SCWO kinetics data to determine parameter values. Moreover, the applicability of this work to commercial SCWO units operating around 600°C is questionable because of the low temperatures employed in the experimental studies, and the strong possibility that the oxidation mechanism at commercial conditions is different from the mechanism at 300°C. Nevertheless, the modeling approach is an appealing one in that it is mechanism based, yet it contains a relatively small number of adjustable parameters.

Summary

Supercritical water oxidation technology has been demonstrated to be effective for treating hazardous and mixed wastes. For organic and hazardous wastes, these demonstrations have occurred at the bench, pilot plant, commercial scales. Mixed waste treatment, on the other hand, has been demonstrated at the bench scale. During SCWO treatment, organic carbon is converted to CO_2 and radioactive elements tend to concentrate in the solid phase. Recovering the solids from the effluent fluid provides a means to reduce significantly the volume of radioactive waste. By destroying the organic portion of a mixed waste, SCWO treatment removes components that would otherwise interfere with the treatment of the radioactive portion by methods such as vitrification.

Research and development work continues to be done to support the improvement of SCWO technology. Reaction kinetics, reactor modeling, corrosion, salt solubility, phase behavior, and thermodynamics are among the main research topics.

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4.6

Thermal Desorption

4.6.1 Thermal Conduction Heating for *In-Situ* Thermal Desorption of Soils

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Introduction

In situ thermal conduction heating is a soil remediation process in which heat and vacuum are applied simultaneously to subsurface soils. In the past decade, it has been applied at a number of sites, and the process has been described in several patents and publications.[1-11] In remediation applications, it is sometimes referred to as *in situ* thermal desorption (ISTD). ISTD has been used in various modes, including surface heating with blankets, subsurface heating with an array of vertical heater/vacuum wells, and *ex situ* blankets.

Radiation heat transport dominates near the heaters, which are operated at 800 to 900°C. However, thermal conduction accounts for most of the heating at greater distances into the soil.

As soil is heated, contaminants in the soil are vaporized or destroyed by a number of mechanisms, including (1) evaporation into the air stream, (2) steam distillation into the water vapor stream, (3) boiling, (4) oxidation, and (5) pyrolysis. The vaporized water, contaminants, and natural organic compounds are drawn by the vacuum into the blankets or wells in a direction countercurrent to the heat flow.

Compared to fluid injection processes, the conductive heating process is very uniform in its vertical and horizontal sweep, evenly heating the entire soil volume. Furthermore, transport of the vaporized contaminants is improved by the creation of permeability, which results from drying and shrinking of the soil. Flow paths are created even in tight silt and clay layers, allowing escape and capture of the vaporized contaminants. The combined effectiveness of both heat and vapor flow yields nearly 100% sweep efficiency, leaving no area untreated.

Furthermore, the contaminants in the heated soil are almost completely removed, with a displacement efficiency approaching 100%. This occurs because the entire soil zone can be heated to high temperatures for many days. (If needed, soil can be heated to temperatures greater than 500°C.) Laboratory treatability studies and field project experience have confirmed that a combination of high temperature and long time results in extremely high overall removal efficiency of even the high boiling point contaminants.

In practice, most of the contaminants are destroyed in the soil before reaching the surface. Contaminants that have not been destroyed *in situ* are removed from the produced vapor stream at the surface with an air pollution control system. The basic vapor treatment train consists of a thermal oxidizer, heat exchanger, carbon bed absorbers, and vacuum blowers. With this system, destruction and removal efficiencies (DREs) in excess of six nines (99.9999%) have been achieved in the stack effluent, with combined *in situ* and above-ground DREs as high as 99.9999998% having been demonstrated.

The thermal conduction processes have been studied in laboratory and full-scale field research tests at Shell's Gasmer Road Field Research Facility in Houston, Texas,[1,5,8] and at General Electric's Corporate Research and Development Center in Schenectady, New York.[2,3] Both thermal wells and thermal blankets have been demonstrated to be highly effective in removing from soils a wide variety of low and high boiling point hydrocarbons, PCBs, pesticides, and chlorinated solvents. ISTD processes have been applied commercially at several contaminated sites by TerraTherm Environmental Services, Inc. (TESI).[4,6,7,9-11,19] The operations were fast, clean, quiet, and odorless and caused little disruption of adjoining neighborhoods. In every case, the projects were successfully completed, and the residual contaminants were well below the remediation goals.

In January 2000, the Thermal Conduction Technology was donated by Shell Oil Company to The Center for Petroleum and Geosystems Engineering at The University of Texas in Austin. The commercial license has been granted to TerraTherm, LLC.[12]

Description of the Process

The thermal conduction process can be used to heat soil for either *in situ* or *ex situ* remediation. In either application, it can be carried out on large volumes of contaminated materials in a single batch. The heat is injected either from areal surface blankets or from vertical or horizontal wells (see Figure 4.6.1.1). Thermal blankets are effective for surficial contamination down to about 3 ft, and thermal wells can be placed to virtually any depth. The fundamental processes, including heat flow, fluid flow, phase behavior, and chemical reactions, are similar for each method. In each case, heat is applied to a soil from a high-temperature surface in contact with the soil, so that radiation heat transfer is effective near the heater, and thermal conduction and convection occur in the bulk of the soil volume. Thermal conduction accounts for over 80% of the heat transfer. A significant feature of the process is the creation of a zone of very high temperature (>500°C), which causes destruction of many contaminants before they exit the soil.

Thermal Blankets

Surface heating and vacuum extraction as an *in situ* process for removing contaminants from surface and near-surface soils is achieved by evacuating the soil under a flexible, impermeable sheet and heating the soil surface up to as much as 900°C with a relatively flat electric blanket heater (see Figure 4.6.1.2). In commercial field application, thermal blanket modules (each 8 × 20 × 1 ft) are configured in groups to cover part or all of a site. Each module is a stainless steel box that contains (1) heating elements that are spaced about 3 in. apart in a furnace belt, and (2) a layer of vermiculite insulation. An impermeable, flexible sheet covers a group of modules and serves as the vapor seal. Modules contain vapor ports that are connected by a manifold system to the process trailer, where unreacted contaminants are oxidized or absorbed from the vapor stream. Each heat treatment of the soil requires 2 to 10 days, depending on the desired depth of treatment, water content of the soil, and other factors. With average soil conditions, about 500 watts/square foot (W/ft^2) of surface can be injected initially, declining to about 300 W/ft^2 after several weeks of heating.

The heat flows downward by radiation and thermal conduction, and the consequent increase in soil temperature results in removal of contaminants from the soil by a number of mechanisms, including boiling, evaporation, steam distillation, pyrolysis, oxidation, and other chemical reactions. Contaminant vapors or volatile decomposition products are convected by the vacuum to the surface, where they are collected into the vapor treatment facility. At remediation sites where a large amount of water vapor is produced, it is sometimes preferable to maintain 100% vapor phase throughout the vacuum treatment system. In other applications, it may be more efficient to trap liquids in condensers and treat a smaller stream of vapors. When a flexible vapor seal is used rather than a rigid module box, the differential pressure between the atmosphere above the flexible sheet and the vacuum under the sheet presses the

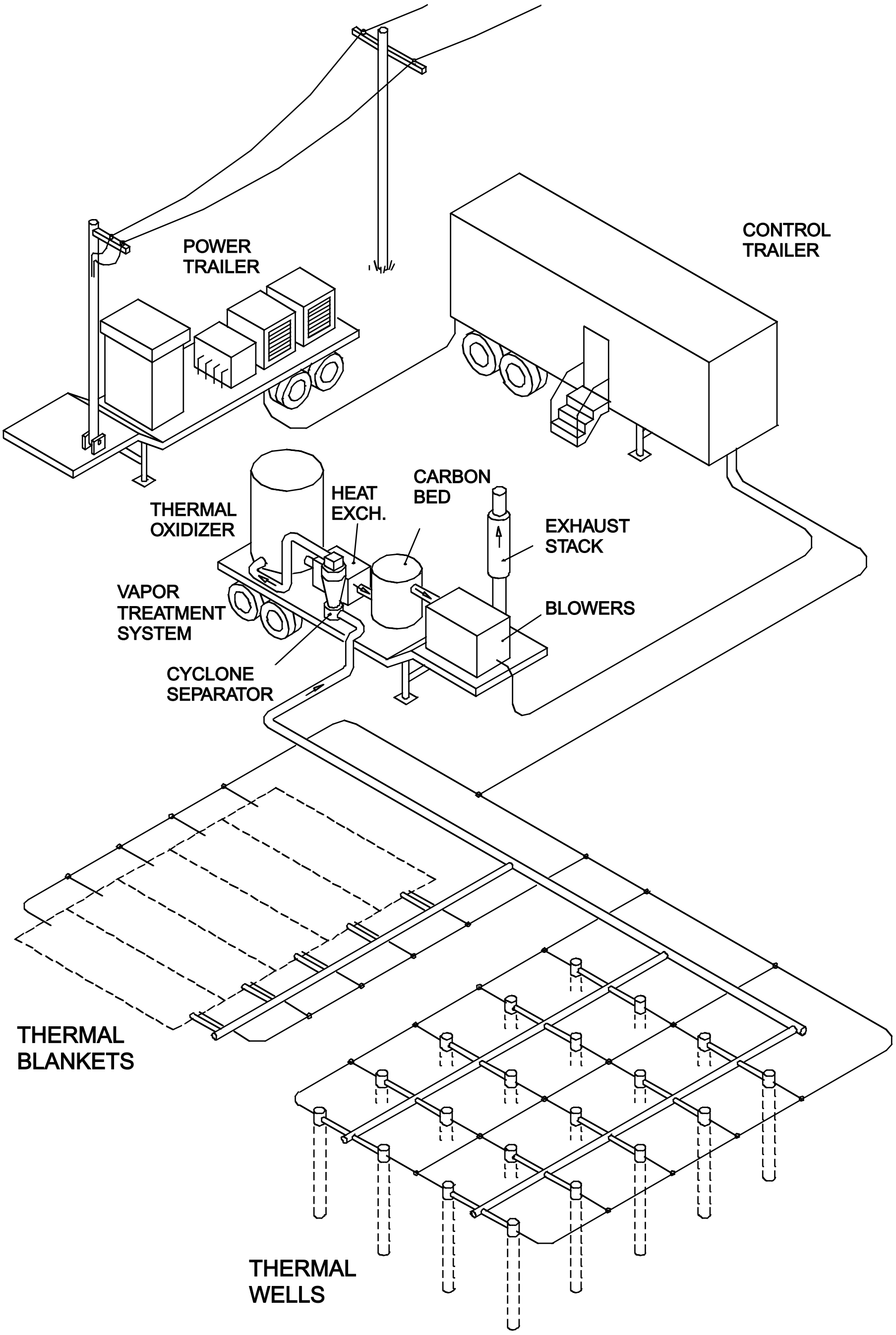

FIGURE 4.6.1.1 Thermal conduction heating with wells and blankets.

sheet, insulation, and heater firmly against the soil. This improves conformance with the surface and increases thermal contact of the heater with the soil. The impermeable sheet may extend areally beyond the surface heater. In this peripheral region, the vacuum seals the sheet directly against the soil. Thus, air, moisture, and contaminants in the soil below the heater are pulled almost vertically to the surface. Atmospheric air, which enters the soil from outside the impermeable sheet, is also produced. Entry of outside air into the central vacuum system is restricted, however, because the air must travel some distance

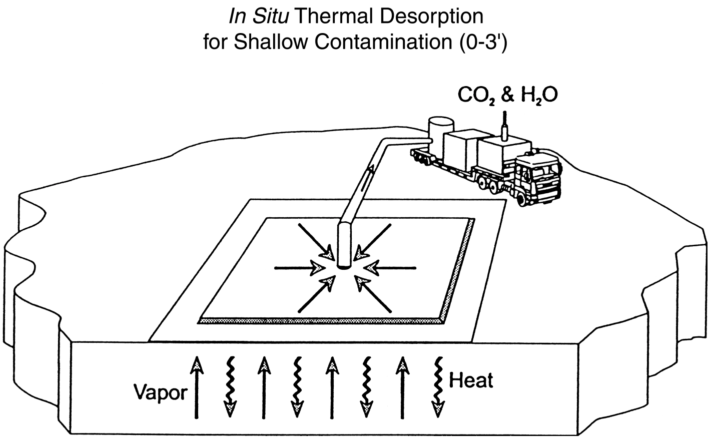

FIGURE 4.6.1.2 *In situ* thermal desorption for shallow contamination (0 to 3 ft).

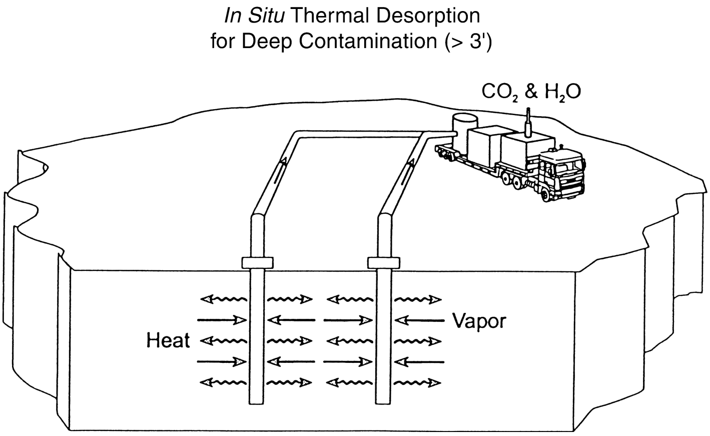

FIGURE 4.6.1.3 *In situ* thermal desorption for deep contamination (>3 ft).

horizontally through the soil. The flow of air through the high-temperature soil serves to evaporate and oxidize contaminants *in situ*, thereby supplementing the boiling and steam distillation mechanisms.

Thermal Wells

For soil contamination at depths greater than 3 ft, heating with surface blankets is ineffective and thermal wells are needed to attain high temperatures in the soil. The principle of *in situ* thermal desorption with heater/suction wells is shown in Figure 4.6.1.3. A standard arrangement is a regularly spaced array of heaters emplaced in screened holes in the soil. The space between wells at the surface is covered with an impermeable sheet that enables a vacuum to be imposed by the wells on the entire targeted soil region. In most applications to date, vertical wells are used; however, slanted or horizontal wells offer attractive alternatives for remediation under buildings, foundations, roads, or other inaccessible areas.

The vertical wells are installed on a triangular grid, typically with a spacing of 5 to 7 ft between wells. Several considerations affect the choice of spacing. First, the well spacing should not exceed the thickness of the heated interval, to avoid excessive heating above and below the target interval. Second, the well spacing, not the length of heated interval, determines the time required to heat the formation. The time required for a project is proportional to the square of the spacing because each well has a nearly fixed power input, but must heat the soil in the hexagonal element of symmetry surrounding it. Third, the amount of power needed to heat the soil is determined by the soil type and moisture content. Fourth,

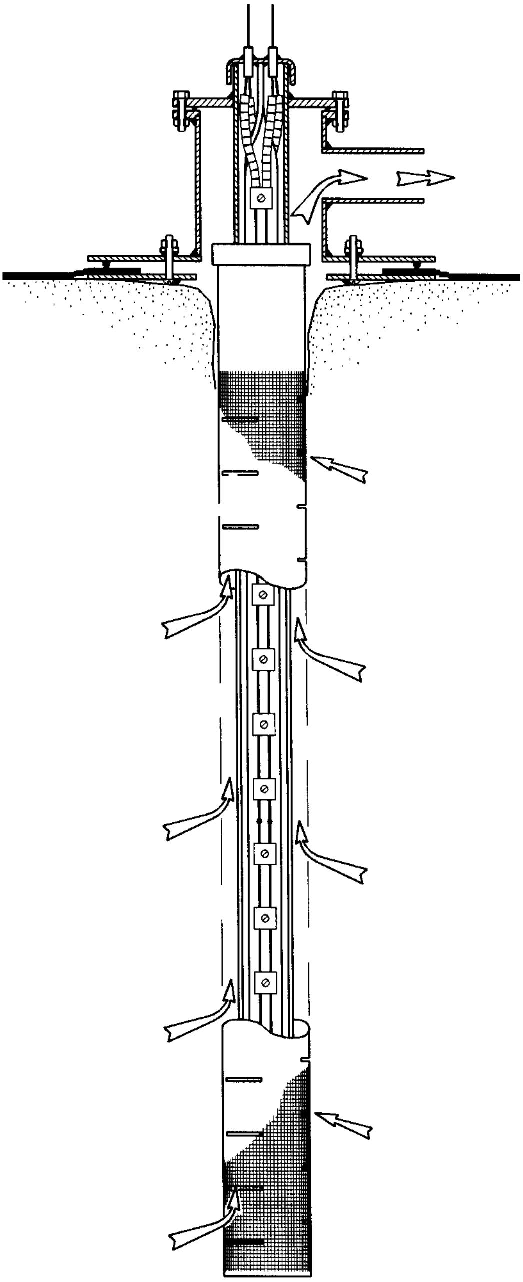

FIGURE 4.6.1.4 Heater vacuum well.

the type of contaminant to be removed determines the temperature to which the soil must be heated. Using a well spacing of 5 ft, soil can be heated to >500°C in 30 to 40 days. Well spacing for thick contaminated zones can be considerably greater if lower temperatures are needed or if longer times are permitted

The heater/vacuum well illustrated in Figure 4.6.1.4 is typically configured in a 6-in. diameter hole with (1) a 10-20 mesh sand-filled annulus between the soil face and the well casing/liner, (2) a 4-in. or 4.5-in. OD stainless steel slotted (0.032 in. × 2 in.) and screened (40 mesh) liner, (3) a 2.5-in. OD pipe sealed at the bottom to provide a "heater can" to isolate the heater element from the product stream, and (4) Nichrome wire heater elements threaded through ceramic insulators. The heaters normally extend 2 ft above and 2 ft below the contaminated layer of soil to apply full temperature to the targeted interval. In addition, to compensate for heat losses at the upper and lower boundaries, these 2-ft intervals are designed to deliver about 25% more power per linear foot than the rest of the heater. This can be accomplished by adding an extra parallel heater or changing the Nichrome wire diameter (e.g., from 0.128 to 0.114 in.). At the surface, the well casing is cemented in the soil and is also sealed to the heater can, thereby providing an annular space in which to apply a vacuum to the well. Thus, the heater/vacuum well provides a means of injecting heat into the soil and countercurrently collecting vapors into the well.

Wells may be completed either as heater/vacuum wells or heater-only wells. Heater-only wells are simply configured with a casing pipe that serves as the "heater can," with the heater elements inside. Because the heater wells do not have countercurrent flow of vapor, they can inject more heat into the soil than the heater/vacuum wells.

One useful triangular array forms a series of hexagonal patterns, with a combination vacuum/heater or production well in the center of each hexagon surrounded by six heater-only wells (see Figure 4.6.1.5). This arrangement of wells is permitted when the producing capacity of the single producer is sufficient to capture vapors generated by all of the associated heater wells.

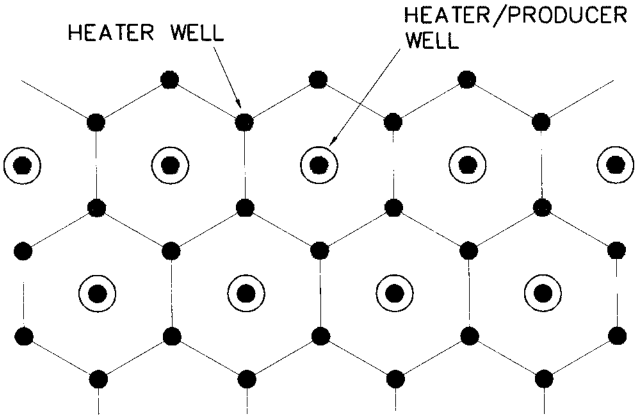

FIGURE 4.6.1.5 Hexagonal well patterns.

Electric heater wells were originally developed for use at depths up to 2000 ft for enhanced oil recovery. However, for ISTD remediation projects, the wells are usually less than 100 ft deep. Depth alone is not a limitation for application of ISTD; however, inflow of groundwater usually increases with depth. Where the recharge rate of groundwater into the site is greater than the boiling rate of the electric well heaters, the soil temperature cannot be raised above 100°C. To dry the soil and reach superheat temperatures in these cases, it will be necessary to control the water influx with temporary bulkheads, freeze walls, or de-watering.

Before beginning heating in a remediation project, it is advisable to produce any liquids that can be pumped or drawn by vacuum from the screened wells. If the target layer is high in the vadose zone, or if the layer is a tight silt or clay, very little liquid will be produced. However, if there is active groundwater flow, it is essential to determine its extent before initiating heating. Groundwater can enter a remediation site from the edges, from the bottom, or from the top. Because horizontal permeability is almost always greater than vertical permeability, the edge-water influx can be the most troublesome. Vertical inflow is usually impaired by even thin clay layers; however, because the area available to inflow is larger than that at the sides, it remains a concern. Inflow from the top can be prevented by proper drainage design of the impermeable sheet covering the area. Groundwater problems are often seasonal, and in those cases, the project should be scheduled to avoid the rainy season. It is more economical to lift out liquid water by pumping than by boiling and producing it as vapor because of (1) the cost of electrical energy to boil the water, and (2) the increased operating costs resulting from the longer time required to reach the process temperature in a wet soil.

Start-up of a remediation begins by imposing a vacuum on all of the screened wells with the vacuum blower. The vapor flow rate will be determined by the soil permeabilities and geometrical factors. The object of imposing the vacuum during heating is the capture of vapors that are generated and of any air that is drawn through the soil. A rule of thumb is that one standard cubic foot of vapor flow per minute is needed for every kilowatt of power injected. Common well headers and subsurface probes can be monitored to confirm that negative pressures are maintained on the heated soils throughout the remediation.

Thermocouples can be placed within the heater wells to control the power input and to monitor the performance of the heating elements. If well controllers are used, a high rate of electrical power is injected until the heater elements reach their maximum operating temperature. As the soil around the wells is heated, the maximum allowable power input slowly decreases. At heater temperatures of 1400 to 1600°F, the wells initially can inject about 500 W/ft, declining to about 300 W/ft over a period of weeks. Another mode of heating is to set the well heaters at the lower limit of power input so that they will not exceed the maximum allowable temperature during the life of the project. Designs for injecting heat without well temperature control are simpler to install and operate, but require somewhat longer times for heating.

The progress of the heat-up of the soil between the heater wells is monitored with thermocouple wells. For triangular patterns, the thermocouples are generally located at the centroid of the triangular area. This location is the most distant from the heaters; consequently, it is expected to be the coldest spot. For sites as deep as 10 ft, thermocouple wells can usually be installed by driving a 1-in. OD, stainless-steel pipe into the soil. The pipes are sealed at the bottom and open to the atmosphere at the top, allowing temperature logging with traveling thermocouples during the heating operations.

Heating at the thermal wells is continued until the target temperatures (based on contaminant properties) are reached at the coldest point between the wells. The temperature history of the soil consists of three periods: heat-up, boiling water, and superheating, as shown in Figure 4.6.1.6. During the first period, the soil minerals and fluids (mainly water) are heated to the boiling point of water. This heat-up is fairly rapid, especially if the soil is fairly dry, because the heat capacities of silicate and carbonate minerals are small. During the second period, the temperature stays at the boiling point until all the pore water is boiled off. The duration of this phase depends on the amount of pore water to be boiled; if additional groundwater flows into the target zone during heating, the boiling time is extended even further. When all the water has been vaporized, the dry soil can be superheated. During this third period, the soil temperature rise is even more rapid than during the first period, because only the soil minerals remain to be heated.

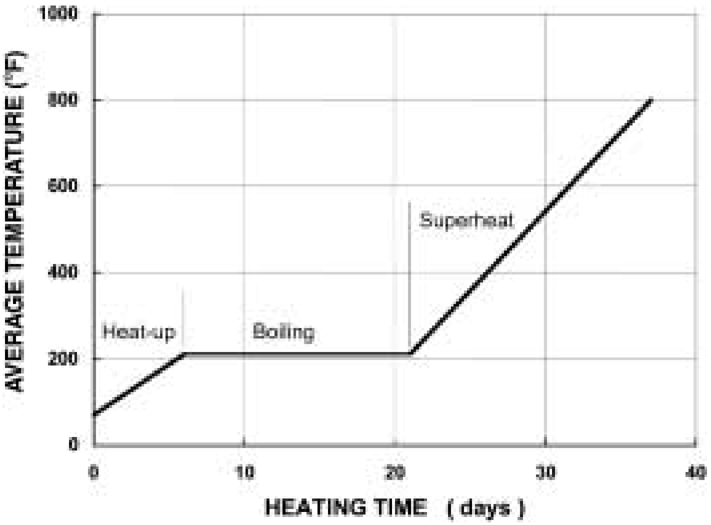

FIGURE 4.6.1.6 Theoretical temperature rise in soil.

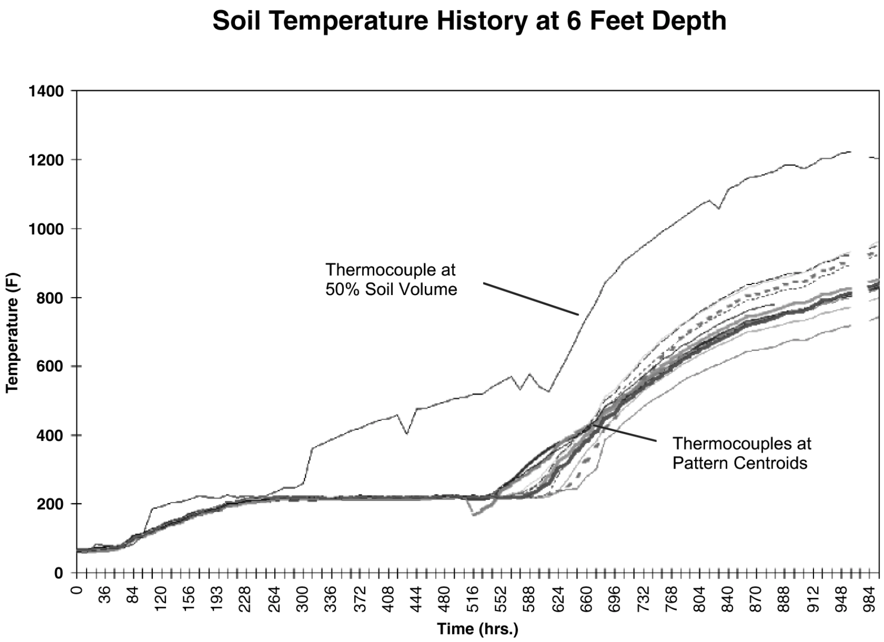

FIGURE 4.6.1.7 Temperature rise in MEW triangular patterns.

Figure 4.6.1.7 shows the actual temperature history of soils at 6-ft depth measured during an ISTD demonstration at the Missouri Electric Works Superfund site in Cape Girardeau, Missouri. The 12 thermocouples shown in Figure 4.6.1.7 were located at the centroids of 12 adjoining triangles with a 5-ft well spacing. The first (heat-up) phase lasted about 250 hr; the second (boiling) phase ended between 560 and 630 hr, with the center and adjoining triangles drying first and the outer triangles later. During the third (superheating) phase, soil temperatures rose rapidly until the heaters were turned off on day 42 (1000 hr). Maximum temperatures over 1000°F were reached at the centers of the triangles, and about 50% of the volume was over 1100°F.

As soil temperatures increase, water, volatile organic compounds (VOCs), semivolatile organic compounds (SVOCs), PCBs, petroleum aromatic hydrocarbons (PAHs), and volatile metals contained in the soil matrix are volatilized by the dynamic heat front and drawn to the wells by the vacuum. If air is present, the contaminants are rapidly oxidized in the hot soil near the heating elements where temperatures typically exceed 1000°F. Remaining contaminants in the product stream (which is composed primarily of air, water, and oxidation products) are drawn through the manifold system to the process trailer for further treatment.

Ex Situ Remediation Using Thermal Conduction Heating

At many sites, contaminated soil has already been excavated or stockpiled. At other sites, small amounts of widely scattered contaminants can be more easily gathered to a single location for treatment rather than dealt with separately in the ground. In these cases, it is more effective to modify the ISTD system and use thermal conduction heating at the surface.

Unlike other *ex situ* processes that are carried out in reactors where residence times are only a few seconds or minutes, the modified *in situ* thermal conduction heating allows treatment times ranging from hours to many days. These longer times are permitted because large volumes can be treated at one time. Thus, heating the interior of large, metallic objects, lumps of soil, concrete, etc., which is a particularly troublesome problem for batch reactors, is easily accomplished by ISTD. Furthermore, irregularly shaped metal objects, vessels, or pipes do not require metal shredding, as is required in conventional thermal desorption reactors or incinerators. Because the permeability of the soil is increased by the high-temperature drying, contaminants can be efficiently removed from even tight clays.

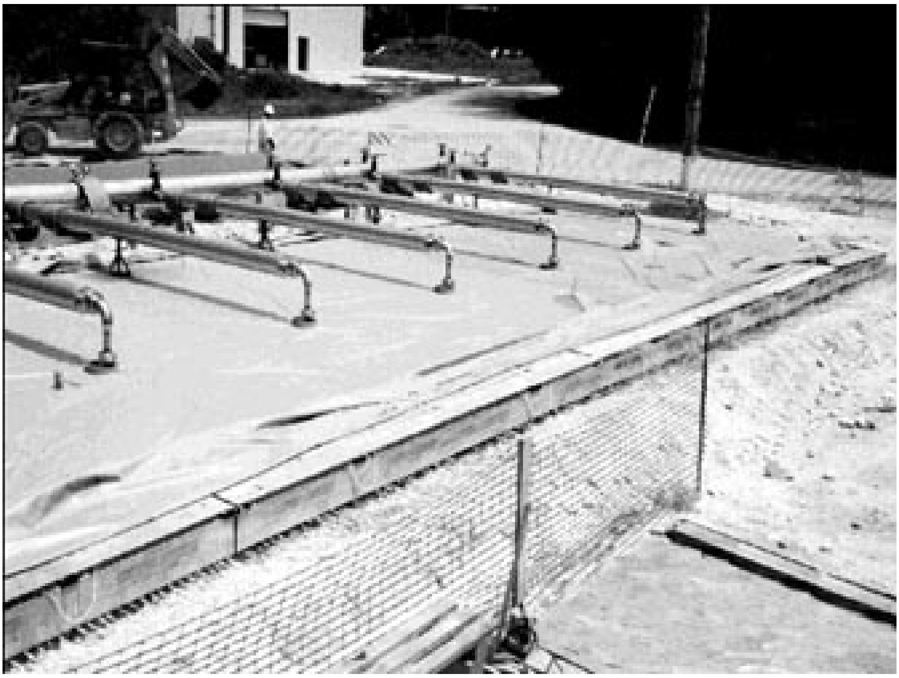

FIGURE 4.6.1.8 *Ex situ* soil remediation, Tanapag, Saipan.

Another advantage of applying thermal conduction heating at the surface is the ease of positioning the heaters in the dirt pile. Heaters can be installed as the soil is being accumulated so that the heating times can be minimized. For example, blanket heaters can be placed both at the top and at the bottom of a layer, or horizontal wells can be placed in shallow trenches.

The flexibility of the ISTD thermal well and thermal blanket system allows it to be adapted to many types of *ex situ* operations. It has been used in a remote location, where the above-ground process equipment was skid-mounted and shipped as a complete unit. Figure 4.6.1.1.8 shows an *ex situ* remediation on the island of Saipan in the Northern Mariana Islands.

ISTD is essentially a "closed-loop" system that eliminates the negative aspects of *ex situ* operations, including the noise, dust, fumes, odors, and material sorting that are inherent in ex situ activities. Most on-site, batch-based systems aggravate these material handling problems due to the limitations on the amount that can be treated at one time, requiring constant loading and unloading, as well as increased sampling activities.

Potential Applications for Thermal Conduction Heating

Because thermal conduction is such a simple means of evenly heating the soil, it offers a variety of uses in soil remediation. Some of these applications are:

1. In its simplest form, widely spaced electric heaters could be driven into the ground to warm the soil slowly over a period of months and thereby optimize temperature for bioremediation of degradable contaminants. Warming to 30 or 40°C would be especially helpful in cold regions where biological activity is low.
2. In the next level of complexity, driven heaters can be used in conjunction with soil vapor extraction in several different modes:
   a. Thermally assisted soil vapor extraction (TSVE) can shorten project life and provide complete clean-up in conventional SVE projects. For example, with conventional vapor extraction wells at service stations, dry-cleaning shops, or industrial sites contaminated with chlorinated solvents

    or fuels, heat injection from driven heaters will accelerate vaporization of contaminants and result in completion of the projects in weeks rather than years.
    b. In another version, the conventional vapor extraction wells can also be heated to prevent condensation.
    c. Thermally assisted, dual-phase extraction (TDPE) is still another application in which contaminants are extracted from soil in both liquid and vapor phases.
3. In the conventional use of thermal conduction heating, both heat and vacuum are applied in the manner described throughout this chapter section to volatilize and destroy or recover contaminants in the vapor phase. Thermal vacuum heating has the potential of complete containment and complete recovery of the contaminants. A wide variety of materials can be treated.
    a. Volatile organic compounds, including gasoline and chlorinated solvents such as trichloroethene (TCE) and tetrachloroethene (PCE), can be removed at medium temperatures (100 to 200°C). Semi-volatile compounds, such as PCBs, dioxins, and MGP wastes, will require higher temperatures (200 to 400°C).
    b. Although not field tested, inorganic contaminants such as mercury, arsenic, antimony, and cadmium, and their compounds are also potential targets for removal or conversion to other less volatile or less water-soluble compounds.
    c. Mixed wastes (those containing a combination of radionuclides and chlorinated hydrocarbons, carcinogens, etc.) present special challenges, but the thermal conduction/vacuum process is effective in removal of the volatile organic components and may reduce the water solubility of the radionuclides.
    d. Contaminants heavier than water, also referred to as dense, nonaqueous-phase liquids (DNAPLs), when they have migrated below the water table into aquifers, may also be amenable to recovery by thermal conduction heating. If the water influx precludes complete vaporization, the DNAPL may be at least partly removed by steam distillation or by reduction in the liquid-phase viscosity.
4. In deep soil contamination, it may be acceptable to carry out thermal conduction processes under a positive pressure rather than with a vacuum. If an active water drive provides containment, the heating and steam distillation could be carried out without significant migration of the contaminant. This method might be visualized as a controlled steam drive, with perfect sweep, not limited by areal or vertical heterogenieties of the soil.

Costs

The cost of thermal conduction remediation, using the applications described above, will vary greatly, depending on the contaminant type and the level of remediation required. Factors that affect costs per ton of soil include the size of the project site, cost of electricity, control of water recharge, depth of contamination, and air discharge limits. In almost all cases, simply injecting heat with electric heaters will be cost competitive with other *in situ* thermal processes.

The conventional ISTD thermal/vacuum process was designed with the assumption that contaminants should be removed from sites, not just dug up and put somewhere else, or capped with a temporary seal. A further assumption was that acceptable levels of contaminants remaining after treatment must be extremely low to meet environmental regulatory requirements. Furthermore, there were rigid constraints to avoid scattering the contaminants or other unwanted effects. With these ground rules, it was concluded that remediation by full, high-temperature *in situ* thermal conduction heating with vacuum and complex vapor treatment was the only process that would meet all of these requirements. TerraTherm has estimated that the cost of such a complete process would be in the range of $50 to $250 per ton of soil. Additional improvements and efficiencies in the process are expected to reduce these costs.

Process and Control Equipment

Process and control trailers are connected to the heating modules and the vapor collection manifold to deliver and control electrical energy to the heating elements contained within the modules and to treat the vapor stream before venting to the atmosphere. Process trailer components include a cyclonic particle separator, an HCl scrubber, a thermal oxidizer, an air-to-vapor heat exchanger, carbon canisters, discharge blowers, a backup generator, a control cabin, a thermal monitoring system, and a continuous emission monitoring system (CEM). See Figures 4.6.1.9 and 4.6.1.10.

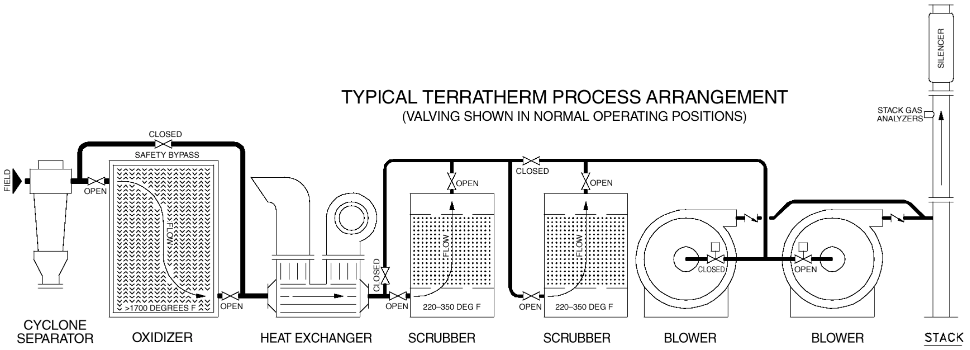

FIGURE 4.6.1.9 Schematic of process treatment equipment.

FIGURE 4.6.1.10 MU 1800 process trailer.

Process Trailer Operations

Process gases removed from the heated soil (primary treatment) typically contain greatly reduced concentrations of original contaminants, oxidation products, water vapor, and atmospheric gases. For example, soil contaminated with chlorinated hydrocarbons will produce CO_2, H_2O, HCl, and small amounts of unreacted contaminant. If the soil naturally contains sufficient carbonates, HCl scrubbing may not be needed. The produced gas stream then receives its initial treatment on the process trailer in the flameless thermal oxidizer (secondary treatment). This operation generates conditions sufficient to reduce residual contamination concentrations in the recovered gas stream by four nines (99.99%) of destruction or more. When combined with oxidation processes occurring in the subsurface, over six nines (99.9999%)

destruction is typically achieved. A high-efficiency thermal oxidizer is not always necessary. For VOCs or nonchlorinated SVOCs, a regenerative thermal oxidizer capable of 95% DRE followed by adsorption on activated carbon often provides sufficient treatment of the recovered gas stream

Heat Exchanger and Carbon Beds

Effluent from the flameless thermal oxidizer passes through a cooler to reduce temperatures prior to carbon adsorption (tertiary treatment). Two carbon beds in series provide redundant adsorption of recovered process gases. When carbon bed adsorption is combined with *in situ* and thermal oxidizer treatment, over eight nines (99.999999%) destruction has been achieved. Process blowers maintain negative pressure on the soils being treated and pull the gas stream through the secondary and tertiary treatment processes on the trailer. This feature prevents uncontrolled atmospheric emissions, in that small leaks anywhere in the treatment train upstream of the vacuum blower will flow into the stream rather than escape to the atmosphere.

Air Emission Controls

The process vapor stream is monitored continuously. This continuous emission monitoring (CEM) utilizes an extractive sample probe and conditioning system. The sample stream is analyzed with a nondestructive infrared analyzer for CO and CO_2. O_2 is measured using a zirconium oxide detector, and total hydrocarbons (THC) are measured using a flame ionization detector. CEM data is collected electronically and displayed graphically. The data is stored using computer software and can be retrieved at any time.

Stack Emissions

Stack emissions are sampled during operations following EPA methods and procedures and analyzed to specific quality assurance and quality control criteria. Emission samples are collected from two sample points. The first is collected after secondary treatment at the post-oxidizer, pre-carbon position, and the second is collected downstream of the carbon beds (this second sample is representative of actual stack emissions).

Electrical Power Generator and Safety Controls

Once the soil has been heated, it is essential that a vacuum be maintained throughout the rest of the remediation. In the event of a power outage, emergency generators kick in to maintain power to the thermal oxidizer and blowers to ensure that gases are processed through the oxidizer and carbon beds. Heater power to the thermal blankets or wells is then automatically shut down to prevent the generation of additional gases.

Control System

The overall process system is controlled by a supervisory programmable logic controller (PLC) located within the control room of the trailer. A visual monitor displays the operating status of system components to the operator through a personal computer. An example of a visual display of the status of a project is shown in Figure 4.6.1.11. In addition to system control, the operator's computer provides extensive data logging and graphing capabilities. The temperatures of the blankets and wells are monitored continuously using Inconel-sheathed thermocouples. This information allows the operator to control blankets or wells individually, if desired. If blanket or well heaters exceed the set operating level, an alarm sounds and the specific blanket or well is shut down. Throughout the air treatment process, vapor stream temperatures are monitored and recorded, with vapor flow rates monitored continuously using inline analog meters. Vacuum pressure is measured continuously using Magnahelic gages, and the temperatures within the oxidizer are monitored continuously using thermocouples. In the event of thermocouple malfunction, the system identifies the defective component, which is then replaced or repaired. The flow rate of combustion air is monitored to ensure that excess oxygen is emitted by the oxidizer. Heat exchanger temperatures are monitored at the hot and cold sides of the stream and tied to the process control system. The temperature and circulation rate of the air in the exchanger are adjusted to control the temperature of the vapor stream feeding the carbon beds to ensure efficiency and safety.

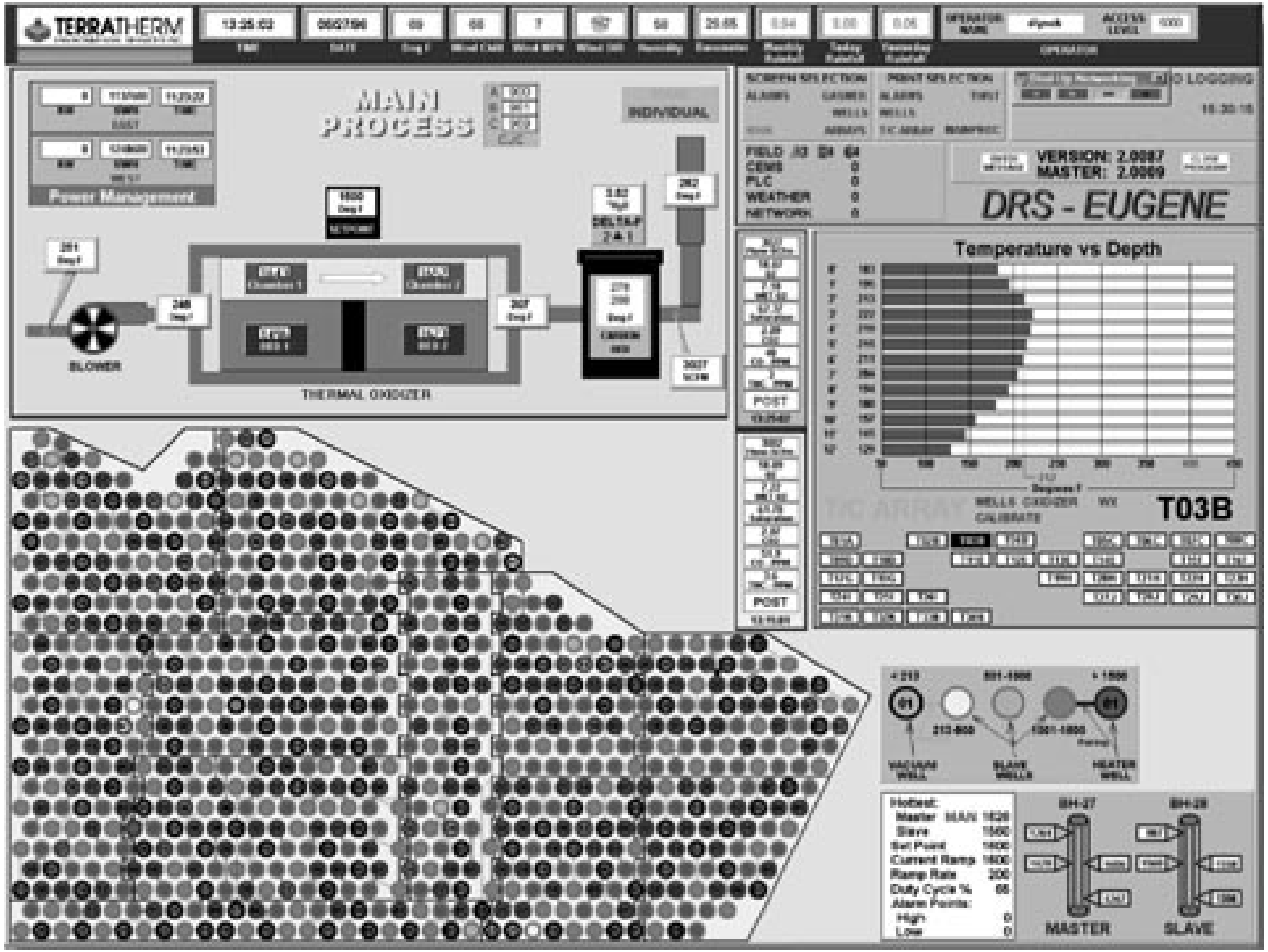

FIGURE 4.6.1.11 Interactive visual display, Eugene Project

FIGURE 4.6.1.11 Interactive visual display, Eugene project.

Removal Mechanisms

Heat Flow

Radiation. Heat flow mechanisms in thermal/vacuum soil remediation processes are a combination of radiation, conduction, and convection. Although conduction heating accounts for most of the heat flow in the soil, radiation is important in transferring heat from the heater elements to the containment sheet or pipe. Efficient radiation requires temperatures greater than 600°C, but has the advantage of instantaneous transfer across empty space. See Appendix 4.6.1.1, Equation (4.6.1.12). This characteristic can be utilized to spread heat evenly at the irregular soil surface under a thermal blanket or to increase the initial area to conductive flow into the soil around the thermal wells. In the latter case, a large-diameter casing allows better heat injectivity of the well.

Conduction. Because thermal conduction in soils is relatively slow acting, the application of heat can be closely controlled. Most remediation operations are carried out under transient heat flow conditions; that is, temperature at a given location changes with time. Because these changes occur very slowly, an operator can safely remediate soil near buildings or underground utilities. For example, thermal blankets have been placed less than a foot from foundations without overheating, and thermal wells, located inside buildings, have been used successfully a few feet from sewer or water lines.

Heat flow by conduction has been described mathematically, both for blankets (linear flow[13] downward into the soil) in Appendix Equations (4.6.1.5) and (4.6.1.6), and for wells (radial flow[14,15] outward from the well casing) in Appendix Equations (4.6.1.7- 4.6.1.10). These calculations predict a very fast temperature fall-off near the heat source, especially for radial flow from wells. For example, after a month of heating, a single heater well can scarcely raise the soil temperature to 500°F only 3 ft away (Figure 4.6.1.12). Fortunately, interwell temperatures reflect the superposition of thermal fronts from all of the heaters in the patterns (see Appendix Equation (4.6.1.11). This results in a temperature peak close to each well, but a more uniform temperature rise over the rest of the soil pattern. (See Figure A-3.) Interwell soil temperatures become even more uniform after long times of heating.

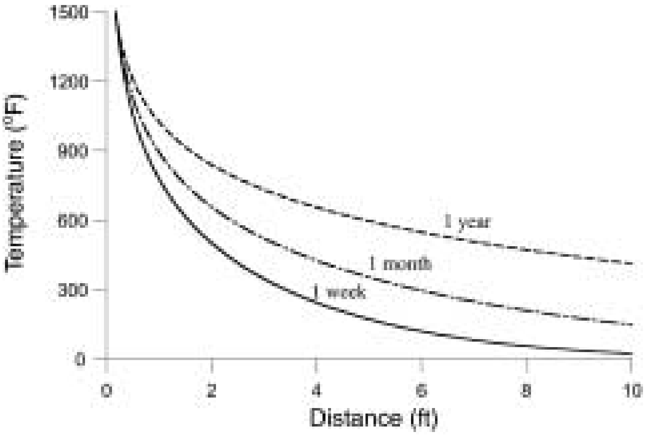

FIGURE 4.6.1.12 Heating times for a single well.

Initially, power input is held constant until the heater reaches its maximum temperature, usually in less than 1 day. If soil properties are uniform and constant, initial temperature changes can be approximated by the constant-power, line-source, exponential integral solution.[14,15] Thereafter, a constant heater temperature is maintained by decreasing the power to the heaters. Temperatures around a constant-temperature cylindrical source are described by the Bessel function solution.

Convection. As evidenced by the propagation of thermal fronts away from typical ISTD heat/vacuum sources when vapors are being drawn into the source, convection heat transfer is less than conduction heat transfer. An exception to this occurs when large amounts of groundwater or air enter the target soil from outside the heated region. Thermal diffusion-driven, high-temperature convection of vapors is another mechanism tending to disperse heat, smoothing the heat fronts.

In practice, in addition to the simple conduction/convection mechanisms discussed above, the actual temperature rise is also affected by the change in thermal conductivity of the soil as it dries and by latent enthalpy changes due to water evaporation and condensation. In addition, the temperature dependence of the thermal properties, and the effects of nonuniform geology, add complexity that is best understood with numerical simulators. Shell's numerical simulator for oil reservoirs (THERM) has been modified for environmental applications and was used to design the initial commercial projects. As actual field experience has been acquired, the need for detailed numerical simulations has lessened, and average soil properties and temperature can be used in the design of most projects. Details of the energy balance, which determines the heating time, are given in Appendix Equation (4.6.1.29).

Vaporization and Phase Behavior

Depending on the process temperature, several mechanisms can contribute to the vaporization of liquids and solids in thermal conduction soil remediation. Contaminants having boiling points ranging from that of benzene (B.P. 80°C) to that of dibenzo(a,h)anthracene (B.P. 524°C) have been successfully removed by the process. Vaporization mechanisms are closely related to vapor pressure, which increases regularly with temperature (see Figure 4.6.1.13.)

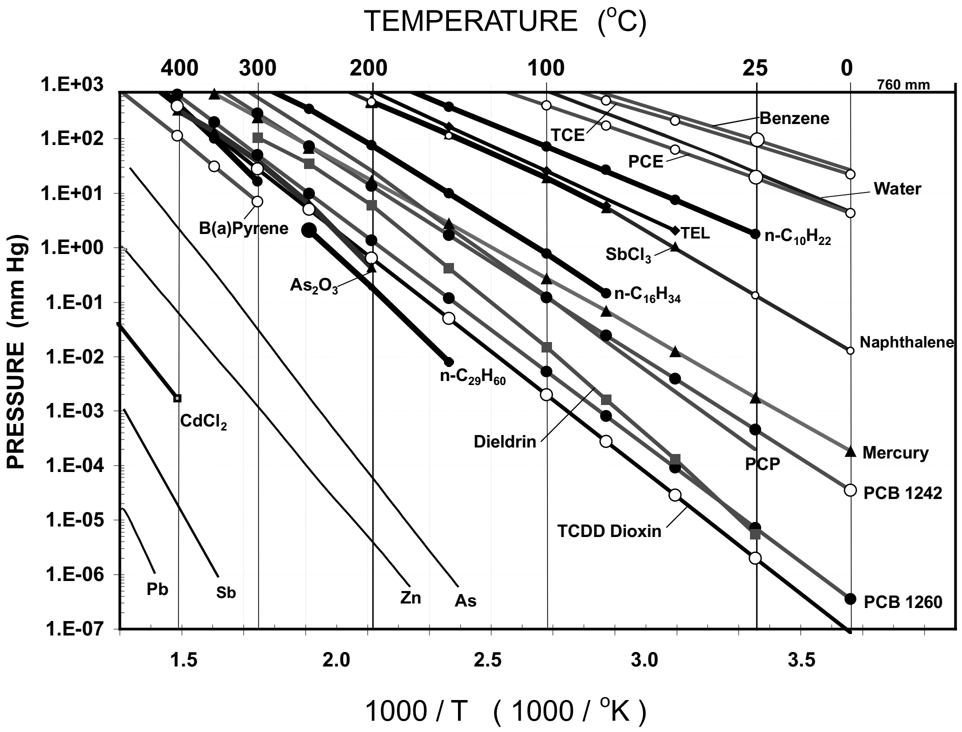

FIGURE 4.6.1.13 Vapor pressure of various contaminants.

Evaporation. If a flowing stream of air or water vapor is present, it is not necessary to raise the temperature to the boiling point of a compound in order to vaporize it. An increase in the vapor pressure increases the mole fraction of a component in the vapor phase, as approximated by Dalton's and Raoult's laws (see Equations (4.6.1.13) and (4.6.1.16)). For heavy, high-boiling-point compounds, an increase in vapor pressure to only a few millimeters of Hg pressure will result in hundreds of parts per million in the vapor phase (see Equation (4.6.1.15)). Thus, substances that are normally not considered volatile can be evaporated in a stream of air that is only mildly heated. Because the masses of flowing air and water are usually much larger than that of the contaminants in the ground, large amounts of even heavy contaminants can be removed in the vapor stream.

Steam Distillation. Water is almost always a major component of soils in the subsurface. As temperature is increased to the boiling point of water (100°C), steam distillation of immiscible compounds occurs. Steam is a more effective evaporant of heavy organic compounds than air because of its lower molecular weight (see Equation (4.6.1.18)). Furthermore, the higher temperature (and higher vapor pressure) of the contaminants provides a richer contaminant fraction in the vapor stream.

Boiling. Even if an evaporant such as air or water vapor is not present, increasing the temperature to 300°C results in vaporization of most organic compounds by simple boiling. At these higher temperatures, thermal diffusion is the only transport mechanism available after all of the lower-boiling connate compounds have been produced. Therefore, some convection of outside air or in-flow water vapor is useful in transporting the remaining high-boiling-point contaminants through the soil to the vacuum source.

Chemical Reactions. At the highest temperatures, oxidation and pyrolysis become important vaporization and destruction mechanisms. Products of chemical reactions - with the exception of coke - are more volatile than the original organic compounds.

In situ Transport of Contaminants

A critical requirement of any remediation process is the efficient transport and collection of the contaminants in the soil. Although contaminants can be vaporized by heating, potential gradients need to be provided and effective flow paths need to be created to transport the fluids out of the soil.

Vacuum Effects. Maintenance of a vacuum is an important feature of the thermal conduction process. The imposition of a vacuum in the heated region of a thermal conduction process not only provides a gradient for flow, but also offers other advantages. Negative pressure in the heated region prevents pressure-driven gradients from spreading the contaminants outside the treatment volume because the other physical flow mechanisms, such as capillarity and diffusion, also direct flow into the heated region. Imposing a vacuum on heater wells prevents the pressure rise that can occur near a heated well, thereby avoiding escape of vapors to the atmosphere.

The liquids in the soil are volatilized by the temperature increase and drawn into the heater/vacuum wells countercurrently to outward heat flow. This flow arrangement also exposes all of the flowing contaminants to high reaction rates in the high-temperature regions near the heater wells (see Equations (4.6.1.19)- (4.6.1.22). Flow into the hot heater-vacuum wells can yield high *in situ* destruction efficiency (90 to 99%) and minimize the amount of treating needed in surface facilities.

Vapor-Phase Flow/Recovery. Another important feature of the thermal conduction process is the opportunity of heating the soil above the boiling point of water, thereby creating a continuous vapor-phase flow regime. The production vapor stream consists of (1) air drawn in from outside the heated zone and from the lesser amount originally in the pores of the vadose zone; (2) water vaporized from pore liquid water in the soil and any groundwater drawn in from outside the heated region; (3) vaporized organic compounds, either naturally occurring or contaminants; and (4) gas-phase combustion products from oxidation and pyrolysis of organic components.

All flow in the heated region occurs in the vapor phase, except for peripheral groundwater influx and a small amount of capillary wicking into the heated regions. Creation of a continuous gas phase throughout the soil provides high-relative-permeability flow paths for removal of contaminants. By vaporizing the last bits of residual liquids, the process also avoids capillary trapping of residual liquid phases that occurs in all of the multiphase flow processes. This feature distinguishes thermal conduction heating from other remediation processes in that it permits complete removal of contaminants.

Creation of Permeability. Another feature of thermal conduction processes is the creation of permeability in the heated, dry regions of subsurface formations. This is important because steam and other vapors that are generated when soils are heated will build positive pressures unless the soil has sufficient permeability to allow the vapors to be withdrawn by an applied vacuum. The permeabilities required to prevent pressure buildup are quite high. For example, Equation (4.6.1.30) predicts that a permeability of 1 Darcy is needed to produce the vapors generated by a 900°C heat source with a vacuum of 10 in. of water. Many natural soils, such as clays and silts, are almost impermeable to fluid flow (<1 millidarcy); however, heating these soils sufficiently to dry them greatly increases the pore permeability and, in some cases, creates a secondary network of high-transmissibility fractures that allows effective transport of the vapors over long distances. The creation of polygonal fractures by the shrinkage of the hydrated minerals, such as clays, is a well-known phenomenon that can be observed at the surface of dry lake beds. Typically, the frequency of these fracture polygons in dry mud is of the order of 1 ft, and the width of fractures is as much as 1 in. Assuming the development of a similar fracture network in the subsurface, one might expect a flow path sequence consisting of a few inches of high-temperature diffusive flow out of the polygons into the fractures and then many feet of convective flow along the fractures to the wells. Even in formations that do not have much shrinkage upon drying, a small local buildup of pressure is sufficient to lift the overburden soil slightly, thereby increasing porosity or creating minute horizontal fractures to the wells.

Experience in field operations has verified that vacuum can be maintained over considerable distances in dry soils, even when a large amount of water vapor is being generated. When vacuum is applied at every heat source, the increase in permeability in the soil occurs faster than the propagation of the boiling front, and no pressure buildup is observed.

In some cases, heat can be applied to the soil at locations that do not have a coincident vacuum. For example, a hexagonal heater well pattern with a single heater/vacuum well at the center of the hexagon can be used (see Figure 4.6.1.5). When mixed well patterns are used, care must be taken to develop permeability with the heater/vacuum wells before full power is applied to the heater-only wells. A reduced rate of heating can be applied initially to the heater-only wells until permeability is created by the drying.

An alternative design can be used in which the heater-only wells are sealed at the surface under an impermeable barrier. In that case, permeability is developed in the region immediately around the heater. This local permeability increase provides a vertical flow path for the vapors produced by heater-only wells to escape to the surface. They can be collected by a vacuum applied to a permeable layer.

Thermal conduction is the only process capable of uniformly drying the formation and heating above the boiling point of water. In view of the adverse experience with soil vapor extraction (SVE) in low-permeability silts and clays, the creation of permeability by thermal conduction drying may be the most critical improvement needed for SVE remediation.

In summary, the ability of thermal conduction heating to achieve dryness and superheat satisfies the requirements for complete vaporization and transport of contaminants via vapor phase to the extraction wells.

Chemical Reactions

In addition to the physical changes in contaminant properties that occur with increases in temperature, a number of chemical changes are also known to occur in these compounds. Products of these chemical reactions are usually more volatile than the original contaminants; hence, they are more easily vaporized.

With even gentle warming, biological activity in soils will increase and promote destruction of organic compounds. In general, chemical reactions at low temperatures are not expected to be useful in batch treatments of contaminants. However, in the *in situ* thermal processes, where the residence time of reactants is sufficiently long, some of these reactions become important.

Oxidation of hydrocarbons and chlorinated hydrocarbons is known to be effective at very high temperatures, but can destroy contaminants even at low temperatures if the residence time for reaction is large. One can reasonably expect a considerable amount of oxidation of contaminants during heating in the 100° to 200°C range because slow oxidation of most organic compounds in air occurs at room temperature, and hydrogen-rich hydrocarbons will spontaneously combust at temperatures above 300°C. In thermal conduction remediation projects, a large amount of air can be drawn through the soil and be made available for these reactions. At higher temperatures (>550°C), even carbon-rich compounds can be oxidized, and pyrolysis will occur in the absence of air. Both oxidation and pyrolysis of contaminants produce volatile compounds that can be more easily mobilized in the vapor phase. Pyrolysis also deposits inert solids such as "dead" carbon that can be safely left in the soil. The gas flowing out of the soil typically contains water vapor, carbon dioxide, and HCl (when chlorinated organic contaminants are present), plus any unreacted components from the soil (see Equations (4.6.1.23- 4.6.1.25)).

In addition to air oxidation, the reactions of organic compounds with water are well known in the production of "water gas" at very high temperatures. Hydrous oxidation reactions have been proposed as a potential method for destroying contaminants at moderate temperatures in *in situ* thermal remediation processes.[16] In all thermal conduction remediation projects, a large amount of naturally occurring water is available for such reactions.

Not much quantitative information is available on chemical reaction as a means of destroying contaminants in thermal remediation. However, in the treatability studies discussed in the next subsection, a significant disappearance of high-boiling-point compounds is observed well below their boiling points.

Treatability Studies

Contaminants

A variety of contaminants have been examined as to their suitability for remediation from soils by the thermal conduction process. These include (1) light hydrocarbons, (benzene, toluene, xylene, and the gasoline range distillates); (2) light chlorinated hydrocarbon solvents (TCE, PCE, DCE, etc.); (3) insecticides (chlordane, lindanes [α-, β-, γ-, δ], 4,4′-DDT, 4,4′-DDE, and 4,4′-DDD); (4) high-boiling-point hydrocarbons (diesel, lube oils, and tar); (5) heavy chlorinated hydrocarbons (including polychlorinated biphenyls [PCB-1248, PCB-1260]), dibenzo-dioxins [TCDD and OCDD], and dibenzo-furans [TCDF]; and (6) manufactured gas plant (MGP) wastes. The removal occurs either by vaporizing and collecting them in the vacuum system or by destroying them in the ground.

Treatability Tests

Treatability tests were devised to determine the temperature and time required for removal of contaminants from soil samples taken from prospective remediation sites. Several kinds of tests were considered, including a heating/convection test with flow-through of air or water vapor. However, a simple heating test with the soil sample in a ceramic crucible has proven adequate for design of field projects.

The treatability tests were carried out by placing soil samples in uncovered crucibles and heating them in a muffle oven.[8] The treatment temperatures were chosen based on the boiling points of the primary constituents of concern. The temperatures were increased over a period of several hours and then held constant at the desired treatment temperature for 1 to 3 days. Pre- and post-treatment analyses were performed to determine the initial and final concentrations of contaminants.

Treatability Results

Although the treatability tests are not scaled to field dimensions and do not replicate the convective mechanisms operative in the field, they appear to be a reasonable guide for field behavior. Table 4.6.1.1 is a summary of some results of these tests, together with results from pre- and post-treatment sampling at field remediation project sites. The results clearly show that contaminants are removed from soils at temperatures considerably below their boiling points. This would not be surprising if the removal mechanism were only evaporation, because efficient drying of water occurs almost 100°C below its boiling point. Because there are a number of vaporization mechanisms that can be operative, the removal of contaminants from soil is more complex. Soil mineral surfaces are known to tenaciously hold a "recalcitrant" fraction of contaminants, and desorption appears to be time dependent.[17] As shown in Figure 4.6.1.14, compounds boiling in the range of 400 to 480°C are largely removed by heating to 400°C for 1 day, but they are even more effectively removed by heating to 300°C for 3 days.

TABLE 4.6.1.1 Summary of Treatability Tests and Field Projects

Type/Treatment	Beginning Conc.	Ending Conc.	Matrix
OCDD	6.9 ppb	0.014 ppb	Silty clay
Chlordane 1 day, 200°C	41 ppb	<0.033 ppb	Sandy silt
4,4′-DDT 1 day, 200°C	3500 ppb	<0.033 ppb	Sandy silt
Lindane 1 day, 200°C	476 ppb	<0.066 ppb	Sandy silt
4,4′-DDE 1 day, 200°C	750 ppb	<0.033 ppb	Sandy silt
4,4′-DDD 1 day, 200°C	510 ppb	<0.033 ppb	Sandy silt
PCB 1260 *Field ~500°C	20,000 ppm	≤0.300 ppm	Clay
PCB 1248 *Field ~200°C	5200 ppm	≤0.950 ppm	Sand
1,1-DCE *Field ~250°C	650 ppb	≤0.53 ppb	Clay
TCE *Field ~250°C	79 ppm	<0.005 ppm	Clay
PCE *Field ~250°C	3500 ppm	<0.005 ppm	Clay
Diesel *Field ~100°C	9300 ppm	<100 ppm	Silt

MGP Waste	Beginning Concen.	Ending Concen. (1 day, 400°C)	Ending Concen. (3 days, 300°C)
Naphthalene	18,000 ppm	<0.033 ppm	<0.017 ppm
Acenaphthylene	1300 ppm	<0.033 ppm	<0.017 ppm
Acenaphthene	750 ppm	<0.083 ppm	<0.042 ppm
Fluorene	3200 ppm	<0.083 ppm	<0.042 ppm
Phenanthrene	7600 ppm	<0.033 ppm	<0.017 ppm
Anthracene	2100 ppm	<0.033 ppm	<0.017 ppm
Fluoranthene	4500 ppm	0.091 ppm	<0.043 ppm
Pyrene	3700 ppm	0.160 ppm	<0.046 ppm
Dibenzofuran	15 ppm	<0.033 ppm	<0.033 ppm
Chrysene	1300 ppm	0.200 ppm	<0.032 ppm
Benzo (*a*) anthracene	1000 ppm	0.130 ppm	<0.025 ppm
Benzo(*b*)fluoranthene	960 ppm	0.410 ppm	<0.054 ppm
Benzo(*k*)fluoranthene	390 ppm	0.140 ppm	<0.020 ppm
Benzo(*a*)pyrene	1100 ppm	0.360 ppm	<0.037 ppm
Dibenzo(*a,h*)anthracene	44 ppm	<0.033 ppm	<0.017 ppm
Benzo(*g,h,i*)perylene	690 ppm	0.570 ppm	<0.041 ppm
Indeno(*1,2,3-cd*)pyrene	400 ppm	0.380 ppm	<0.071 ppm
1-Methylnaphthalene	2700 ppm	<0.066 ppm	<0.033 ppm
2-Methylnaphthalene	8000 ppm	<0.066 ppm	<0.033 ppm

Note: ≤ represents a detectable quantity where multiple samples were tested.

Every compound that has been studied can be removed from soil by heating for only a few days. Concentrations of benzene in coal tar were reduced from 39,000 µg/kg initially to only 22 µg/kg after as little as 1 day of heating at 200°C. Benzo-(*a*)-pyrene and other PAHs boiling in the range of 500 to 525°C were reduced by a factor of 10,000 as a result of heating 3 days at 300°C (see Figure 4.6.1.1.15). Field projects typically maintain even higher temperatures for longer periods of time; consequently, they can be expected to attain better destruction efficiency.

Field Projects

In addition to the field research and development program at Shell's Gasmer Road Field Research Facility in Houston, Texas,[1,5,8] there have been a number of field remediation demonstrations[2-4,6,7] and commercial field projects[9-11,19] at contaminated sites.

ISTD has been used in a number of modes (surface heating, heating from wells, *ex situ* blankets, coincident heat/vacuum sources, and separate heaters and vacuum sources). A wide variety of high- and low-boiling-point contaminants have been remediated in these and other projects (Table 4.6.1.4.6.12). A few of these field projects will be reviewed to show the range of applications.

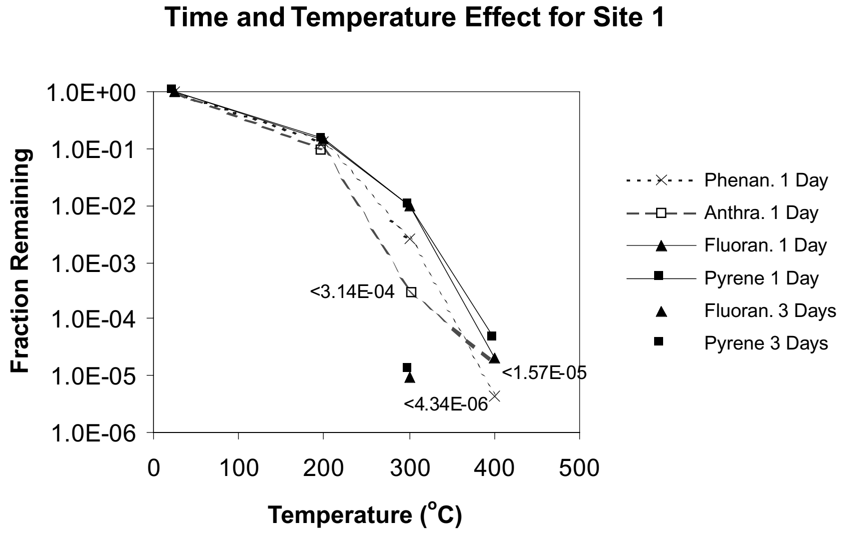

FIGURE 4.6.1.14 Treatability tests: PAHs (400- 480°C B.P.).

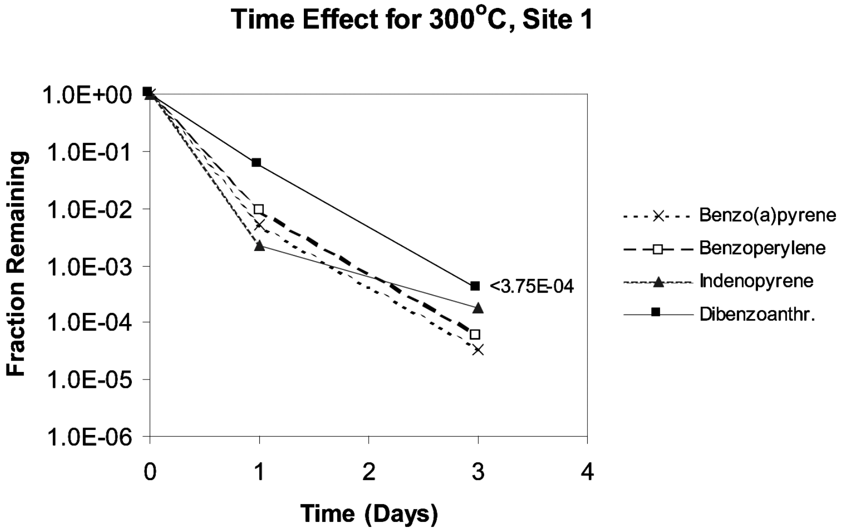

FIGURE 4.6.1.15 Treatability tests: PAHs (500- 525°C B.P.).

Missouri Electric Works (PCBs)

Both thermal wells and thermal blankets have been demonstrated to be highly effective in removing PCBs from soils. In a field demonstration at the Missouri Electric Works (MEW) Superfund site in Cape Girardeau, Missouri, ISTD thermal blankets and wells were shown to remediate high-concentration PCB contamination from shallow and deep clay soils.[6-7] The MEW site was contaminated with PCBs in both shallow and deep soils during past operations that included servicing and remanufacturing transformers, and recycling dielectric fluids containing PCBs. The natural stratigraphy is brown clay soil; the water table is located about 40 ft below ground surface.

The objectives of the MEW field test were to (1) clean up clay soils contaminated with high concentrations of the highest-boiling-point PCB (Aroclor 1260), to less than 2 ppm, (2) demonstrate that stack discharges were in compliance with state and federal standards for PCBs and polychlorinated dibenzo-

TABLE 4.6.1.2 Summary of Thermal Conduction Field Projects

Location	Project	Soil Type	Depth (ft)	Process	Number of Blankets or Wells
S. Glens Falls, NY	Demo	Sand	0- 0.5	Blanket	5- 8×20 ft
Cape Girardeau, MO	Demo	Clay	0- 1.5	Blanket	2- 8×20 ft
Cape Girardeau, MO	Demo	Clay	0- 12	Wells	12
Mare Island , CA	Demo	Silt/Clay	0- 14	Wells	12
Portland, IN	Commercial	Clay	0- 12	Wells	15
Portland, IN	Commercial	Clay	0- 20	Wells	130
Tanapag, Saipan	Commercial	Carbonate/sand	0- 2	Blanket box	28- 8×20 ft
Eugene, OR	Commercial	Sand/silt/clay	0- 11	Wells	761
Centerville Beach, CA	Commercial	Sand	0- 15	Wells	53

Location	Contaminant	Initial Conc. (ppm)	Final Conc. (ppm)
S. Glens Falls, NY	PCB 1248/1254	5000	<0.8
Cape Girardeau, MO	PCB 1260	500	<1
Cape Girardeau, MO	PCB1260	20,000	<0.033
Mare Island , CA	PCB 1254/1260	2200	<0.033
Portland, IN	1,1-DCE	0.65	0.053
Portland, IN	PCE/TCE	3,500/79	<0.5/0.02
Tanapag, Saipan	PCB 1254/1260	10,000	<1
Eugene, OR	Gasoline/diesel	3500/9300 + free product	N.D. Benzene, 250,000 # free product removed
Centerville Beach, CA	PCB 1254	800	<0.17

dioxins/polychlorinated dibenzofurans (PCDDs/PCDFs), and (3) obtain a system DRE for PCBs greater than 99.9999%. The demonstration was conducted in support of TerraTherm Environmental Services' application for a modification of the TSCA permit for alternate PCB treatment. EPA Region VII and the Missouri Department of Natural Resources (MODNR) monitored the demonstration.

For the blanket demonstration, two heater blankets were placed side-by-side in an area where PCB concentrations had averaged 510 ppm near the surface and 2.7 ppm at 12 to 18 in. The target treatment depth was 18 in.

For the well demonstration, 12 heater/vacuum wells were completed in a multiple triangular array with a 5-ft well spacing to a depth of 12 ft. The area chosen had PCB contamination as high as 19,900 ppm near the surface and still above 2 ppm at the target depth of 10 ft. During the demonstration, electrical heating and vacuum were applied to the wells for a period of 42 days.

In the blanket demonstration, the soil was successfully remediated to a depth of 18 in. The upper 1 ft of soil was non-detect for PCBs (i.e., <33 ppb), and averages at all depths met the remedial objective of <2 ppm.

In the well demonstration, temperatures above 1000°F were achieved in the interwell regions. Maximum temperatures over 1000°F were reached at the center of the triangles, and about 50% of the volume was over 1100°F. Sampling after 42 days showed complete clean-up of all contaminants to levels below 1 ppm to a depth of 10 ft below ground surface. Eighty-one samples in the treatment zone were non-detect (<33 ppb) by EPA Method 8080. Sampling down to 15 ft in the center of the treated zone showed that no vertical migration of contamination had occurred.

Emission stack sampling by EPA methods demonstrated that the discharge of PCBs and combustion by-products complied with state and federal ambient air requirements. Stack testing of emissions from the process indicated 99.9999998% DRE of the PCBs by combined *in situ* and surface treatment. The sampling and analysis results of EPA Method 680 analysis performed on the stack samples indicate that a total of 0.10 mg PCB was emitted from the stack from a conservative estimate of 40 kg PCB in the treated area.

Post-treatment soil samples composited vertically and areally from the treated zone were analyzed for PCDD and PCDF and exhibited 2,3,7,8-tetrachlorodibenzodioxin equivalent (TEQ) levels from non-detect to 6.84 parts per trillion (ppt), with an average of 3 ppt. This is below the background level of 8 ppt for uncontaminated soil in North America.

Centerville Beach, California (PCBs)

A commercial PCB remediation utilizing 53, 15-ft deep heater wells was successfully performed at a Navy base at Centerville Beach, California. Residual PCB levels below 1 ppm were achieved in all target zones.

Portland, Indiana (Chlorinated Solvents)

The first full-scale commercial application of ISTD was performed by Shell Technology Ventures, Inc., at a Shell site in Portland, Indiana[9,10] (see Figure 4.6.1.16.) The site contained difficult-to-remediate, tight clay soils contaminated with high concentrations of tetrachloroethene (PCE) to depths as great as 18 ft. The size of the Indiana project included an area of about 6500 sq. ft^2 to a depth of 18 ft, or about 5600 tons. The impacted area was adjacent to and beneath a loading dock at a plastics manufacturing facility, which was located across the street from a residential neighborhood (see Figure 4.6.1.17.) At the Indiana site, as at many other sites, there is a wide variation in permeabilities ranging from tight clays to the high-permeability fill located above the target zone. A large amount of surface runoff water at the site drained into the vadose zone above the normal water table at 22 ft. Water influx during heating was partially controlled with perimeter drains.

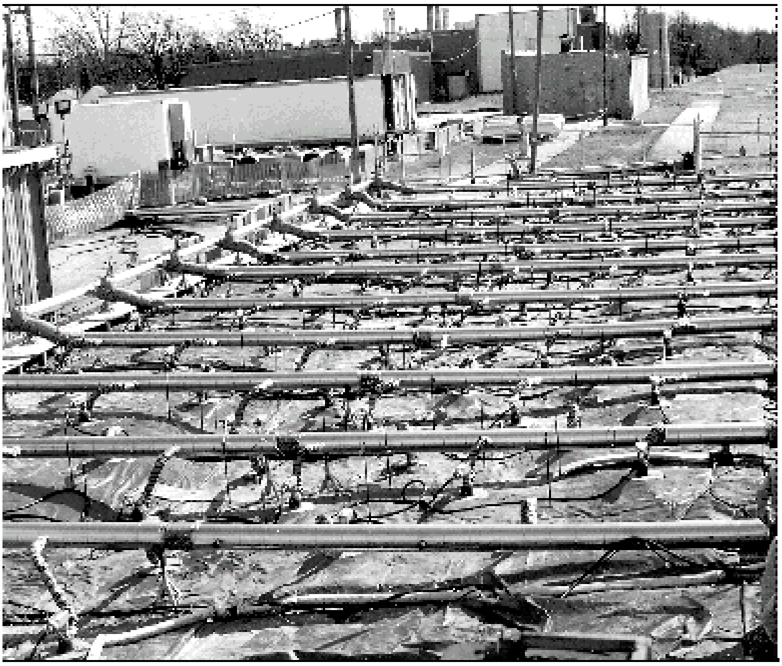

FIGURE 4.6.1.16 Portland, Indiana, thermal wells.

This area was treated with 130 vacuum/heater wells on 7.5-ft triangular spacing, including 26 wells that had to be drilled through the concrete loading dock to remediate the underlying soil. The site was successfully remediated by reducing initial concentrations of PCE that were as high as 3500 ppm to less than the Tier 2 Industrial Standards established for the site (<8.01 ppm for depths greater than 2 ft). In fact, after thermal treatment, all samples below 2 ft had less than 0.5 ppm PCE remaining.

A separate smaller area (30 × 20 ft) of 1,1-dichloroethene (1,1-DCE) contaminated soil at the same facility was also treated successfully with 18 vacuum/heater wells installed on 7.5-ft spacing to depths of

FIGURE 4.6.1.17 Portland, Indiana, remediation site.

12 ft. The entire site was remediated *in situ* without disruption to the adjacent residential neighborhood from noise, dust, and odors that would likely have been associated with alternative remedial options such as excavation.

Before the heating was discontinued, soil samples were taken with a hollow sampling probe at the coldest locations (centroids of the triangular patterns) furthest from each heater well. These were analyzed and used to decide whether additional heating was required. The sampling data, temperature profiles, and absence of HCl in the stack were all used to determine when remediation was complete. For quality assurance, confirmatory samples were taken after heating when the soil had cooled below 100°F.

After the remediation operation was completed, the wells were removed and the holes were grouted to the surface. After the winter, new grass growth reappeared naturally, without re-seeding. Later, revegetation was accelerated by resodding; and after 1 year, the site was completely restored. No damage was observed to the nearby trees.

Eugene, Oregon (Diesel And Benzene)

The largest ISTD field project to date was a 3/4-acre Shell diesel loading facility in Eugene, Oregon.[11] This site had free-product LNAPL (diesel and gasoline with benzene). Hydrocarbon contamination was observed in cores to depths of 12 ft. The lithology was gravel and sand fill above silty sands, with a water table that varied seasonally from 5 ft depth to 12 ft depth.

The project utilized 761 wells, with an ISTD well pattern that included hexagonally heater-only wells surrounding center heater-vacuum wells. (The ratio of heater-only wells to heater-vacuum wells was 2 to 1.) A ring of dewatering wells was used to control the water influx. A visual display of the Eugene project heater wells from the computer display inside the instrument truck is shown in Figure 4.6.1.11. Approximately one fourth of the heater wells were drilled inside buildings through the concrete floors. The wells also extended down an alleyway adjacent to apartment buildings and straddled a sewer line in the alleyway.

The site was heated for 110 days, utilizing 4.5 MW of electric power. During the heating, some 250,000 pounds of organic compounds were removed from the soil. After the remediation, sampling wells showed no remaining free product, and all samples were non-detect for benzene.

Safety

In situ thermal desorption operations have been carried out by TerraTherm Environmental Services, Inc., with careful attention to safety and health of on-site operators and nearby residents and with concern for the long-term impact of operations on the environment. Enclosed by fencing, the operations were so clean, quiet, and trouble-free that normal activities of nearby businesses and residents were continued with scarcely any interruption.

In future ISTD projects, attention to safety is of continuing importance. Because the process uses large amounts of electrical power and high temperatures, it is essential to keep a high profile on safety with active management controls of ongoing activities and with continuing education of site personnel.

As expected with all new technologies, a number of concerns have been expressed by regulators and site owners. These have been addressed by TESI's R&D efforts as follows.

Underground Fires

Ignition of hydrocarbons and other organic materials in soils during heating by the ISTD Process was examined to assess the possibility of uncontrolled subsurface fires. Typically, the oxidation reactions take place in porous soils that consist of about 60% by volume of rock minerals (either silicates or carbonates) and 40% pore space. The large amount of rock minerals absorbs reaction energy, so that even for a soil laden with 10,000 ppm THC (total hydrocarbons), complete combustion would raise the temperature to only about one half of a flame temperature. To burn that much hydrocarbon would require hundreds of pore volumes of air. In practice, the amount of air present in the pore space of even a dry vadose zone is sufficient to burn only about 20 ppm of the THC, and that amount of combustion would raise the soil temperature only a few degrees. These are the reasons sand is used to extinguish fires.

Underground fires associated with coal mines occur because of oxygen supplied by the coal itself and the presence of large mine shafts that can convect large amounts of air. In soil remediation, uncontrolled fires are not likely, and if oxidation ever became excessive, it could easily be quenched by drawing water into the soil with the vacuum.

Migration of Contaminants

Theoretical and numerical simulation studies have indicated that ISTD can be used to remove contaminants from a region of subsurface soils without dispersion of contaminants beyond the boundaries of the treated zone. One reason for this is the negative pressure imposed by the vacuum wells in the soil that draws the mobilized contaminants inward. Because of continued questions on this matter, TESI made a large effort to detect migration in our field experiments and demonstrations. None of these investigations found evidence of migration after a completed thermal treatment. The reason for this is the abruptness with which the temperature falls off with distance from the heat sources. In large projects, the potential edge dispersion zone is miniscule compared to the dimensions of the treated zone.

Contaminants naturally migrate due to subsurface flow of water driven by hydraulic gradients. Removing this influence by de-watering, and removing the source of the plume by superheating with ISTD, prevents further migration.

Formation of Toxic By-products

The question of whether dioxins and furans are formed in the wells as by-products of the ISTD can be addressed by noting that the reaction rate of formation is slower than the destruction rate of a by-product at the process temperatures of the heaters through which all of the products pass. In addition, by-products have comparable volatility to the original compounds so that even if they had been formed in the soil, they would be vaporized and drawn to the wells. Aside from these theoretical arguments, we have proven in field experiments that dioxins or furans remaining after thermally treating PCB-contaminated soils were less than the average concentration in uncontaminated soils in North America.[6]

Fugitive Emissions

Toxic stack emissions in the field projects are typically two orders of magnitude below EPA ambient air criteria. This is a result of the *in situ* destruction, highly efficient thermal oxidizers, and final carbon-bed absorbers. The escape of fugitive emissions at the edge and at the surface of the treated soil is prevented by a combination of an impermeable sheet covering the surface and the imposition of a vacuum on the entire region. Verification of the absence of escape of contaminants was carried out at field sites.[6]

Fate of Buried Drums

Many sites contain wastes that had been placed in sealed drums and buried in shallow ditches. Typically, these drums corrode after a few years and no longer present any hazard of over-pressuring when heated. To investigate the potential problem with new sealed drums, we conducted field tests on new 30-gallon drums, crimped at the ends and sealed with conventional rubber-gasketed bungs. The drums were filled with liquid ethanol and buried, standing vertically and lying horizontally, 2 ft below the surface. These drums were heated by several nearby heater wells, and the ethanol was successfully remediated from the drums without any event recorded on a nearby seismometer. The experiment was repeated with the bungs welded in. At about 100 psi internal pressure, the vertical drum failed and blew out the overburden 2 ft of sand.

These experiments demonstrated the hazard of tightly sealed vessels that might build sufficient pressure to fail and erupt at the surface. As a precautionary measure, buried drums near the surface could be perforated with a driven rod. Deeply buried drums will leak at the crimped ends before building sufficient internal pressure to burst and crater.

A hazardous condition exists at any site containing unexploded ordnance or high-pressure gas bottles. At suspected sites, detailed location of metallic objects with ground-penetrating detectors will be required; and during remediation, the site area must be shielded and isolated from personnel.

Discussion

After 10 years of development and field applications, thermal conduction heating with vacuum extraction is now a technically mature soil remediation process. Being versatile and robust, it has met or exceeded remediation goals at every contaminated site where it has been used. The reason for this success is that, although simple in concept, thermal conduction heating has a number of unexpected advantages for soil remediation:

1. Thermal conduction heating from high-temperature heaters allows large amounts of heat energy to be injected without fluid injection. Avoidance of fluid injection is an important advantage in that the entire subsurface region being heated can be maintained at sub-atmospheric pressure, thereby preventing spreading of contaminants to surrounding regions.
2. The injection of heat energy by thermal conduction is very uniform compared to convective heat flow. The high sweep efficiency results from the regularity of areal patterns of heat injection wells and the uniformity of heat flow into the variable layers of natural soils. Thermal conductivities of dry soils differ by a factor of only about two for various soil types. In contrast, fluid flow permeabilities of sedimentary layers may vary by a factor of 100,000,000. Furthermore, unlike fluid flow, heat flow is self-correcting because thermal conductivity decreases with an increase in temperature, whereas permeability increases with displacing phase saturation. Use of electric heaters allows heat to be injected exactly where it is needed over the vertical profile. The net result is that the entire volume of contaminated soil can be heated to a desired process temperature, regardless of variability in the subsurface geology.
3. Because the soil can be heated to high temperatures, the process is effective in recovering any contaminant that can be volatilized. The high displacement efficiency results from the nature of the vaporization in the microscopic pores of the soil. Several mechanisms contribute to the vaporization of contaminants. If soil is heated to the boiling point of a contaminant, it is readily mobilized in the vapor state; however, even heating below the boiling point increases the vapor pressure of the contaminants and permits evaporation into a carrier stream of air that may be drawn in by the vacuum. Steam distillation is even more effective in vaporizing the contaminants. Most natural formations contain large amounts of liquid water compared to contaminants. Boiling this pore water provides a water vapor stream that is an important means of volatilizing the

contaminant. If air is present when contaminants pass through soils that have been heated, they are destroyed *in situ* by oxidation. At higher temperatures (>350°C), air oxidation is nearly instantaneous, and even reactions with water occur. In the absence of air and water at these high temperatures, the contaminants are altered by pyrolysis to form more volatile compounds. The overall result is that low- and high-boiling-point contaminants are all efficiently volatilized and made available for vapor-phase transport. Treatability studies of soil samples in the laboratory have shown that removal of contaminants from soils can be a function of both temperature and time. Unlike *ex situ* thermal processes, the *in situ* processes have very long residence times, which are favorable to the removal mechanisms that might be time dependent. Heating times for natural soils are necessarily longer than vaporization or desorption times; thus, complete removal can be achieved if the soil is heated to an adequate temperature, which is nominally the boiling point of the contaminant.

4. Another important feature of the *in situ* thermal conduction process is the creation of permeability in heated dry regions of subsurface formations. The increase in permeability allows the process to be applied to low-permeability clays and silts where other processes cannot be used effectively. The major increase in microscopic permeability can occur in soils when the pore water is evaporated. In addition, the drying of a layer of clay-rich soil creates a polygonal network of wide cracks. Such a drainage network would explain the effective removal of contaminants out of dried silt/clay soils that is observed with widely spaced wells in field projects.

The ability of thermal conduction heating to achieve dryness and to superheat the soil fulfills both process requirements essential for perfect remediation: complete vaporization of contaminants and effective transport via vapor phase to the extraction wells.

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Appendix 4.6.1: Design Equations for *In Situ* Thermal Desorption[18]

The proper design of an *in situ* thermal desorption (ISTD) project depends on an understanding of several mechanisms that occur in the soil during application of heat. These mechanisms are described by the fundamental equations that predict (1) fluid and heat flow, (2) vaporization and chemical reactions of contaminants, and (3) mass and energy balances. Although actual design computations are usually carried out in numerical simulators, the simplified analytical expressions given below will illustrate the *in situ* process behavior.

Fluid Flow (Steady State)

Flow of fluids in a porous medium is described by a Darcy equation for each of the flowing phases. In most *in situ* soil remediation processes, we need to account for flow of aqueous and oleic liquid phases and of a gas phase composed of air, water vapor, and lesser amounts of oleic vapors. The linear form of Darcy's equation, as given in Equation (4.6.1.1), generally describes flow in the thermal blanket process. The radial form, as given in Equation (4.6.1.2), describes flow in the thermal well process.

In the Darcy equations, the soil properties (absolute permeability and porosity) are differentiated from fluid properties (viscosity and density). The interference of dissimilar fluids in multiphase flow is described by a relative permeability correction that is a function of the saturations of each of the phases. All properties may vary with temperature, and in this way the flow of viscous oil, water, and vapors is properly described throughout the entire process.

Heat Flow

Conduction (Steady State)

Heat flow by conduction in porous media is described by the temperature/heat flow equations that are similar in form to the pressure/fluid flow equations. For steady-state, linear, conductive heat flow, Fourier's equation, given in Equation (4.6.1.3), is applicable. The Fourier equation for steady-state, radial, conductive heat flow is given in Equation (4.6.1.4).

Conduction (Transient)

Because heat flow is so much slower than fluid flow, transient solutions are needed to describe this process. For linear flow, the rise in temperature as a function of time and distance from a plane heater blanket is given by Equation (4.6.1.5). This equation incorporates the bulk thermal properties of soil and the heat input rate per unit area of the heater. For pure conduction without convection, the temperature fall-off with distance is described by the complementary error function as given in Equation (4.6.1.6) and Figure A.1. The line source solution, given in Equation (4.6.1.7), is a good approximation for radial conduction heat flow from a thermal well. The shape of the resulting temperature profile with radial distance from the line source is defined by the exponential-integral function given in Equations (4.6.1.8) through (4.6.1.10) and Figure A.2. When an array of heater wells is installed in a volume of soil, the temperature rise at any interwell location is the superposition sum of each of the heaters in the pattern, as shown in Equation (4.6.1.11) and Figure A.3. Although the contribution to the temperature rise from distant wells is less than from closer ones, each well in the array contributes to the temperature rise. The effects of this superposition in the regions between the wells become most important after long heating times, when the soil heat-up is surprisingly uniform.

Radiation

Radiation heating is important only in the very high-temperature region near the heaters. Typically, at heater temperatures less than 1000°F, radiation heat transfer becomes insufficient for practical heating rates from blankets or wells. The Stephan-Boltzmann equation shows radiation heat transfer to have a fourth-power dependence on the absolute temperatures. This is given in Equation (4.6.1.12).

Vaporization

Dalton's Law

At moderate levels of heating, most *in situ* liquids will vaporize by boiling, evaporation into air, or steam distillation. For immiscible liquids, the fractions of individual components in the gaseous phase are described by Dalton's law, which states that the total pressure of a gaseous mixture is the sum of the partial pressures of the components (see Equation (4.6.1.13). Because the liquids are immiscible, each component vaporizes independently of the others, as determined by its single-component vapor pressure, which is a function only of the temperature. The mole fraction of a component is directly related to the partial pressure, as shown in Equations (4.6.1.14) and (4.6.1.15).

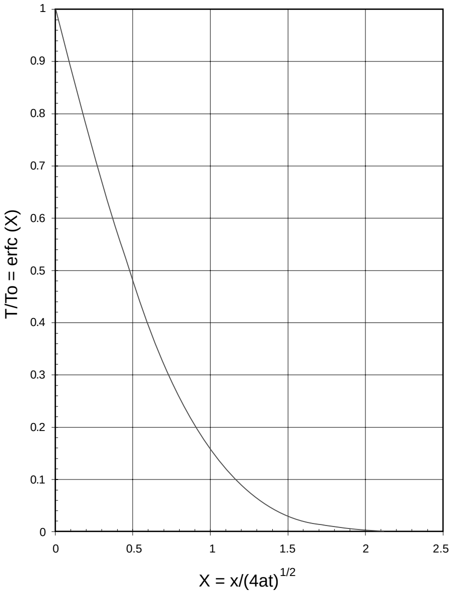

FIGURE A.1 Complementary error function.

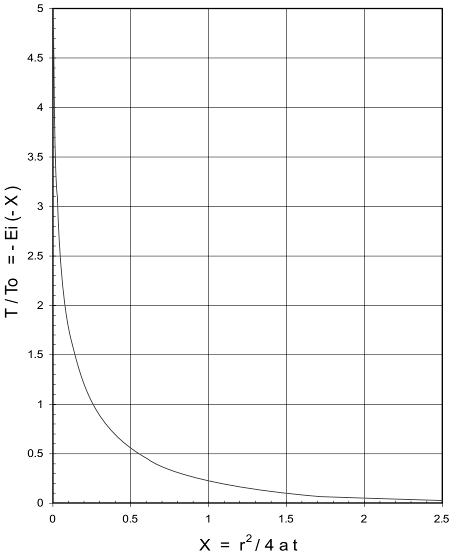

FIGURE A.2 Exponential integral function.

Raoult's Law

If the liquids are miscible, the partial pressure of a component is reduced by its mole fraction in the liquid phase (see Equation (4.6.1.16). For example, the slight solubility of benzene in water will reduce the partial pressure of benzene in the vapor phase, provided there is no excess liquid benzene present. This will retard vaporization of the last trace of benzene until all of the liquids are vaporized.

Steam Distillation/Air Evaporation

The weight fraction of an oleic contaminant that can be carried in a stream of air or of steam is given in Equations (4.6.1.17) and (4.6.1.18). This formulation assumes that a liquid contaminant residue is

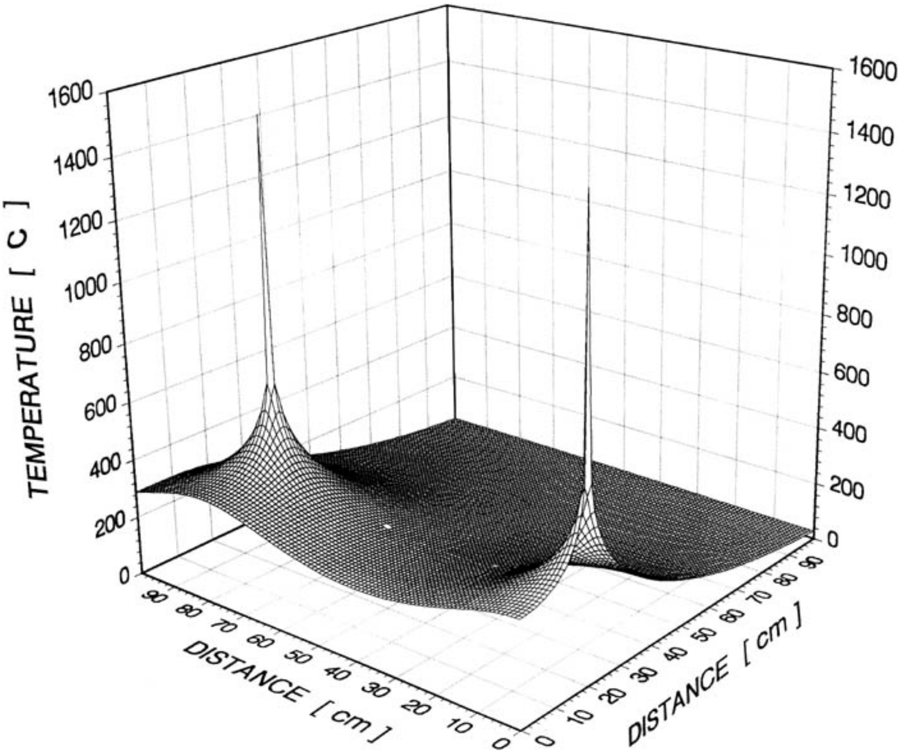

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FIGURE A.3 Superposition of exponential integral functions.

being evaporated in a stream either of air or of water vapor. Equation (4.6.1.18) shows that the weight fraction of contaminant in the vapor stream is dependent on the molecular weights and the pure component vapor pressures. (Subscript 1 refers to the contaminant and subscript 2 refers to either air or steam.) In the *in situ* thermal conduction processes, the total pressure of the vapor stream is slightly below 1 atm. Therefore, for high-boiling-point contaminants, the partial pressure of the air or steam is very nearly equal to the total pressure. Because steam has a lower molecular weight than air, it is a more effective distilling medium than air. The large amount of water vapor present in the subsurface also makes steam distillation an important mechanism for recovery of contaminants at temperatures well below their boiling points.

Chemical Reaction Kinetics

When high temperatures are generated in situ and sufficient air is present, most of the contaminants are destroyed in the subsurface. The long residence time of reactants at elevated temperatures in the ISTD process favors completion of chemical reactions. Assuming first-order reactions, the kinetic behavior can be represented as shown in Equations (4.6.1.19) and (4.6.1.20). These equations, when combined with the Arrhenius Equation (4.6.1.21), provide a combined expression for completion of a chemical reaction, as a function of time and temperature (see Equation (4.6.1.22)). Our experience in field projects has shown that 90 to 99% of the chemical reactions take place in the subsurface soil. The remaining unreacted compounds are reacted in a high-temperature thermal oxidizer, achieving as much as 99.999999+% destruction efficiency for the combined process. The resulting products are carbon CO_2, H_2O, and HCl, all of which are readily vaporized at even moderate effluent temperatures.

Stoichiometry

A generalized stoichiometric equation for reaction of chlorinated hydrocarbons with air is given in Equation (4.6.1.23). This formulation assumes the air stream to be composed of 20% O_2 by volume. By monitoring the effluent stream for CO_2, the amount of remediated hydrocarbon removed from the soil can be calculated (see Equation (4.6.1.24)). Similarly, by monitoring the effluent stream for HCl, the amount of remediated chlorinated hydrocarbon can be determined (see Equation (4.6.1.25)).

Material Balance

Material balances of fluid components in the ISTD process are carried out at a particular site with the following conditions and assumptions:

1. The system volume is that bounded by the periphery of the treated volume of subsurface soil and the surface treatment equipment out to the effluent stack.
2. The simple balance can be stated as (Mass of a component initially present in the soil) + (Mass of component flowing into the treated volume from adjacent soil) = (Mass of component produced during the treatment) + (Mass of component remaining in the treated soil at the end of the process).
3. Individual components include:
   a. The oleic contaminant, (Equation (4.6.1.26)).
   b. Water (Equation (4.6.1.27)).
   c. Air (Equation (4.6.1.28)).
4. The initial mass of oleic contaminant in the soil is obtained by analysis of soil samples. Depending on the frequency of this sampling at the site, the total contaminant target can be readily obtained by construction of iso-concentration maps and comparing the initial amount in place with the produced amount as determined by Equation (4.6.1.24) or (4.6.1.25). In a well-designed project, essentially no contaminant is released to the atmosphere, no contaminant is allowed to resaturate the cleaned volume, and almost no residual contaminant will be left in the heated volume.
5. The initial amount of water in the target zone can also be determined from core sampling. In general, there is much more water than oleic contaminant. In addition, the movement of groundwater into the target region occurs at many sites and in some cases can even exceed the amount of water initially present in the target region. All of this water must be vaporized if it is not removed by dewatering wells. Typically, the amount of water in the product stream is 20 to 50% by volume. At the end of a successful project, all of the liquid water will have been vaporized. The mass of water vapor remaining in the target zone is negligible.
6. The mass of air initially in the soil is negligible, even in dry soils, because of the low density of air compared to the liquid components. Because of the high mobility of air, one normally expects to draw in a large volume from outside the heated region. Thus, the produced air almost entirely originates from outside the treatment area.

Energy Balance

An energy balance for the process is more easily obtained than the mass balance of components. Because the soil temperatures are a good measure of the completeness of remediation, the energy balance, which takes into account electrical and thermal energies, provides an independent means of monitoring progress of the operations. This is accomplished using the heat capacity of the soil and the thermal properties of the liquids and gas to estimate the average temperature attained from injection of a quantity of electrical energy. Equation (4.6.1.29) is a simple energy balance that does not take into account conductive heat losses from the surfaces of the heated region or water that originates from outside the treated volume.

Also not included in this energy balance are the exothermic oxidation reactions of *in situ* organic compounds with the inflowing air. This additional energy source, however, is not easily incorporated into the process design because the distribution of hydrocarbon contaminants and the flow paths of air are not well-defined. When the amount of heat energy released by oxidation reactions is large, there is incentive for allowing air to enter some wells in patterns that evenly distribute the air in the heated zone and for varying the power input in the heater wells to avoid overheating.

Permeability-Heat Flow/Gas Flow Balance

An estimate of the permeability required to withdraw the vapors as they are generated by a thermal conduction heat front can be obtained by equating Fourier's Equation (4.6.1.3) with Darcy's Equation (4.6.1.1) (see Equation (4.6.1.30)). Pressure drop is assumed to be small compared with absolute pressure so that the incompressible Darcy equation is used. The solution is identical for either linear or radial flow. Gas flow rate is equated to the rate of generation of steam at the boiling front. For simplicity in this calculation, the gas flow is assumed to be a linear, steady-state stream of water vapor.

Numerical Simulators In Process Design

Successful design of *in situ* thermal remediation projects requires an understanding of the wide range of technical concepts described above. Processes can be applied in complex geological settings, in which multiphase, multicomponent fluids flow in response to the heat injection. In addition, a number of options exist for optimizing injection and production of fluids. In these cases, the use of numerical thermal simulators that incorporate the formulations discussed above provides additional insight for the successful design of a project.

Equations Used in Calculation of *In Situ* Thermal Desorption

Fluid Flow (Steady State)

Linear:

$$q_L = \frac{kk_r A}{\mu}\frac{\Delta p}{\Delta l} \tag{4.6.1.1}$$

Radial:

$$q_R = \frac{2\pi kk_r h\Delta p}{\mu \ln(r_e/r_w)} \tag{4.6.1.2}$$

Heat Flow (Steady State)

Linear:

$$q_{hL} = \lambda A\frac{\Delta T}{\Delta L} \tag{4.6.1.3}$$

Radial:

$$q_{hR} = \frac{2\pi\lambda h\Delta T}{\ln(r_e/r_w)} \tag{4.6.1.4}$$

Heat Flow: Conduction (Transient)

Linear:

$$\Delta T(x, t) = \frac{2F_o}{\lambda}\left\{\left(\frac{\alpha t}{\pi}\right)^{1/2} e^{-\frac{x^2}{4\alpha t}} - \frac{x}{2}erfc\left(\frac{x}{2\sqrt{\alpha t}}\right)\right\} \tag{4.6.1.5}$$

$$erfc(X) = 1 - \frac{2}{\sqrt{\pi}}\int_0^X e^{-t^2}dt = 1 - \frac{2}{\sqrt{\pi}}e^{-X^2}\sum\left\{\frac{2^k X^{2k+1}}{(2k+1)!!}\right\} \tag{4.6.1.6}$$

where $(2k + 1)!! = 1\cdot 3\cdot 5\ldots(2k + 1)$

and $X = \dfrac{x}{2\sqrt{\alpha t}}$

Radial:

$$\Delta T(r, t) = \frac{-F_i}{4\pi\lambda} Ei\left[-\frac{r^2}{4\alpha t}\right] \tag{4.6.1.7}$$

For $0 < Ei\,(-X) < 3$:

$$Ei(-X) = \ln(\gamma X) + \sum_{n=1}^{\infty}\left[\frac{(-N)^n}{n \cdot n!}\right] \tag{4.6.1.8}$$

where $X = \dfrac{r^2}{4\alpha t}$

and

$$\ln\gamma = \int_0^1 \frac{1 - e^{-t}}{t}\,dt - \int_1^{\infty} \frac{e^{-t}}{t}\,dt \tag{4.6.1.9}$$

$$\ln\gamma = 1 + \sum_{n=2}^{\infty}\left[\frac{1}{n} + \ln\left(\frac{n-1}{n}\right)\right] \tag{4.6.1.9a}$$

For $3 < Ei\,(-X) < 10$:

$$Ei(-X) = \left(\frac{1}{Xe^X}\right)\left(\frac{X^2 + 2.334733X + 0.250621}{X^2 + 3.3330657X + 1.681534}\right) \tag{4.6.1.10}$$

Well patterns:

$$\Delta T(x, y, t) = \frac{-F_1}{4\pi\lambda}\left[\sum_{n=1}^{m}\left\{Ei\left(-\frac{(x - x_n)^2 + (y - y_n)^2}{4\alpha t}\right)\right\}\right] \tag{4.6.1.11}$$

Heat Flow: Radiation (Steady State)

Linear:

$$F_o = S(T_1^4 - T_2^4)\left(\frac{1}{\frac{1}{e_1} + \frac{1}{e_2} - 1}\right) f \tag{4.6.1.12}$$

Vaporization

Dalton’s law:

$$p_t = \overset{\circ}{p}_1 + \overset{\circ}{p}_2 \ldots \overset{\circ}{p}_n \qquad (4.6.1.13)$$

$$f_1 + f_2 + \ldots f_n = 1 \qquad (4.6.1.14)$$

$$f_1 = \frac{\overset{\circ}{p}_1}{\overset{\circ}{p}_1 + \overset{\circ}{p}_2 + \ldots + \overset{\circ}{p}_n} \qquad (4.6.1.15)$$

Raoult's law:

$$p_t = x_1\overset{\circ}{p}_1 + x_2\overset{\circ}{p}_2 + \ldots + x_n\overset{\circ}{p}_n \qquad (4.6.1.16)$$

Steam distillation:

$$f_{w_1} = \frac{w_1}{w_1 + w_2} \qquad (4.6.1.17)$$

$$f_{w_1} = \frac{1}{1 + \left(\frac{M_2}{M_1} \cdot \frac{\overset{\circ}{p}_2}{\overset{\circ}{p}_1}\right)} \qquad (4.6.1.18)$$

Kinetics: First-Order Reactions

$$-\frac{dc}{dt} = k_1 c \qquad (4.6.1.19)$$

$$\frac{c}{c_o} = e^{-k_1 t} \qquad (4.6.1.20)$$

Arrhenius equation:

$$\ln(k/k_o) = -\frac{\Delta E}{RT} \qquad (4.6.1.21)$$

Combined equation:

$$\frac{c}{c_o} = e^{-k_o t e^{-\frac{\Delta E}{RT}}} \qquad (4.6.1.22)$$

Stoichiometric Reaction of Chlorinated Hydrocarbons

$$4\ C_x\,H_y\,Cl_z + (4x + y - z)\ O_2 + 4\ (4x + y - z)\ N_2 \Rightarrow$$

$$4x\ CO_2 + 2\ (y - z)\ H_2O + 4z\ HCl + 4\ (4x + y - z)\ N_2$$

$$w_{HCl} = w_{CHC} \cdot z\frac{M_{HCl}}{M_{CHC}} = w_{CHC} \cdot \frac{(36.5 \cdot z)}{(x \cdot 12 + y \cdot 1 + z \cdot 35.5)} \qquad (4.6.1.23)$$

$$w_{CHC} = \left(\frac{M_{CO_2}}{V_{M\,@\,STP}}\right)\left(\frac{M_{CHC}}{x \cdot M_{CO_2}}\right)\int_0^t c_{CO_2} q_p dt \qquad (4.6.1.24)$$

$$w_{CHC} = \left(\frac{M_{HCl}}{V_{M\,@\,STP}}\right)\left(\frac{M_{CHC}}{z \cdot M_{HCl}}\right)\int_0^t c_{HCl} q_p dt \qquad (4.6.1.25)$$

Material Balance

Contaminant:

$$m_c + \rho_c \int_0^t i_c dt = \rho_c \int_0^t q_c dt + r_c \qquad (4.6.1.26)$$

Water:

$$m_w + \rho_w \int_0^t i_w dt = \rho_w \int_0^t q_w dt + r_w \qquad (4.6.1.27)$$

Air:

$$\int_0^t i_a dt = \int_0^t q_a dt \qquad (4.6.1.28)$$

Energy Balance

$$lwh\{[\rho_R C_R(1-\phi) + \rho_w C_w \phi S_w](T_f - T_i) + \rho_w h_w \phi S_w\} + q_a t \rho_a C_a (T_f - T_i) = \frac{lwh}{A} F_1 t \qquad (4.6.1.29)$$

Permeability–Heat Flow/Superheat Gas Flow Balance

$$k_g = \frac{\mu_g V_M \lambda \Delta T}{\Delta p M_w\{h_v + C_w \Delta T_w + [(1-\phi)\rho_r C_r \Delta T_w / \phi S_w \rho_w] + C_g \Delta T\}} \qquad (4.6.1.30)$$

Nomenclature

Fluid Flow

$q_{L,R}$ = Flow rate [l^3 t^{-1}]
k = Absolute permeability [l^2]
k_r = Relative permeability
A = Area [l^2]
Δp = Pressure drop [m l^{-1} t^{-2}]
Δl = Flow path length [l]
μ = Viscosity [m l^{-1} t^{-1}]
r_e = Outer radius [l]

r_w = Well radius [l]
h = Length of well [l]

Conductive Heat Flow

ΔT = Temperature change [T]
x = Linear distance [l]
t = Time [t]
F_o = Heat injection rate/unit area [m t^{-3}]
λ = Thermal conductivity of soil [m l t^{-3} T^{-1}]
α = Thermal diffusivity of soil = λ/ρ C [1^2 t^{-1}]
ρ = Density of soil [m l^{-3}]
C = Heat capacity of soil [l^2 t^{-2} T^{-1}]
F_1 = Heat injection rate/unit length [m l t^{-3}]
q_{hL} = Linear heat flow rate [ml^2 t^{-2}]
q_{hR} = Radial heat flow rate [ml^2 t^{-2}]
r = Radial distance [l]
x,y = Well distances N- S and E- W [l]
m = Total well count
X = Argument of erfc and Ei functions
k, n = Integers
$\ln \gamma$ = Euler's constant = 0.577215665

Radiant Heat Flow

S = Stephan-Boltzmann constant [m t^{-3} T^{-4}]
e = Emissivities
f = Shape factor
T_1 = Emitting temperature [T]
T_2 = Absorbing temperature [T]

Vaporization

Dalton's law:

p = Total pressure [m l^{-1} t^{-2}]
$\overset{\circ}{p}_{1,2\ldots,n}$ = Vapor pressure of pure components [m l^{-1} t^{-2}]
$f_{1,2\ldots,n}$ = Mole fraction of pure components in vapor

Raoult's law:

$x_{1,2\ldots,n}$ = Mole fraction of miscible pure components in liquid
$\overset{\circ}{p}_{1,2\ldots,n}$ = Partial pressure of component in vapor [m l^{-1} t^{-2}]

Steam Distillation/Air Evaporation:

w_1 = Weight of high-boiling-point oleic contaminant in vapor [m]
w_2 = Weight of water or air in vapor [m]
f_{w_1} = Weight fraction of oleic contaminant in vapor
M_1 = Molecular weight of oleic contaminant [m mole^{-1}]
M_2 = Molecular weight of water or air [m mole^{-1}]

Kinetics

c = Concentration [eq m^{-1}]
c_o = Base concentration [eq m^{-1}]
k_1 = Kinetic constant [t^{-1}]
k_o = Reference kinetic constant [t^{-1}]
ΔE = Activation energy [m l^2 t^{-2} mole^{-1}]
R = Gas constant [m l^2 t^{-2} T^{-1} mole^{-1}]
T = Temperature [T]

Stoichiometry

w_{CHC} = Weight of chlorinated hydrocarbon produced [m]
w_{HCl} = Weight of HCl produced [m]
M_{CO_2} = Molecular weight of CO_2 [m mole^{-1}]
M_{CHC} = Molecular weight of chlorinated hydrocarbon [m mole^{-1}]
M_{HCl} = Molecular weight of hydrogen chloride [m mole^{-1}]
$V_{M@STP}$= Molar volume of a gas [l^3 mole^{-1}]
x = Number of C atoms/molecule
y = Number of H atoms/molecule
z = Number of Cl atoms/molecule
c_{CO_2} = Fractional concentration of CO_2 in product streams
c_{HCl} = Fractional concentration of HCl in product streams
q_p = Total flow rate of gas in product stream [l^3 t^{-1}]

Material Balance

m_c = Mass of contaminant [m]
ρ_c = Density of contaminant [m l^{-3}]
i_c = Inflow rate [l^3 t^{-1}]
q_c = Production rate [l^3 t^{-1}]
r_c = Residual contaminant [m]

Energy Balance

l = Length of site [l]
w = Width of site [l]
h = Height of site [l]
ρ_w = Density of water [m l^{-3}]
ρ_R = Density of mineral grains [m l^{-3}]
C_R = Heat capacity of mineral [l^2 t^{-2} T^{-1}]
ϕ = Porosity [-]
ρ_w = Density of water [m l^{-3}]
C_w = Heat capacity of water [l^2 t^{-2} T^{-1}]
S_w = Water saturation
q_a = Flow rate of air [l^3 t^{-1}]
ρ_a = Density of air [m l^{-3}]
C_a = Heat capacity of air [l^2 t^{-2} T^{-}]
T_f = Final temperature [T]
T_i = Initial temperature [T]
h_w = Heat of vaporization of water [l^2 t^{-2}]
F_1 = Well heat injection rate/unit length [ml t^{-3}]
t = Time of heating [t]
A = Area/injection well [l^2]

Permeability–Heat Flow/Superheat Gas Flow Balance

C_g = Heat capacity of gas [l^2 t^{-2} T^{-1}]
C_w = Heat capacity of liquid water [l^2 t^{-2} T^{-1}]
k_g = Gas permeability of heated soil [l^2]
h_v = Heat of vaporization of water [l^2 t^{-2}]
M_w = Molecular weight of water [m mole^{-1}]
Δ_p = p_b - p_s, vacuum needed to maintain negative pressure in soil [ml^{-1} t^{-2}]
T_b = Boiling temperature [T]
T_o = Initial soil temperature [T]
T_s = Source heater temperature [T]

ΔT = T_s - T_b, temperature change from vacuum source to boiling front [T]

ΔT_w = T_b - T_o, temperature change from ambient to boiling [T]

μ_g = Viscosity of gas [$\mathrm{ml}^{-1}\ \mathrm{t}^{-1}$]

4.6.2 *Ex Situ* Thermal Desorption

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Introduction

Definition of *Ex Situ* Thermal Desorption

Ex situ thermal desorption is defined as "a process that uses either indirect or direct heat exchange to heat organic contaminants to a temperature high enough to volatilize and separate them from a contaminated solid medium" (U.S. EPA, 1991). *Ex situ* thermal desorption is typically used for the treatment of contaminated soil sediments. *Ex situ* treatment includes excavation, treatment, and on-site backfill of impacted soil. The contaminants in the off-gas can be either destroyed or captured for off-site disposal by an emission control system.

History
The first commercial use of *ex situ* thermal desorption was at the McKin site in Grey, Maine, in 1987. This site consisted of 17,500 tons of VOC contaminated soil. Since this first use of the technology, many contractors have designed and constructed mobile systems that can be moved from site to site to process contaminated media. With public concerns and the high cost associated with incineration, thermal desorption became the technology of choice in the late 1980s and early 1990s for remediating sites with semivolatile organic contaminants.

Advantages of Thermal Desorption
Ex situ thermal desorption has several advantages that make the technology more attractive than incineration in many circumstances. The key advantages of *ex situ* thermal desorption over incineration for treatment of organic contaminated soils include:

- More rapid startup and shutdown time due to a lack of refractory in the primary heating chamber
- Lower soil exit temperatures
- Process operating conditions can be readily adjusted to meet soil treatment criteria
- Higher soil throughputs, thus reducing remediation schedules and costs
- Typically easier to gain community acceptance

Thermal desorption also competes with other remedial technologies such as capping, bioremediation, etc. Advantages of thermal desorption over these technologies include:

- Treatment results can be reliably estimated through laboratory-scale treatability tests
- Achievable residual concentrations of contaminants are typically less than 1 mg/kg or lower, depending on the vapor pressure of the contaminants present and the exit soil temperature from the desorber

- Application of thermal desorption to remediate a site usually requires much less time than other technologies
- Thermal desorption is a permanent solution because contaminants are removed at a very high efficiency, thus resulting in very low residual risks

Evaluation of the costs and advantages of using thermal desorption instead of other alternatives is typically a complicated process and highly site specific.

Thermal Desorption Theory

General Theory

Thermal desorption systems are based on the principle that the vapor pressure of organic contaminants increases as a function of temperature. As the contaminated soil is heated, organic compounds are vaporized and driven from the contaminated soil into a purge gas stream for collection or further treatment. Contaminants generally must be heated to temperatures near their boiling points for thermal desorption to be effective. In systems that operate under vacuum conditions, the boiling point of the contaminants present in the soil being treated are depressed proportional to the amount of vacuum applied.

Contaminant Types

Thermal desorption is applicable for the remediation of several different types of contaminants, including petroleum contaminants, volatile and semivolatile organics, polychlorinated biphenyls (PCBs), pesticides,, and dioxins/furans. In general, thermal desorption has minimal impact on the removal of inorganic contaminants with the exception of mercury, which has a very low boiling point. Thermal desorption has typically been utilized to treat organic contaminated soil, but it has also been utilized to remediate mercury contaminated soil.

Energy Requirements

To facilitate vaporization of contaminants, the contaminated soil must be heated from ambient conditions to the desired treatment temperature. Soil requiring treatment typically contains moisture at concentrations ranging from 5 to 40 wt%. The moisture must be heated and vaporized from the soil before the solid portion of the soil can be heated to reach the desired treatment temperature. A major portion of the energy required to treat contaminated soil is usually associated with vaporization of moisture. Figure 4.6.2.1 shows the energy required to heat the feed soil (soil and moisture) from 60 to 600°F as a function of the starting moisture content. The data presented in Figure 4.6.2.1 includes only the energy required to heat the soil and moisture in the feed and excludes the energy required to heat the combustion products and excess air from the heat source. Figure 4.6.2.1 also shows that even at a relatively low moisture content (10 wt%), over half of the energy is needed to heat and vaporize the moisture.

Treatment Time and Temperature

Each site typically has clean-up goals established for the contaminants of concern. To achieve the established clean-up goals, a combination of residence time and treatment temperature must be maintained. Various combinations of treatment temperature and residence time can achieve the same clean-up goal for a given contaminant. Increased residence time at a given treatment temperature, or increased temperature at a given residence time, will typically reduce the residual concentration of the contaminants in the treated soil. As the concentration of an organic contaminant increases, so does the treatment time and/or treatment temperature required to achieve a given residual contaminant concentration. Treatability testing or historical data is commonly used to determine the treatment temperature and residence time required to achieve clean-up goals.

Typical soil treatment temperatures and residence times for *ex situ*, continuous-feed thermal desorbers are in the range of 260 to 650°C (500 to 1200°F) and 5 to 40 min. Residence time for batch-feed thermal desorption systems are typically in the range of 2 to 4 hr. A graph of full-scale data showing the residual concentration of beta-BHC (beta-benzene hexachloride) as a function of soil treatment temperature is shown in Figure 4.6.2.2. The data trend in Figure 4.6.2.2 is typical for residual contaminant concentrations as a function of soil treatment temperature.

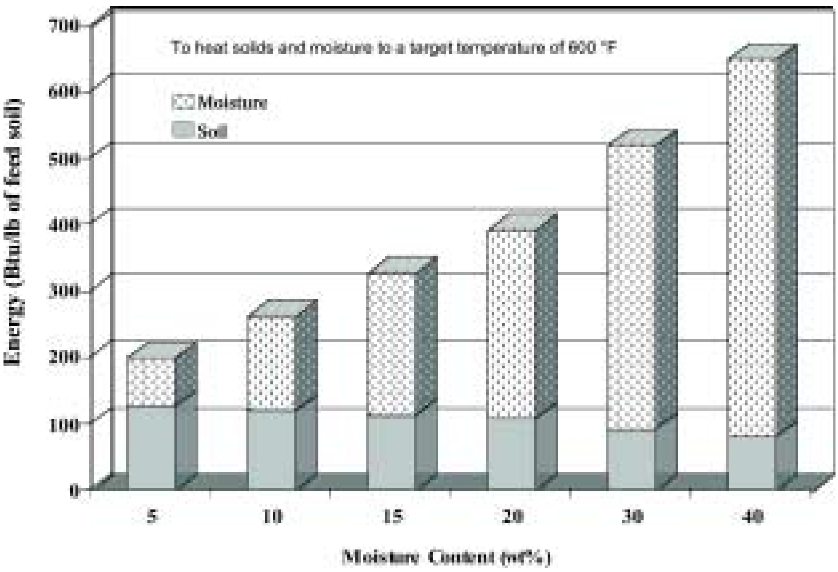

FIGURE 4.6.2.1 Energy requirements diagram.

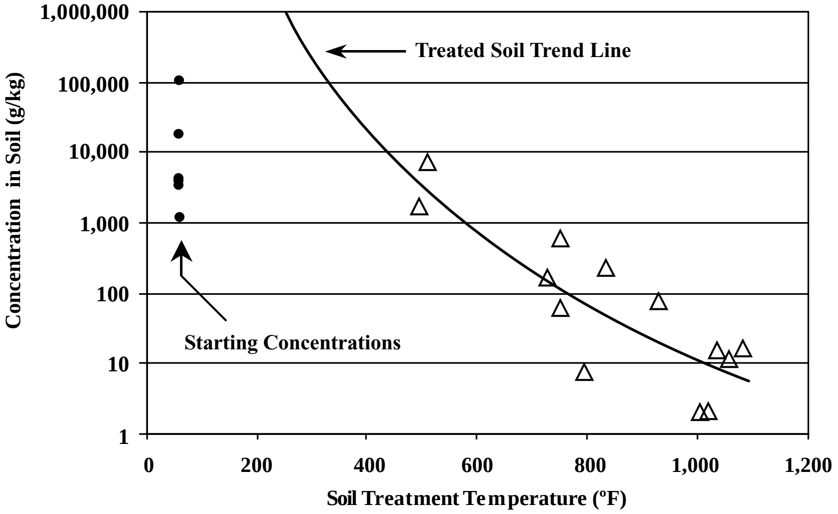

FIGURE 4.6.2.2 Residual beta-BHC vs. soil exit temperature.

The maximum soil discharge temperature that an *ex situ* thermal desorber can attain is a function of the construction material of the primary chamber. The maximum soil discharge temperature for thermal desorbers made from carbon steel is approximately 371°C (700°F). Higher treatment temperatures would require the primary chamber of the desorber to be made from alloy materials.

Soil Type

Soil type has several effects on the application of *ex situ* thermal desorption. These effects include the ability to pretreat and feed contaminated soil, the removal kinetics of organic compounds from the contaminated soil, and the degree of particulate carry-over from the thermal desorber into the emission control system.

Soil that has a high clay content tends to agglomerate as the moisture content increases, making it difficult to handle and feed to the thermal desorber. Wet soil can stick to materials transfer equipment, screens, and feed belts if the moisture content exceeds the Atterberg limit (ASTM Method 4318-93). Sandy soils are not cohesive and typically are much easier to handle.

Adsorption is primarily a surface phenomena. Therefore, contaminants bound to materials with high surface-to-volume ratios are much more difficult to desorb than contaminants on materials with a low surface-to-volume ratio. Therefore, contaminants adsorbed on granular, free-flowing materials such as sand and gravel are much easier to desorb than contaminants adsorbed on clay soils.

Clay soils have much lower permeabilities than sand, thus decreasing the rate of heat transfer and rate of diffusion of organics out of the soil matrix. Clay soils also have a high surface-to-volume ratio compared to sand, which enhances the adsorption of contaminants to soil particles, thereby decreasing desorption rates.

The fraction of particulate carry-over from the primary heating chamber of a thermal desorber is impacted by the following factors:

- Grain size distribution of the soil
- Soil cohesion characteristics
- Type and degree of solids mixing within the thermal desorber
- Gas velocity through the thermal desorber
- Gas/solids flow pattern in the thermal desorber

The fraction of particulate carry-over from the primary heating chamber of a thermal desorber to the emission control system may range from 1 to 30% of the feed material, depending on the factors listed above.

Application of *Ex Situ* Thermal Desorption

Basic Designs

There are numerous designs and configurations of *ex situ* thermal desorbers commercially available for conducting remedial actions. Figure 4.6.2.3 provides a general schematic for *ex situ* thermal desorption processes. The basic design consists of (1) a primary heating chamber and (2) an emission control system (ECS).

The primary heating chamber can be either directly or indirectly heated. Directly heated systems utilize an auxiliary fuel-fired burner to produce a hot gas that is contacted directly with the soil to desorb the contaminants. The volatilized contaminants are mixed with the hot gas produced by the burner and exhausted to the ECS for collection or further treatment. Figure 4.6.2.4 provides a general diagram of a directly heated primary chamber, showing the hot gas from the primary burner in direct contact with the contaminated soil. Indirectly heated systems transfer heat through a shell to heat the soil. Figure 4.6.2.5 provides a general diagram of an indirectly heated primary chamber, showing that the hot gas from the primary burners is contained in an annulus around the rotating shell which contains the contaminated soil. Heat is transferred by conduction from the hot gas to the soil through the metal shell of the rotating chamber. With this configuration, the off-gas volume is much smaller than for a directly heated desorber; therefore, the emission control system equipment is typically smaller.

ECSs can be either of "destructive-type" or the "recovery-type." Destructive-type systems use a thermal oxidizer to destroy organic contaminants and use various combinations of cyclones, baghouses, venturi scrubbers, and packed scrubbers to remove particulates and acid gases from the off-gas stream. Because destructive-type systems oxidize the organic contaminants, there are no residual streams requiring off-site disposal. Recovery-type systems typically use wet scrubbers, condensers, and granular activated carbon to recover organics from the off-gas stream. The process residuals from a recovery-type system include spent activated carbon, organic liquid condensate, organic sludge, and filter cake. Residual streams from recovery-type systems are typically shipped off-site for further treatment at a commercial treatment, storage, and disposal facility.

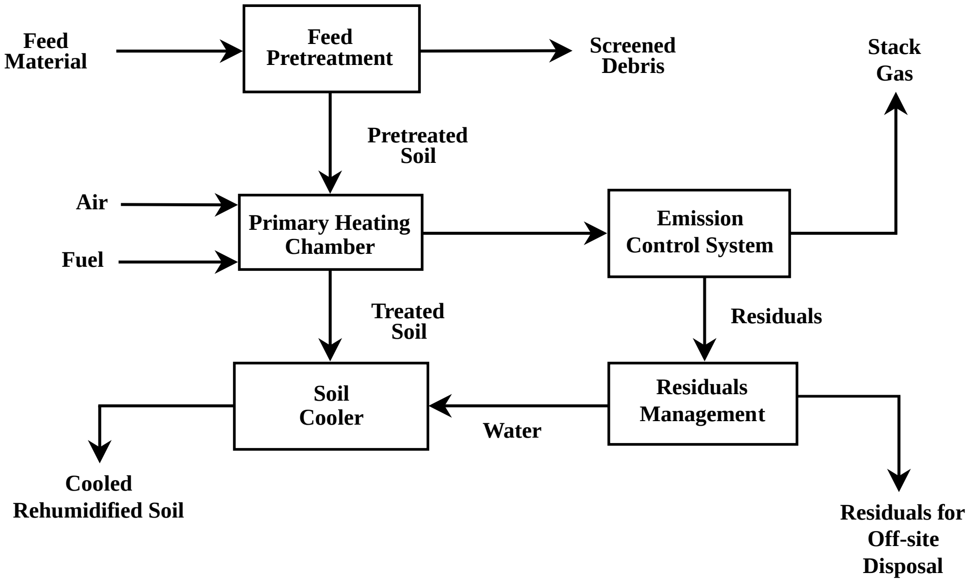

FIGURE 4.6.2.3 Thermal desorption process components.

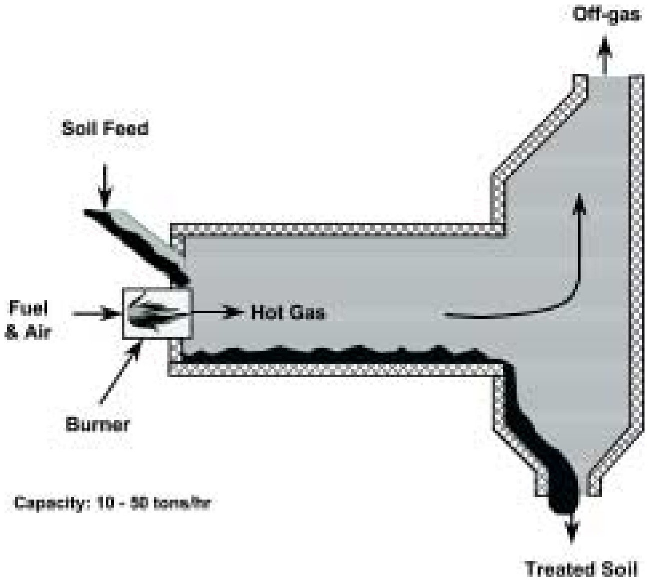

FIGURE 4.6.2.4 Directly heated rotary dryer.

A brief description of two typical process configurations is presented below.

Directly Heated Rotary Dryer: Destructive Emission Control System

A directly heated rotary dryer consists of a cylindrical chamber that is inclined slightly to the horizontal. Soil is fed into one end of the cylinder by a belt or screw conveyor. The dryer rotates and conveys the solids through the dryer. A series of lifters mounted inside the dryer shell lift the soil and drop it through the hot gas. Rotary dryers can be either co-current (soil and process gas flow in the same direction) or countercurrent (soil and process gas flow in opposite directions).

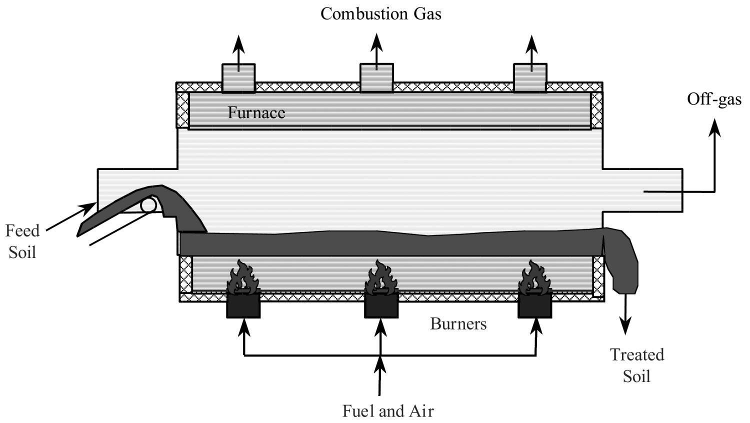

FIGURE 4.6.2.5 Indirectly heated rotary dryer.

Directly heated rotary dryers utilize a burner (propane, natural gas, or fuel oil) mounted at one end of the rotating cylinder as a heat source. The hot gas from the burner is discharged into the rotating cylinder in direct contact with the contaminated soil. The hot gas heats the soil, and the contaminants are volatilized and swept from the thermal desorber along with the hot gas produced by the burner into the ECS. Because the hot gas from the burner is mixed with the volatilized contaminants, the gas flow rate entering the ECS is relatively large compared to the gas flow from an indirectly heated system.

Directly heated systems typically operate with thermal desorber gas velocities in the range of 1.5 to 4.5 m/s (5 to 15 ft/s) which can result in 5 to 30% particulate carry-over, depending on the soil characteristics and the flow pattern (countercurrent vs. co-current). Throughputs for directly heated systems can range from 10 to 50 tons/hr, depending on the specific process and characteristics of the soil requiring treatment.

The ECS typically includes a cyclone, baghouse, afterburner, quench chamber, and wet scrubber. The cyclone and baghouse remove particulates, the afterburner destroys organic contaminants, the quench chamber cools the gas, and the wet scrubber removes acid gases.

Figure 4.6.2.6 is a photo of a typical directly heated thermal desorber with a destructive-type ECS.

Indirectly Heated Rotary Dryer: Recovery Emission Control System

Indirectly heated rotary dryers utilize a cylindrical metal shell that rotates inside a furnace. A series of burners are fired into the space between the inside of the furnace wall and the outside of the dryer shell. Heat is transferred through the dryer shell to the contaminated soil. The contaminants are volatilized and exhausted to the ECS. The combustion products from the burners do not mix with the volatilized contaminants and are exhausted through a separate set of stacks. Because the combustion products from the heat source are kept separate from the desorbed contaminants, the gas flow exiting to the ECS is very low, consisting only of the moisture and organic materials that were volatilized from the feed soil and any air that leaked into the system.

Because of the lower gas flow rates, indirectly heated systems typically operate at thermal desorber gas velocities much lower than for directly heated systems. Gas velocities in indirectly heated systems are typically 0.15 to 0.6 m/s (0.5 to 2 ft/s). The fraction of particulates carried over from the primary heating chamber of a thermal desorber to the ECS may range from 1 to 5% of the feed material. Throughputs for indirectly heated systems range from 5 to 25 tons/hr, depending on the specific process and characteristics of the soil requiring treatment.

Indirectly heated rotary dryers almost always use a recovery-type ECS that may include a number of unit operations. Typical types of unit operations in the ECS include a quench chamber and/or wet scrubber, baghouse, condenser, reheater, and vapor-phase activated carbon adsorption.

Figure 4.6.2.7 is a photo of a typical indirectly heated thermal desorber with a recovery-type ECS.

FIGURE 4.6.2.6 Directly heated thermal desorber: destructive ECS.

FIGURE 4.6.2.7 Indirectly heated thermal desorber: recovery ECS.

Other Configurations

The two process configurations summarized above are the predominant configurations used for thermal desorption systems. In some cases, directly heated desorbers with recovery-type ECSs or indirectly heated desorbers with destructive-type ECSs have been used to remediate sites. Other designs such as infrared vacuum systems have also been used.

The infrared vacuum system is a batch treatment unit consisting of a rectangular chamber with a set of hinged doors that allows a tray of contaminated soil to be placed in the chamber. Propane-fired radiant tube heaters mounted near the top of the unit provide indirect heating of the contaminated soil. A vacuum of approximately 550 to 660 mmHg is pulled on the system prior to initiation of the heating cycle. The soil is typically heated to a temperature ranging from 149 to 232°C (300 to 450°F). Residence time for each batch of soil typically ranges from 2 to 4 hr, and the off-gas from the system is managed with a recovery-type ECS.

Figure 4.6.2.8 provides a summary of the relative utilization rates of different process configurations for remediation of CERCLA (Comprehensive Environmental Response, Compensation and Liability Act; Superfund) sites.

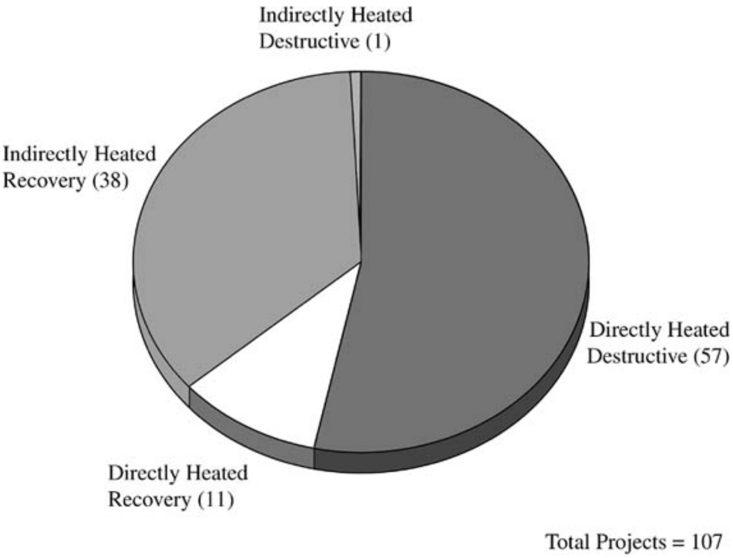

FIGURE 4.6.2.8 Configuration utilization.

Site Factors

Key site factors that affect the application, performance, and treatment cost of *ex situ* thermal desorption at contaminated sites include:

- Site size
- Soil characteristics
- Organic content
- Feed solids moisture content
- Potential for acid gas formation
- Contaminant clean-up goals

A brief discussion of these key factors is presented below.

Site Size. Site size can range from a few hundred tons to over 100,000 tons. For sites containing less than 30,000 tons, both indirectly and directly heated desorbers have competed equally for the market. For sites with soil quantities in excess of 30,000 tons, directly heated desorbers are more commonly used because of the higher throughput capabilities that can decrease the duration of the remedial action and facilitate a reduced cost.

Soil Characteristics. Sandy soil is typically drier and much more easily handled than clay soil. Throughputs are typically much higher for a sandy soil than for a clay soil if all other factors are equivalent (moisture content, organic content, clean-up levels, etc.). Thermal treatment of soil with a high clay content (more fines) will result in increased carry-over of soil to the ECS. The fines are typically captured in the ECS and combined with the treated soil. If the fines contain significant concentrations of the contaminants of concern and the clean-up goal is relatively low, the process may fail to achieve the clean-up goal for the treated soil.

Soil characteristics also impact material handling operations. Soils must be excavated, transported, and conveyed into the thermal desorption process. Clay soil containing moisture in excess of the plastic limit can agglomerate to the handling equipment and be difficult to screen and convey into the thermal desorber. Sandy soils typically do not agglomerate and are much easier to manage.

Organic Content. The concentration of organics in the feed impacts several key elements of the thermal desorption process, including:

- Residence time and temperature required to achieve treatment standards
- Safety considerations related to the concentration of the organics in the off-gas
- Quantity of residuals generated and requiring off-site disposal

As the concentration of organics in the feed increases, a corresponding increase in the exit soil temperature or residence time may be required to maintain compliance with the clean-up goals.

If a recovery-type ECS is used, the organic content of the starting soil may have an impact on the quantity of residuals that can be generated from processing of the soil. Also, high-boiling-point organics that are vaporized at treatment temperatures can sometimes condense and foul emission control equipment. It is very important to evaluate the quantity and characteristics of organics in the feed soil that may be imparted to the ECS if a recovery-type emission control system is used. A common mistake made in this evaluation is to only consider the measured concentrations of contaminants of regulatory concern. Evaluation of the organic content of the feed soil should consider all organic material that has the potential to be vaporized at the process operating conditions, and not just the contaminants of regulatory concern.

Applications in which the feed soil has a total organic content in excess of 2 wt% must be carefully evaluated to determine if explosive environments could be generated. Sufficient organic vapors (>25% of the lower explosive limit [LEL]) and a minimum oxygen content (MOC, typically >8 vol% O_2, but dependent on the specific organic material) must be present in the off-gas to cause potential problems.

Moisture Content. The feed soil moisture content has a major impact on the amount of energy required to evaporate the moisture from the soil. As the feed moisture content increases, process throughput decreases and treatment costs increase. Figure 4.6.2.9 shows the theoretical impact of moisture content on the throughput of a thermal desorption system. Throughput decreases drastically with increasing moisture content.

Moisture content also affects the material handling properties of clays. Clay soils exhibit cohesive characteristics at moisture contents above the Atterberg plastic limit and can be difficult to feed to the system and treat because of the tendency to stick to process equipment and consolidate into larger pieces. These large pieces can also inhibit heat transfer in the thermal desorber.

Acid Gas Formation. The contaminants of concern in the soil feed to thermal desorbers are often chlorinated. The organic chlorine atoms are often stripped from the contaminants of concern and can form hydrogen chloride (HCl), which must be managed in the ECS. Some sites may also contain sulfur in the feed soil that can be converted to sulfur dioxide (SO_2) and form sulfuric acid ($H_2 SO_4$) in the ECS. Both HCl and $H_2 SO_4$ must be considered in the application of thermal desorption technology both from a corrosive and emission perspective.

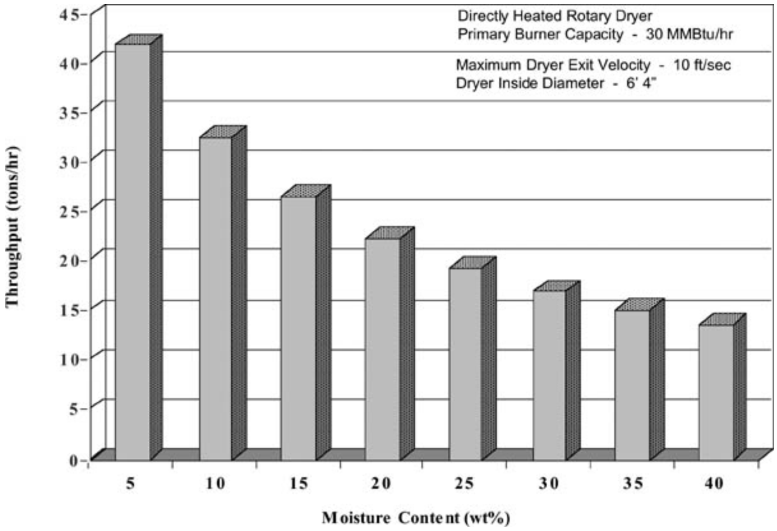

FIGURE 4.6.2.9 Impact of moisture content on throughput.

Contaminant Clean-Up Goals. Clean-up goals for specific sites are often risk based and can be low, requiring long residence times and high exit soil temperatures to meet clean-up goals. Clean-up goals are often established near or below the detection limits for applicable analytical methods used to demonstrate compliance. In these cases, negotiations with the applicable regulatory agency are required to establish a contingency plan for when analytical results are non-detectable at concentrations above the clean-up goal.

Site Layout and Space Constraints

Contaminated sites are sometimes small with space constraints that must be carefully considered. A detailed evaluation of space requirements must be conducted early in the planning phase to assess the adequacy of space for the equipment and support facilities. For *ex situ* thermal desorption to be accomplished, space must be provided for the following:

- Parking
- Office trailers
- Shop and maintenance area
- Thermal desorber footprint
- Feed and treated soil management area (pretreatment and stockpiles)
- Wastewater treatment and storage
- Debris and treatment residuals storage
- Equipment decontamination stations

In addition, during development of the site layout, the following must be considered:

- OSHA (Occupational Safety and Health Administration) work zones
- Traffic patterns (haul roads, site access, exit from contaminated zone)
- Site drainage
- Existing site conditions (trees, roads, railroads, wells, buildings, etc.)

It is often necessary to obtain access to adjacent property to provide sufficient space for remedial activities. However, gaining access to adjacent properties can be a difficult and lengthy process, depending on relationships with adjacent property owners. Again, early and thorough planning is critical.

Residuals

Ex situ thermal desorption processes generate residuals that must be managed. Thermal desorption processes can generate some or all of the following residuals:

- Debris
- Treated soil
- Baghouse dust
- Treated water
- Filter cake
- Organic condensate
- Vapor-phase granular activated carbon
- Aqueous-phase granular activated carbon

Debris is typically decontaminated and shipped off-site for disposal. Treated soil is typically cooled, rehumidified, and backfilled on-site. Baghouse dust is typically combined with the treated soil to be cooled and rehumidified prior to backfilling on-site. The rehumidified treated soil is sampled and analyzed to determine if the clean-up goals have been achieved. A wastewater treatment process is necessary to manage water blowdown from the ECS. Treated water from the wastewater treatment system is typically used to quench the off-gas or cool and rehumidify the treated soil. Filter cake from the wastewater treatment system is typically reprocessed or disposed of off-site. In some cases, filter cake may meet clean-up goals and can be blended with treated soil and backfilled on-site. This typically would be the case when a process with a destructive-type ECS is used.

If a process with a recovery-type ECS is used, the filter cake, organic condensate, and spent activated carbon residuals are more likely to be generated.

The quantity of residuals generated by a recovery-type ECS can add significant operating cost, depending on the quantity of residuals. The quantity of residuals generated is primarily a function of the organic content of the feed soil, characteristics of organics imparted to the off-gas, and the operating conditions of the ECS. Treatability testing is required to effectively estimate the quantity of residuals that may be generated from a thermal desorber with a recovery-type ECS.

Treatment Costs: *Ex Situ* Thermal Desorption

Cost Components

Total treatment costs associated with the execution of an *ex situ* thermal desorption project can be categorized as fixed costs and unit costs. Components of the fixed costs include:

- Project planning and design
- Site preparation
- Mobilization, erection, or assembly
- Startup and shakedown
- Performance testing
- Decontamination and demobilization
- Site restoration

Components that are typically unit costs include:

- Excavation
- Thermal treatment

- Backfill
- Off-site disposal

The actual costs of each component are site specific. For example, site preparation costs may be significant if the site is not near a major road or existing utilities. The cost of extending access roads and utilities (power, water, phone lines, etc.) can vary significantly from one site to the next. The unit cost for thermal treatment can be very site specific, as described below.

Thermal Treatment Unit Cost

The magnitude of the unit cost for thermal treatment is also very site specific. The primary factors affecting the magnitude of the unit cost for thermal treatment include:

- Site size
- Moisture content
- Throughput capacity
- Residual disposal costs

A brief description of how each of these factors impact the unit cost for thermal treatment is provided below.

Site Size. Given a larger site (i.e., a relatively large quantity of soil to treat), contractors will be able to keep equipment and personnel busy for longer periods of time. This can be a significant incentive to lower the unit cost for treatment and win the job.

Moisture Content. As previously described, the moisture content of the feed soil can have a significant impact on material handling, fuel requirements, and throughput. Typically, the higher the moisture content, the higher the unit cost for thermal treatment.

Throughput Capacity. There is a minimum labor force required to operate a thermal desorption system, regardless of the throughput of the unit. As the throughput capacity of the thermal desorption system increases, additional labor may need to be added; but in general, the cost of labor per unit of soil treated decreases as the throughput of the system increases.

Residual Disposal. The cost for off-site disposal of residuals is typically included in the unit cost for treatment. Therefore, as the mass of residuals requiring off-site disposal per unit mass of soil treated increases, the unit cost for thermal treatment also increases.

Total Treatment Costs

The total treatment cost for completing an *ex situ* thermal desorption project, including all the cost components previously listed, is highly site specific and currently ranges from $100 to $200 per ton of soil, with the average cost being approximately $155 per ton. Figure 4.6.2.10 presents the cost components and the relative portion that each component is of the total treatment cost. Figure 4.6.2.10 is based on actual bids from eight sites received during the 1992 to 1998 time frame. The average site size for these eight sites was 29,000 tons. This figure shows that the treatment cost is the largest component (approximately one half) of the total treatment cost.

Summary

Ex situ thermal desorption is a full-scale remedial technology that has been proven to be technically sound and cost-effective at numerous contaminated sites. Several factors impact the effectiveness and cost of applying thermal desorption to a specific site. Each of these factors must be carefully considered to determine whether application of thermal desorption is appropriate.

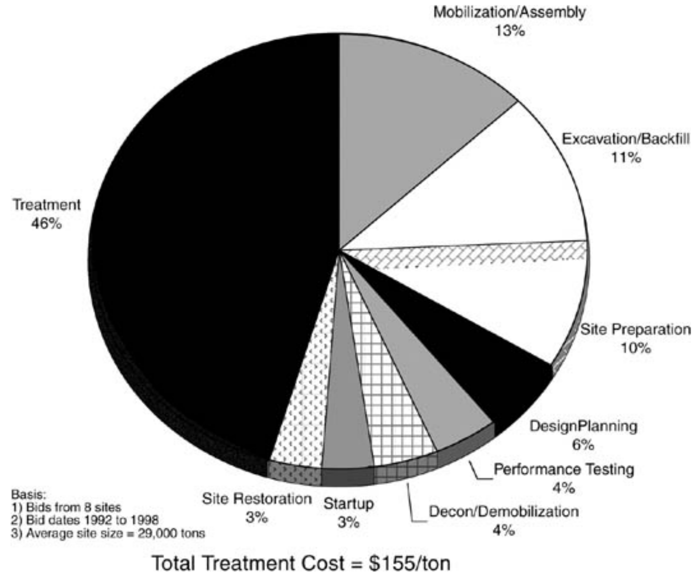

FIGURE 4.6.2.10 Breakdown of total treatment costs.

Defining Terms

BHC: Benzene hexachloride.

CERCLA: Comprehensive Environmental Response, Compensation and Liability Act (often referred to as Superfund).

Destructive-type: Refers to a thermal desorption system that uses an afterburner to completely destroy the organics discharged from the primary heating chamber of the thermal desorption system.

ECS: Emission Control System. Also called air pollution control system (APC system).

LEL: Lower Explosion Limit. This is the lowest concentration of a compound or material in air that could explode if an ignition source is present.

MOC: Minimum Oxygen Concentration. This is the minimum concentration of oxygen required to sustain an explosive reaction in the presence of an explosive material. If the oxygen concentration is less than the MOC, an explosion is not likely to occur. The MOC varies with specific materials.

OSHA: Occupational Safety and Health Administration. This is a branch of the federal government that is responsible for establishing worker safety laws and requirements. Specific regulations that govern workers at CERCLA sites are contained in 40 CFR 1910.120.

PCBs: Polychlorinated biphenyls.

Recovery-type: Refers to a thermal desorption system that is designed to condense and capture organics discharged from the primary heating chamber of the thermal desorption system. The captured organics form residuals that must be shipped off-site for disposal.

U.S. EPA: United States Environmental Protection Agency.

VOC: Volatile organic compound.

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For Further Information

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4.7

Molten Salt Oxidation

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Introduction

Molten salt oxidation (MSO) is a promising alternative to incineration for the treatment of a variety of organic wastes. It is a non-flame thermal treatment process and it completely destroys (oxidizes) the organic constituents of mixed wastes or hazardous wastes, including energetic materials, while retaining inorganic and radioactive constituents in the salt.

MSO technology is not new. Rockwell used the process more than 30 years ago for coal gasification, and also demonstrated its effectiveness for destroying certain hazardous organics, such as PCBs and trichloroethylene.[1] Extensive experience with laboratory-, bench-, and pilot-scale MSO units has been obtained at Rockwell, Oak Ridge National Laboratory, and Lawrence Livermore National Laboratory since the technology's introduction.[2-4] Within the past 5 years, MSO also has been demonstrated as an effective method for destroying mixed waste oils and energetic materials. Unlike incineration, in MSO the large thermal mass of molten salt provides a stable heat-transfer medium that resists thermal surges, ensures uniform temperature, and tolerates rapid process fluctuations. Flame-outs are completely avoided because MSO is a non-flame process that proceeds by catalytic, liquid-phase oxidation reactions. MSO generates less off-gas than incineration because it does not require supplemental fuel to sustain a flame. The MSO system operates at temperatures hundreds of degrees cooler than flame-combustion temperatures, which minimizes emissions of radioactive materials from mixed wastes. Acid gases are "scrubbed" by alkali salts, eliminating the need for a wet off-gas scrubbing system. Lower operating temperatures, containment of toxic metals and acid gas precursors, and related features are expected to simplify permitting of a commercial MSO system.

Process Description

MSO is a robust thermal treatment process for destroying organic waste. In this process, organic wastes are injected with a stoichiometric excess of oxidant air under a pool of molten carbonate salts at temperatures between 700 and 950°C. Flameless oxidation takes place within the salt bath converting the organic components of the waste into CO_2, N_2, and H_2O. The product off-gas leaving the processor is treated to remove any entrained salt particulate and essentially all water vapor before being discharged to the facility off-gas system. Halogens and heteroatoms such as sulfur are converted into acid gases, which are then "scrubbed" and trapped in the salt in forms such as NaCl and Na_2SO_4. Using sodium carbonate (Na_2CO_3) in the processor, this process occurs according to the reaction shown in Equations (4.7.1) through (4.7.4), where X represents generic halogens.

$$2C_aH_b + (2a + b/2)O_2 \rightarrow 2aCO_2 + bH_2O \tag{4.7.1}$$

For nitrogen-bearing organic wastes,

$$C_aH_bN_c + O_2 \rightarrow CO_2 + H_2O + N_2 + NO_x \tag{4.7.2}$$

For halogenated organic wastes,

$$C_aH_bX_c + c/2Na_2CO_3 + (a + (b - c)/4)O_2 \rightarrow (a + c/2)CO_2 + b/2H_2O + cNaX \tag{4.7.3}$$

For sulfur-containing organic wastes,

$$C_aH_bS_c + cNa_2CO_3 + (a + b/4 + 3c/2)O_2 \rightarrow (a + c)CO_2 + b/2H_2O + cNa_2SO_4 \tag{4.7.4}$$

Other non-oxidizable inorganic constituents, heavy metals, and radionuclides are held captive in the salt, either as metals or oxides, and are easily separated for disposal.

The salt remains in the bed catalyzing the destruction of waste until either the viscosity increases above acceptable levels or the carbonate salt is transformed into halide or heteroatom salts. Inorganic constituents captured in the bed eventually increase the bed viscosity above acceptable limits. These viscous salts are processed through the salt recycle system to remove the inorganic constituents and the salt is recycled to the bed.

Wastes that contain acid gas precursors such as chlorine, sulfur, and other heteroatoms eventually displace most of the carbonate in the salt to form the corresponding salts (e.g., sodium chloride). These salts are easily disposed of, especially in comparison to the similar volume of salts from an acid gas scrubber that must be disposed of when the wastes are processed in a conventional thermal treatment system.

Molten Salt Reaction Mechansim

The oxidation of organic wastes in the molten salt has been demonstrated by several research groups over past 30 years. While the chemical reactions shown in Equations (4.7.1) to (4.7.4) represent the overall reaction, the carbonate moiety actually plays a major role in the oxidation/reaction of wastes.[5,6] The formation of sodium peroxide in the molten sodium carbonate and its role in the oxidation of carbon and hydrocarbons are important. Dunks et al.[8] reported on the oxidation of carbon in the presence of sodium carbonate. The effect of sodium carbonate is to lower the oxidation temperature by 150°C, thus acting as a rather efficient catalyst for the oxidation. The mode of the catalytic effect is believed to be the formation of sodium peroxide,[7,8] which then participates in an oxidation/reduction cycle with sodium oxide, oxygen, carbon, carbon monoxide, and carbon dioxide. Consistent with electrochemical studies, which have shown that peroxide ion is formed directly from molten alkali carbonates and oxygen,[9] the sequence of reactions for the oxidation of carbon in molten sodium carbonate given by Equations (4.7.5) through (4.7.9) was proposed.[8]

$$Na_2CO_3 + 1/2\ O_2 \rightarrow Na_2O_2 + CO_2 \tag{4.7.5}$$

$$Na_2O_2 + C \rightarrow Na_2O + CO \tag{4.7.6}$$

$$Na_2O + 1/2\ O_2 \rightarrow Na_2O_2 \tag{4.7.7}$$

$$Na_2O_2 + CO \rightarrow Na_2O + CO_2 \tag{4.7.8}$$

$$Na_2O + CO_2 \rightarrow Na_2CO_3 \tag{4.7.9}$$

The sum of the sequence is represented by Equation (4.7.10).

$$C + O_2 \rightarrow CO_2 \tag{4.7.10}$$

Salt Selection

The use of molten salts as a medium for organic reactions has been known for a long time. A reaction temperature as low as 200°C is possible in low-melting-point salts such as $AlCl_3$. The use of molten salt for waste destruction was not studied until about 30 years ago. Rockwell International initiated a research program aimed at using molten salt oxidation for waste destruction at high temperature using ceramic crucibles. The process efficiency and quality of the product gas was found to be very sensitive to the salt temperature. For a thermal process, process efficiency improves as the salt temperature rises; however, NO_x levels in the product gas also increase. Therefore, careful selection of the salt temperature and salt composition is important for the MSO process. Table 4.7.1 shows the melting points of several candidate salts for the MSO process.

TABLE 4.7.1 Melting Points of Carbonate-Based Salt Mixtures

Melting Point, (°C)	Compositions, (wt. fraction)				
	Na_2CO_3	K_2CO_3	Li_2CO_3	K_2SO_4	KCl
890		1.000			
850	1.000				
723			1.000		
710	0.525	0.475			
680	0.782		0.218		
680	0.450	0.506	0.044		
680	0.501	0.304		0.195	
680	0.455	0.479			0.066
580	0.664		0.336		
580	0.375	0.503	0.122		
580	0.414	0.359			0.227

Comprehensive testing and demonstration at Lawrence Livermore National Laboratory showed that process efficiencies as high as 99.9999% can be achieved at salt temperatures above 900°C.[3,4]

Recent Activities in MSO Technology Development

Currently several organizations are actively engaged in the development of MSO technology for waste treatment. These organizations include Lawrence Livermore National Laboratory (LLNL); Indian Head Division of the U.S. Navy; Los Alamos National Laboratory (LANL); ATG, Inc.; and the Molten Salt Oxidation Corporation (MSO Corp.).

MSO Activities at LLNL

Lawrence Livermore National Laboratory (LLNL) was tasked by the U.S. Department of Energy's Office of Environmental Management (DOE/EM) to demonstrate the MSO technology for the treatment of organic-based mixed wastes. Since early 1990, the the LLNL MSO team has built several MSO units of different sizes, ranging from bench-scale units, a two-stage unit, to the 8-in. ID engineering-scale reactor unit (EDU). In 1997, the team built a facility in which an integrated pilot-scale MSO treatment system was demonstrated. This integrated system was designed and engineered based on the operational experience with the EDU and extensive laboratory development on salt recycle and final forms preparation. Treatment of over 30 different feed streams was demonstrated in the integrated MSO system from October 1997 to May 1999. These feed streams included surrogates and real waste streams, both liquid and solid. Results of the demonstrations have been documented and reported.[3,4]

The integrated MSO demonstration system, shown schematically in Figure 4.7.1, consists of several subsystems. It includes a reactor vessel, an off-gas treatment system, a salt recycle system, and a ceramic final waste forms immobilization system. The waste, either in liquid or solid form (solid particle size

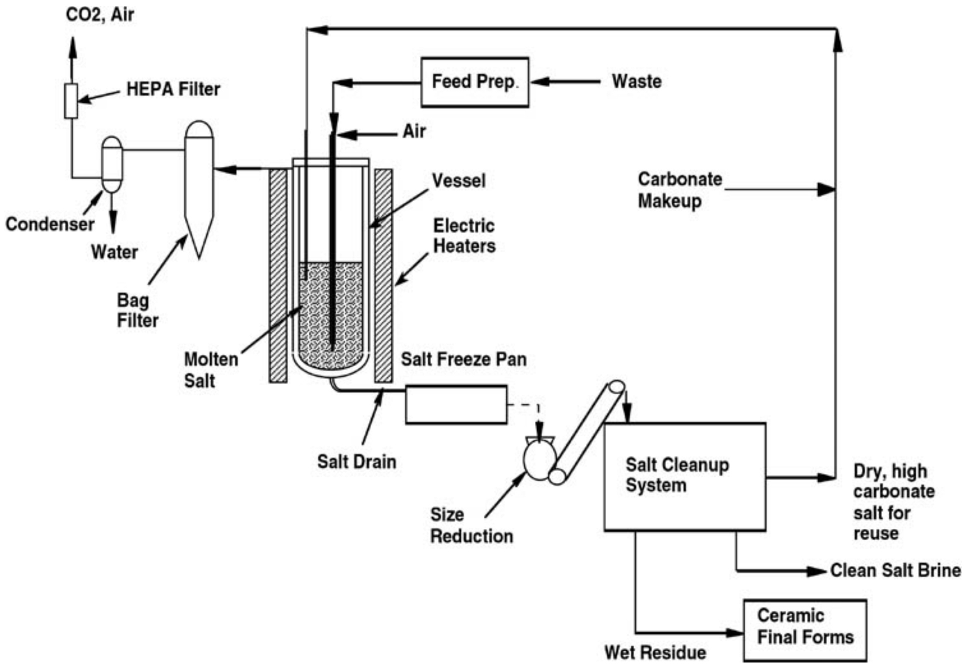

FIGURE 4.7.1 Integrated MSO system.

down to 1/8 in. after a feed preparation step), is fed to the reactor vessel along with oxidant air using a top-feed injection system designed for solid and liquid waste streams at throughputs up to 8 kg/hr for chlorinated solvents. Product gases exiting the vessel are then treated in the off-gas system to remove entrained salt particulates, water vapor, and traces of gas species such as CO and NO_x. As waste is injected into the MSO vessel, residues of inorganic components build up in the salt bed, which necessitates periodic removal of salt and replenishment with fresh salt to maintain process efficiency. Because many of the metals and/or radionuclides captured in the salt are hazardous and/or radioactive, without further treatment the removed spent salt would create a large secondary waste stream. A salt recycle system is needed to segregate these materials to minimize the amount of secondary waste, and to reduce the consumption of fresh salt.[10] The segregated inorganic residues are then encapsulated in a ceramic matrix for final disposal. Each subsystem is described below.

Reactor Vessel

The MSO reaction is contained in a 2.74-m tall processor vessel, as shown in Figure 4.7.2. The processor is 38.1 cm inside diameter over the top half and 29.8 cm inside diameter over the bottom half, with a 30.5-cm long, tapered transition zone in between. The normal salt load is 160 kg and fills the vessel to the bottom of the transition zone when quiet. When air and feed injection is occurring, the salt level froths up to the top of the transition zone. The freeboard area of the vessel above the salt level provides a disengagement zone for salt spray to separate from the off-gas before it exits. There are baffles in this region to assist in separating the salt spray. The air and feed material enter through an injector lance extending through the vessel cover to the bottom of the vessel. The injector is insulated and air-cooled to keep the feed temperature low until it leaves the injector and contacts the molten salt.

The vessel is fabricated from 1.27-cm thick Inconel 600® material. Corrosion tests at LLNL have shown an acceptable corrosion rate for Inconel 600® in Na_2CO_3 and NaCl salt mixtures at operating temperature.[11] The most severe corrosion occurs at high NaCl contents. The vessel is protected against overpressure by placing close limitations on maximum feed rates, by closely monitoring the off-gas system to prevent buildup of salt deposits that may cause plugging, and by a rupture disk on a dedicated vessel nozzle. The rupture disk is a low-pressure disk that discharges into a separate exhaust vent stack.

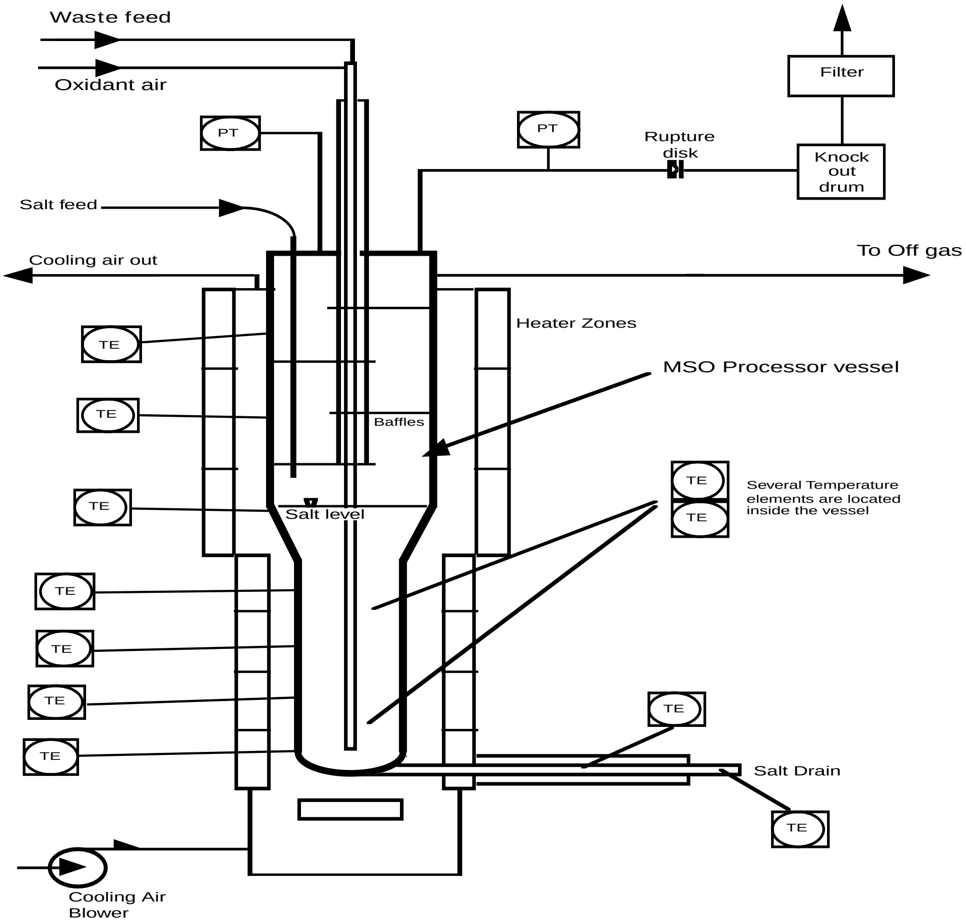

FIGURE 4.7.2 MSO reaction vessel.

The heaters are radiant electric type and are made up of two major subassemblies: one assembly covering the top half of the vessel and a second subassembly covering the bottom half. The heaters are separately supported from the vessel support stand. The vessel has a salt drain pipe extending from the bottom of the vessel to outside the heated zone to drain the salt out when salt replacement is necessary. The vessel temperature is maintained by the control system. The heaters are segregated into several zones, each of which is separately controlled to a temperature determined by sensors mounted in blocks on the outside of the vessel. When exothermic materials are being fed, the vessel must be cooled to prevent overheating. A blower is provided to blow ambient air though the annular space between the heaters and the vessel wall for cooling.

Off-gas System

The purpose of the off-gas system is to remove entrained salt particulates, moisture, and traces of CO and NO_x from the off-gas and to ensure that clean gas exits the off-gas system. This is accomplished by the following components: a piping section with a gas-to-air cooler, an air cylinder and salt trap, a ceramic filter, a heat exchanger and condenser, an electrical heater, a high-efficiency particulate air (HEPA) filter, and catalytic converter. Figure 4.7.3 depicts the off-gas system.

The off-gas exiting the reaction vessel is first cooled by the gas-to-air cooler, which consists of two concentric pipes with an annular gap between them. As the gas stream cools, the entrained salt cools and sticks to the inner pipe wall. Salt buildup is removed by a wire brush on the end of a rod that is driven and retracted by the air cylinder. The dislodged salt falls into the vessel on the forward stroke and

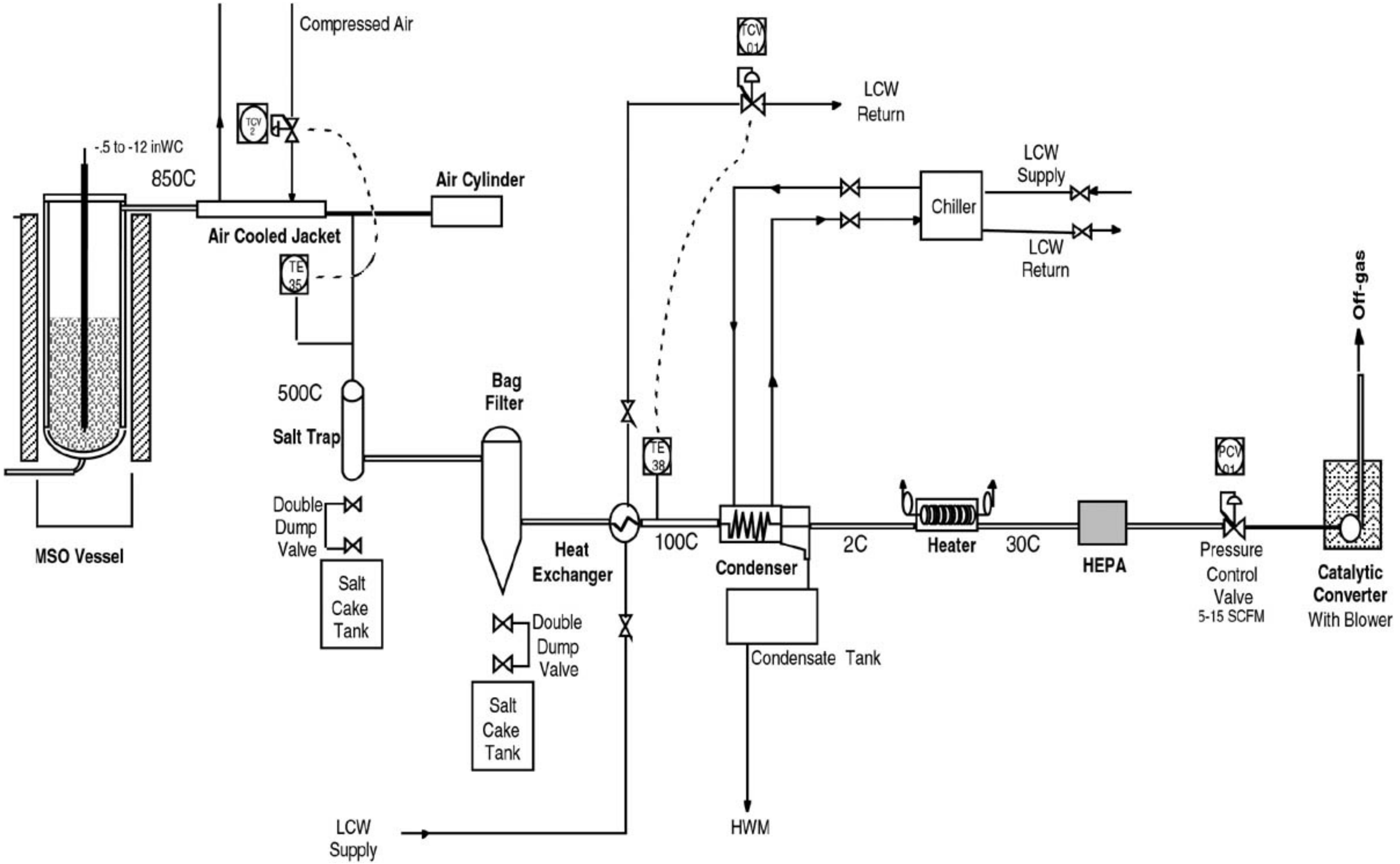

FIGURE 4.7.3 Off-gas system.

falls into the salt trap on the reverse stroke. The smaller entrained particles are captured in the pulsating, self-cleaning ceramic filter. The ceramic filter captures particles Š 0.5 µm in size and can withstand gas temperatures up to 700°C. Six silicon carbide filter elements are pulsed with compressed air to remove caked-on salt when the pressure drop across the elements reaches 2.74 kPa (11 in. water). The captured salt in the salt trap and ceramic filter is removed by cycling double dump valves that allow the salt to fall into a drum below them.

The filtered off-gas is then cooled to 100°C by a shell-and-tube heat exchanger using low-conductivity water. The moisture is removed when the gas is cooled to 2°C by the condenser using propylene glycol from a chiller. The gas is then heated to 30°C by an electrical heater to ensure that dry gas enters the HEPA filter. The HEPA filter serves two purposes: it acts as a prefilter for the catalytic converter and a barrier for remaining particles in the off-gas. Thus, no salt particles escape the process off-gas system. The catalytic converter is designed to abate 50,000 ppm CO and 30,000 ppm NO_x. It converts CO into CO_2 in a catalyst bed at elevated temperatures. It is also equipped with an ammonia injection system that converts NO_x into N_2 and H_2O by selective catalytic reduction. The off-gas leaving the catalytic converter is very clean and is exhausted to a building stack via a ducting system.

Salt Recycle System

As waste is injected into the MSO vessel, residues of inorganic components build up in the salt bed; this necessitates periodic removal of salt and replenishment with fresh salt to maintain process efficiency. Because many of the metals and/or radionuclides captured in the salt are hazardous and/or radioactive, without further treatment the removed spent salt would create a large secondary waste stream. A salt recycle system is needed to segregate these materials to minimize the amount of secondary waste, and also to reduce the consumption of fresh salt. The segregated inorganic residues are then immobilized as a ceramic final form for disposal.

The salt recycle system, shown in Figure 4.7.4, receives spent salts from the MSO reactor vessel and off-gas system. The size of spent salt is reduced to approximately 6.3 mm using hand tools, air-power tools, and a crusher inside a dedicated enclosure with glovebox for operational safety. Small salt particles are then transferred to tank T-101 by a spiral conveyor. Salt samples are taken during salt crushing for analysis. Salt dissolution is performed in tank T-101 using either deionized or clean recycled water. The salt dissolution step is controlled at 30 to 40°C by an immersion heater and a temperature controller to minimize the amount of water required. Most of the mineral residues and ashes precipitate as hydroxides and oxides during the dissolution step. Chemical reagents such as sodium hydroxide, hydrochloric acid, and dithionite are used at various stages of the process to adjust pH and/or facilitate metals removal. Reagents such as alum $[Al_2(SO_4)_3]$ and activated silica are added to facilitate the coagulation and precipitation process to avoid an excessive holding time in the dissolver tank. These reagents can be fed into the T-101 or T-102 tanks by metering pumps or by opening the hatch.

Once precipitated, these solids can then be removed by pumping the solution through filter F-101. The filter has a 1-µm filter element and will efficiently remove solid particles from the salt solution. The filter element is precoated with a thin layer of diatomaceous earth to facilitate the filtration process. At various stages, the filter cake must be removed by opening the filter vessel and relocating the filter cartridge into the wash-off area inside the enclosure. Air and water are used to assist in cake removal. The wet cakes are then sent to the Final Forms for immobilization. The filtration operation is performed inside an enclosure.

After metals precipitation, the salt solution goes to a spray-dryer, ion exchange columns, and/or portable containers, depending on the concentrations of carbonate and radionuclides. If the spent salt contains a high level of carbonate, then the solution is pumped to tank T-103 for spray-drying. If it contains low levels of carbonate and traces of uranium and thorium, then the salt solution is pumped to the ion exchange columns E-101/E-102 for removal of radionuclides. In some instances, such as salt containing high chloride, it is not for reuse, and the salt solution is pumped to portable containers and then shipped to a hazardous waste management facility.

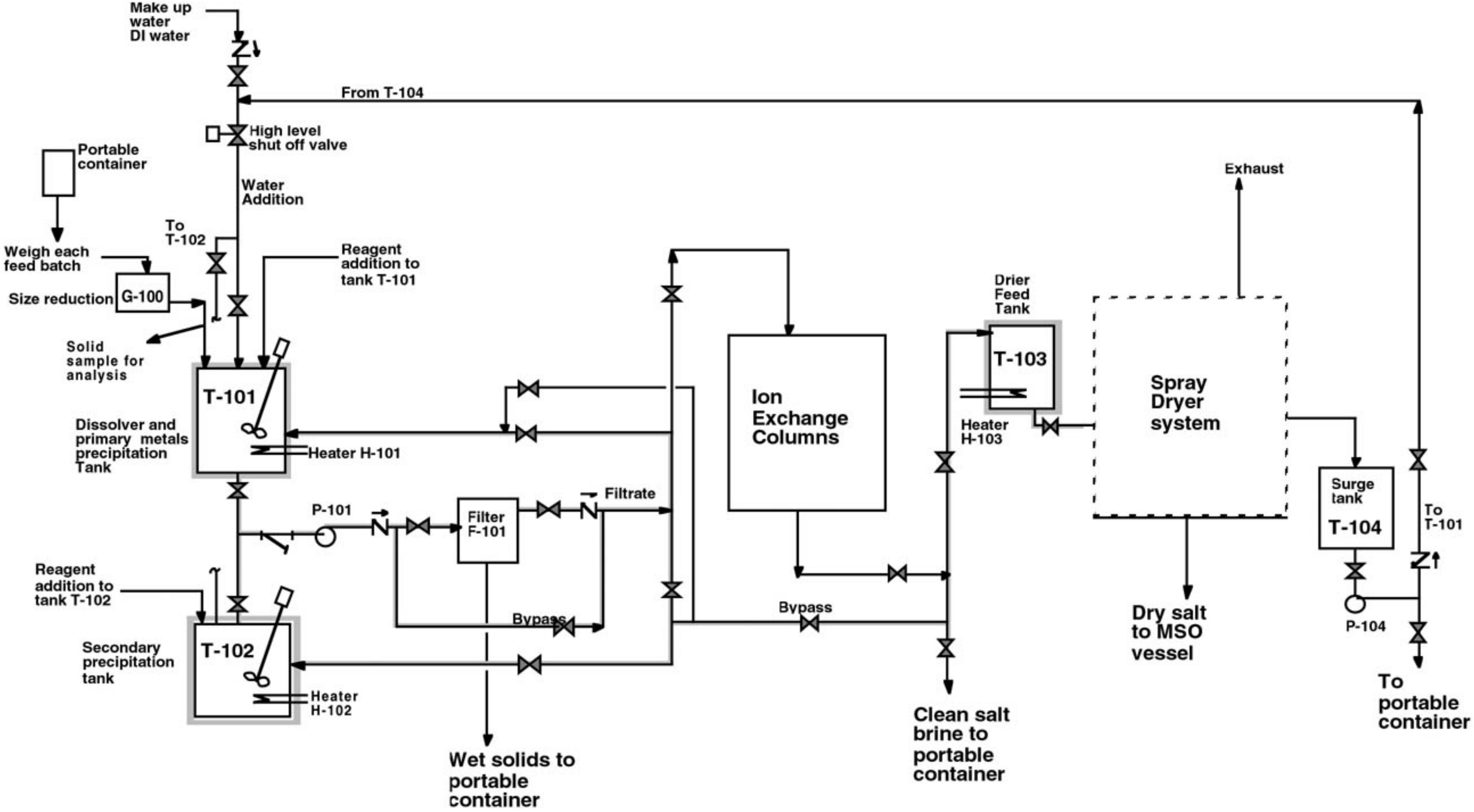

FIGURE 4.7.4 Salt recycle system flow diagram.

The spray-dryer is part of the salt recycle system. It receives clean salt solution from tank T-103. The system includes a natural gas-fired air heater, a dryer using hot air as heating medium, a cyclone separator for collecting clean dry salt, and a venturi scrubber as well as an absorber for gas cooling and dust control. The clean dry salt is collected in well-sealed drums for reuse. The air leaving the absorber passes through a HEPA filter and exhausts. The spray-dryer is operated at slight vacuum. Condensate blowdown is pumped to tank T-104 for reuse or discharge.

Ceramic Final Forms

The wet filter cake produced by the salt recycle system contains residues from the MSO process itself, typically deriving from a variety of input wastes, and compounds introduced by the salt recycle process. In addition to metals and oxides, there may be some carbonates, phosphates, sulfates, sulfides, borides, carbides, and nitrides. Overall, LLNL residues from LLNL wastes have been dominated by Si, Al, Mg, Zn, Ca, and Fe. Any of a wide variety of elements may be present in minor or trace amounts. The ceramic final waste form must immobilize the hazardous and radioactive elements present; both the ceramic material and the process to make it must be adaptable to the variable composition of the filter cake; and a high waste loading is desirable. The ceramic is intended to satisfy both federal and California leach resistance standards.

The ceramic material comprises several crystalline phases. They were chosen because they (1) can be fabricated as a durable ceramic using standard and economical ceramic processing methods; and (2) can incorporate, either as major constituents or by ion substitution, all of the dominant elements just mentioned, and most of the hazardous and radioactive elements of concern. A recipe is calculated for each residue batch (i.e., filter cake), based on its elemental content, and waste loadings are optimized by blending residue batches.

The main equipment items in the Final Forms subsystem include a standard fumehood for weighing and mixing powders, a recirculating attrition mill for wet blending and comminuting the formulation, a rotary calciner for drying the slurry and calcining the dried mixture, a rotary granulator in which the calcined powder is formed into ~1-mm granules, an automatic pellet press to form the "green" pellets, a large tube furnace with a retort and programmer-controllers for sintering the pellets, and a small tube furnace with a retort and programmer-controllers for process-control test sintering.

The system also includes a variety of quality-control, process-control, and lab-scale processing equipment. Control is local to each equipment item; process monitoring and data collection is direct to the Final Forms computer. The production capacity is presently limited by the sintering step; it could be doubled by adding a second tube furnace. LLNL conducted a limited demonstration on the Ceramic Final Forms in 1999.

Status

The LLNL integrated MSO system has been transferred to ATG, Inc. In 2000, ATG began reinstalling the system in its mixed waste facility at Richland, Washington, in an effort to demonstrate the MSO technology with real waste streams at the industrial scale.

For more information, readers can visit the Web site at www-ep.es.llnl.gov/www-ep/aet/waste/wt.html.

In a parallel development, LLNL has been funded since 1992 by the U.S. DOE Defense Programs and Department of Defense (DOD) - Air Force and Army to demonstrate the MSO technology for the destruction of energetic materials. Several MSO systems of EDU size have been built and tested with a variety of energetic materials, including ammonium picrate, HMX, K-6 (keto-RDX), NQ, NTO, PETN, RDX, TATB, TNT, Comp. B, LX-10, LX-16, LX-17, PBX-9404, and XM46.

LLNL is currently building an MSO plant for the treatment of TNT-contaminated sludge and TNT-contaminated spent activated carbon, both of which will result from a 155-mm artillery shell melt-out operation. The plant is designed to treat 21 kg/hr of explosives slurry and it will be installed in a U.S. Army/ROK demilitarization facility in South Korea in March 2001. LLNL also plans (in 2001) to build an MSO system to be installed at Bluegrass Army Depot in Kentucky to destroy TNT sludge.

MSO Activities at Molten Salt Oxidation Corporation

Molten Salt Oxidation Corporation (MSO Corp.) was spun off from Ajax Electric in 1997 with the sole mission to design and fabricate MSO systems for government and industrial applications.[12] Since its inception, MSO Corp. has received three orders from Naval Surface Warfare Center (NSWC) Indian Head Division (IHD), a confidential industrial client, and Los Alamos National Laboratory.

Energetic Waste Destruction Unit at the U.S. Navy Naval Surface Warfare Center (NSWC), Indian Head Division (IHD)

The Indian Head Division of the Naval Surface has been operating a 6-in. ID MSO unit since 1997, destroying solid feed energetic materials.[13] The IHD has contracted the construction of a new treatment reactor to MSO Corp. The reactor is a 12-in. ID prototype unit and was delivered in 2000.

The reactor incorporates a number of features that offer some benefits. The features include:

1. *Retractable electrodes.* Internal electrodes are a common method for heating molten salt baths through efficient coulombic heating (salts are electrically conductive). Startup of this size unit with internal electrodes is expected to be accomplished in approximately 4 h, thereby allowing the electrodes to be withdrawn to a position above the molten salt.
2. *Screw feed injection.* The screw feeder is outfitted with multi-port injections to allow for the feed of gases, liquids, slurries, and even energetic solids. The unit has been designed to inject the feed streams into the bottom of the molten salt bath. Air is used as a cooling medium and as oxidant gas within the screw feeder.
3. *Salt drain valve.* This feature allows the unit to be operated continuously as it provides a method for removing a metered amount of spent salt. Replacement of salt is accomplished through the addition of salt in the screw feeder.
4. *Inconel vessel.* A specially treated Inconel vessel is able to withstand the highly corrosive nature of molten salt. The results are longer vessel life and therefore reduced life cycle cost.
5. *Multi-zone cooling.* This feature may increase the throughput capacity of the unit, which is usually limited by the passive heat loss through the vessel walls. In addition, control of the extraction of heat from the vessel allows good temperature control of the inner vessel wall. The unit operates at a low wall temperature to "freeze" a layer of salt to the surface of the vessel. The frozen layer of salt further protects the vessel from the corrosive molten salt.

Salt Recovery Unit for a Commercial Client

MSO Corp. is building a large MSO unit (78 ft high × 13 in. ID) for a confidential client to recover a blend of salts. The proprietary production process creates a slurry of salts contaminated with chlorinated hydrocarbons. Utilizing an MSO system, it will be possible to remove the chlorinated hydrocarbons by oxidizing them in the molten salt bed (to gaseous CO_2 and H_2O). After redissolving the salts in water, the recovered salt stream is pumped to a neighboring plant for utilization. The MSO unit is constructed of stainless steel; it will be lined with a specialty brick able to withstand corrosive molten salt.

An aqueous slurry of salts contaminated with chlorinated hydrocarbons is pumped into the MSO unit through four feed injectors that introduce the feed near the bottom of the MSO vessel. The oxidizing air required in the molten salt bed is also fed through the feed injectors. The salt is continuously removed from the unit through an overflow port. The molten salt overflow then flows into a dissolution system and is eventually pumped to a neighboring chlor-alkali plant for reuse.

To provide a higher level of control over the reaction in the vessel, active heating and cooling is provided. This MSO unit is outfitted with six pairs of electrodes to internally heat the salt bed. External air cooling will be provided around the molten salt bed portion of the vessel.

Los Alamos National Laboratory Glovebox Unit for Transuranic Waste Volume Reduction and Plutonium Recovery

LANL is testing the MSO process for reducing the number of shipments of transuranic waste shipments that LANL needs to send to the Waste Isolation Pilot Plant (WIPP) in New Mexico. LANL has asked

MSO Corp. to build a 10-in. ID MSO reactor for the effort. The integration of MSO processing and aqueous chemical separation offers a method for recovering plutonium from combustible transuranic (TRU) waste at LANL. TRU combustible waste includes cellulose rags and polyethylene/polyvinylchloride plastics with plutonium contamination. By utilizing an MSO system, LANL will be able to destroy the combustible portion of the waste by oxidation in the molten salt bed. The plutonium remains in the molten salt, where it can be recovered in a subsequent aqueous chemical separation process.

The complete glovebox line for the process consists of three gloveboxes. A size reduction glovebox houses a cryogenic shredder to prepare the feed solids for introduction into the MSO unit. A 10-in. ID MSO unit is housed in an adjoining glovebox. Attesting to the scalability of the NSWC energetic waste destruction unit design, that particular MSO unit design is scaled down to fit in the required glovebox for this application.

Conclusions

MSO technology is effective in treating some difficult waste streams such as low-level mixed wastes, chlorinated solvents, PCB-contaminated oils, and energetic materials. It operates at lower temperatures than incineration, and generation of secondary wastes such as spent salt appears to be manageable. It offers a valuable alternative to incineration. The further implementation of MSO technology at the industrial scale with real waste streams is very important to bring the technology into wider acceptance by the public and the waste management industry.

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4.8

Fluidized-Bed Calcination

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Introduction

The Idaho Nuclear Technology Engineering Center (INTEC) (formerly called Idaho Chemical Processing Plant, ICPP[*]) at the Idaho National Engineering and Environmental Laboratory (INEEL) processed spent nuclear fuels for the separation and recovery of uranium from 1953 until 1992. They were primarily fuels of highly enriched uranium. The two major categories processed were Zircaloy fuels from naval reactor cores and aluminum fuels from the Advanced Test Reactor and other test reactors at the INEEL and throughout the world. A variety of other types were also processed, such as stainless steel fuels from the EBR-II reactor and graphite Rover fuel, in which uranium carbide spheres coated with pyrolytic carbon were dispersed in a graphite matrix; the particles also contained niobium carbide. The Zircaloy fuels were dissolved in hydrofluoric acid (HF) and, after complexing the excess HF with aluminum nitrate, nitric acid was added. The aluminum fuels were dissolved in nitric acid, catalyzed by mercuric nitrate. One tankful (1×10^6 L) of acid-deficient waste was generated from nitric acid-mercuric ion catalyzed dissolution of uranium-aluminum fuel with ammonium hydroxide used to provide the acid deficiency and the salting strength for solvent extraction of the uranium. The stainless steel fuels were either dissolved in sulfuric acid or electrolytically in nitric acid. Rover fuels were processed by burning the graphite in fluidized-bed burners. Then the residual ash from the fuel particles, in which the uranium and niobium carbides had been converted to oxides, were dissolved in nitric and hydrofluoric acids, after which excess fluoride was complexed with aluminum nitrate.

The first-cycle extraction raffinate that resulted after solvent extraction separation of the uranium consisted of the radioactive waste products, the fuel cladding and matrix material, and the reagents used to dissolve them. The fluoride wastes were adjusted with aluminum nitrate to result in free HF concentrations that were acceptable for long-term storage. The wastes were temporarily stored as acidic solutions in 1×10^6-L stainless steel underground tanks. Other acidic liquid waste that was accumulated in the tanks was sodium-bearing waste (SBW). It was generated from sodium carbonate scrubbing of the tributyl phosphate extractant used in the separations process and from decontamination solutions. The SBW was blended with the second-cycle extraction raffinates in tanks separate from the first-cycle extraction raffinate tanks; thus, earlier nomenclature for the blended waste was second-cycle waste. In later years, other wastes generated from activities such as HEPA filter leaching were included.

In 1963, solidification of these wastes was begun, using a fluidized-bed calciner. This was the first solidification process for high-level liquid radioactive wastes to be put into practice. In the 1960s and 1970s, a number of high-level waste solidification processes were investigated. High-level liquid wastes (HLLWs) are the first-cycle extraction raffinates generated from the processing of spent nuclear fuels

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[*] ICPP is used when describing activities performed when that title was in place.

for the recovery of uranium and plutonium. Their characteristics influence the type and chemistry of the solidification process and affect the nature of the off-gas that must be treated. There are, in general, four types of HLLW: acidic or basic that are concentrated in fission products or diluted with salts of nonradioactive "inert" constituents. Those generated from the processing of commercial LWR fuels from the chop-leach PUREX process are highly concentrated in fission product radionuclides. The raffinate that is produced is acidic in nitric acid and that is the primary liquid waste form. In the case of the West Valley (USA) wastes, the raffinates were neutralized and made basic for interim storage and contained sludge. As described above, defense HLLW, from the processing of naval Zircaloy fuels at the ICPP in the United States were acidic nitrate solutions with complexed fluoride. Dissolved nonradioactive fuel constituents and associated process chemicals made up the bulk of the liquid waste solutes; the activity levels of these wastes were orders of magnitude less than those of commercial LWR wastes. Other ICPP wastes, primarily from processing aluminum and stainless steel fuels, also contained substantial nonradioactive diluents, although not as much as the zirconium wastes. Defense waste solutions at Hanford and Savannah River have been neutralized and made basic.

Of the waste solidification processes investigated, three have emerged as practical systems: (1) fluidized-bed calcination in use at the ICPP/INTEC in the United States; (2) rotary kiln calcination with vitrification developed in France (AVM process) and implemented in France and the United Kingdom; and (3) liquid-fed ceramic melter developed in Germany and the United States and built at the Savannah River site and at West Valley in the United States. Preconcentration of wastes by evaporation prior to solidification is sometimes used. This section describes the fluidized-bed calcination process as applied to acidic wastes.

Fluidized-Bed Calcination Technology

Calcination

The fluidized-bed calcination process was developed at Argonne National Laboratory (Jonke et al., 1957; Loeding et al., 1961) and the INEEL (Brown et al., 1962; Wheeler et al., 1962; Brown et al., 1964a; Brown et al., 1964b; Lakey et al., 1965; Buckham et al., 1964; Grimmett, 1966; Hickok and Madachy, 1961; Evans, 1961). The original calciner with a 4-ft (1.2-m) diameter bed was built to serve as a hot demonstration pilot plant for calcining aluminum nitrate wastes and was called the Demonstration Waste Calcining Facility (DWCF) during its cold testing from 1961 to 1963. It began processing radioactive waste in December 1963 and operated so well that it served as an operating plant until March 1981 and was called the Waste Calcining Facility (WCF). During that period, approximately 15,000 m^3 of wastes were converted to 2200 m^3 of calcined solids (Berreth and Dickey, 1982). In September 1982, the New Waste Calcining Facility (NWCF) became operational. Its bed section is five ft (1.5 m) in diameter. The system is depicted in Figure 4.8.1 and a picture of the calciner vessel is shown in Figure 4.8.2.

A comprehensive compilation of the operating history of the calciners is provided by Staiger, (1999). The report includes an inventory of the calcine produced during the period December 1963 to May 1999 and the range of chemical compositions of the calcine. Information provided includes calciner startup data, waste solutions analyses and volumes calcined, and calciner operating schedules.

In this process, the acidic high-activity aqueous waste is sprayed through an atomizing nozzle into a fluidized bed of particles heated to 400 to 600°C. The particles are fluidized by a flow of air through a distributor plate with holes at the bottom of the bed. The superficial velocity is 0.18 to 0.36 m/s. The water and nitric acid are flash-evaporated, and the residual salts and oxides are deposited on the surface of the bed particles or create new particles. A minimum dissolved solids concentration in the feed stream is needed to build a bed. The required concentration depends on feed type and appears to be a function of the calcine particle density produced: 150 g/L for zirconium waste, 120 g/L for SBW with aluminum nitrate additive, and 90 g/L for aluminum waste. Particle size is maintained by a balancing grinding action that is controlled by adjusting the nozzle air-to-feed ratio. The fluidization maintains a constant and uniform temperature throughout the bed. As the bed level increases from particle formation and growth, it is drawn off and pneumatically transported to stainless steel storage bins in concrete vaults.

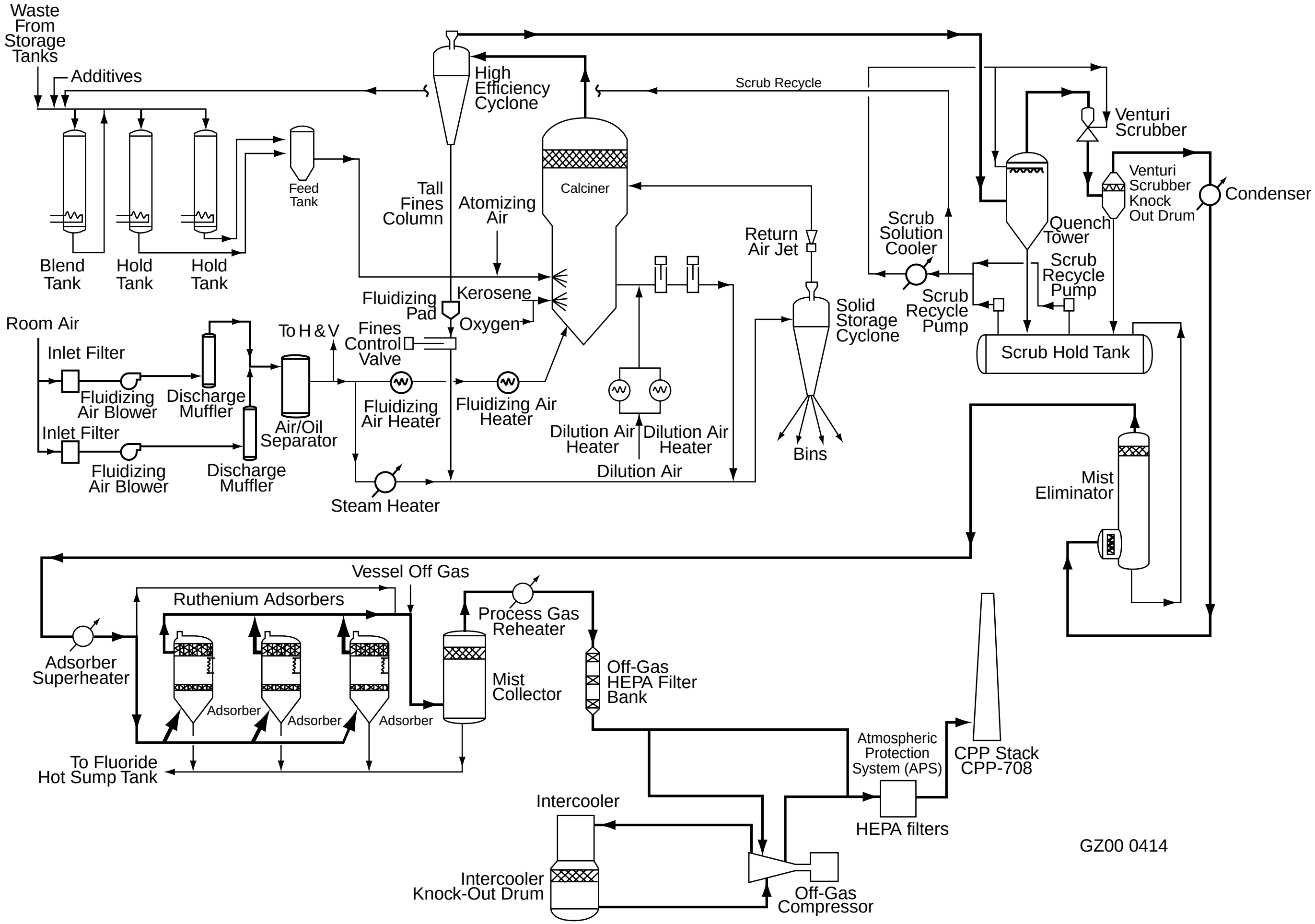

FIGURE 4.8.1 Calciner and off-gas treatment system - NWCF.

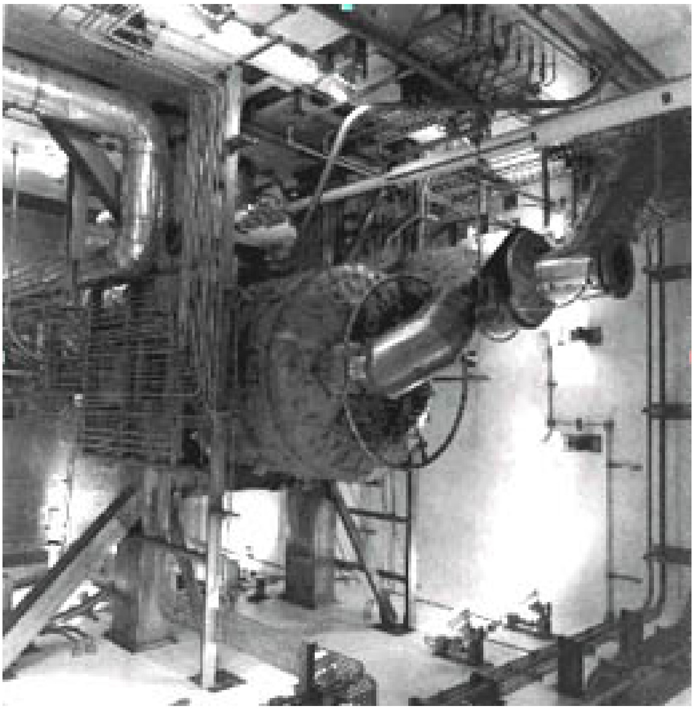

FIGURE 4.8.2 NWCF vessel showing off-gas cyclone and 2.1-m diameter solids deentrainment section above the 1.5-m diameter fluidized bed.

The particle size is affected by the waste being processed. The composition of the solution must be adjusted to produce calcine particles of appropriate hardness that will not agglomerate or "clinker," but that will not be so soft as to grind to a powder. When zirconium fluoride wastes are calcined, $Ca(NO_3)_2$ is added to hold the fluorine in the bed as CaF_2 [Brown et al., 1964a; Hickok and Madachy, 1961; Petrie et al., 1965). A nominal Ca:F atom ratio of 0.55 was used for those wastes. When sodium-bearing waste was blended with the zirconium fuel fluoride raffinate, the calcine became more attrition resistant and nodules grew on the particles, this made fluidization difficult and clinker formation (growth of large, hard chunks) would sometimes occur. Increasing the Ca:F atom ratio to 0.7 eliminated this effect. Most of the nitrates are dissociated to the oxides. However, sodium and potassium nitrates in the SBW do not completely dissociate and this waste could not be calcined by itself. The sodium and potassium nitrates melt at calcination temperatures. These wastes were calcined by blending them with the aluminum or zirconium (which contained aluminum nitrate) (Newby, 1979) wastes or with aluminum nitrate additive so that $NaAlO_2$ formed. In the case of the acidic fluoride (zirconium) waste blending, cryolite (Na_3AlF_6) was possibly formed (Brown et al., 1964a; Bower, 1973; Newby, 1979).

When dissolved aluminum is present in the waste feed, the aluminum nitrate decomposes to both amorphous and crystalline (alpha and gamma) alumina in varying amounts, with as much as 90% alpha-alumina being produced under certain conditions (Brown et al., 1962; Wheeler et al., 1962). A factor that affects formation of alpha-alumina is the presence of oxides of nitrogen and water vapor in the gaseous atmosphere. It is formed, also, only if a small amount of sodium ion is present in the alumina product (Murray and Rhodes, 1962).

Particle fines that are entrained into the off-gas system and removed by the scrubbing solution (see subsection entitled "Integrated Off-gas Treatment System") must dissolve to avoid excessive buildup of solids in the scrubbing system. The amorphous alumina dissolves readily in the hot nitric acid scrubbing solution, but the alpha-alumina is highly insoluble. The alpha-alumina is also softer and produces more fines. Therefore, a small amount of boric acid is added to the feed; this effectively suppresses the formation of the crystalline alumina, apparently by preventing the formation of crystalline sodium nitrate (Murray and Rhodes, 1962). Boron-to-sodium molar ratios as low as 1 to 8 were effective. A concentration of 0.01 *M* boric acid was added to the feed solution during calcination of aluminum waste (Brown et al., 1964a). During blending of SBW and aluminum nitrate cold chemical in the NWCF, boric acid was added to bring the boron molar concentration to the greater of 0.03 or $0.2364(C_{Na} + C_K) - 0.0450$ (Newby and O'Brien, 2000).

The ammonium nitrate waste from the acid-deficient dissolution of aluminum fuels was blended with acid aluminum raffinate waste for calcining (Brown et al., 1964a; Lohse and Hales, 1970). When calcining the acidic sulfate waste from the dissolution of stainless steel fuels, aluminum nitrate was added to form and retain nonvolatile aluminum sulfate in the bed and prevent the vaporization of sulfuric acid (Brown et al., 1964a; Wielang and Freeby, 1973).

A portion of the atomized liquid evaporates to a dry powder before striking the surface of a bed particle, and the particles undergo a grinding process. Thus, a fraction of the dried waste forms "fines," small particles that are entrained in the off-gas or act as seed particles for bed growth. The calcine and powdery solids range in size from 0.05 to near 1 mm; the ideal mass mean particle size is 0.35 to 0.45 mm. In practice, it ranged from 0.25 to 0.60 mm. Also, ruthenium, under oxidizing conditions, can volatilize. An extensive off-gas treatment system is needed to remove these particulate and volatilized ruthenium species.

The ratio of the quantity of product to fines (P/F) is a function of the attrition resistance index (ARI)* and the residence time of the calcine in the fluidized bed. The ARI of the calcine varies with the type of feed, for example, aluminum, zirconium, sodium-bearing, or simulated LWR HLLW (specifically, AGNS** waste). For example, the ARI of aluminum calcines is high (60 to 80) and an acceptable P/F ratio is obtained during operation. Zirconium wastes, however, yield a very friable product with an ARI of only 12, and a large percentage of fines results.

A low ARI may be due to two causes: the particles may have a low resistance to abrasive wear, or the particles may be friable and easily broken into smaller particles. If the abrasion mechanism prevails, additives are needed to increase the hardness of the calcine product; to reduce particle breakage, an additive is required to increase the internal binding of the particles.

Most of the evidence indicates that low ARIs for calcine are due to friability. This immediately suggests the need for a material (e.g., small amounts of sodium nitrate) that is known to cause agglomeration of particles when present in significant quantities.

A study was conducted to determine the quantitative correlation between sodium concentration and ARI (Christian, 1975). The concentrations of the major components of several calcine feed solutions (and some product compositions), along with the measured ARIs of the calcine product, are listed in Table 4.8.1. The zirconium calcines have the lowest attrition resistance; but when second cycle/SBW feed is mixed with the zirconium feed, the ARI of the product is vastly improved.

Examination of Table 4.8.1 shows that, aside from the dilution factor resulting from blending, the major difference between the zirconium feed and the mixed feed solution is the markedly higher sodium concentration in the zirconium-SBW blend. In the calcined products, $NaNO_3$ is present in significant quantities in the blended system (the 4.2:11 weight ratio of Na:NO_3 is near-stoichiometric), but absent in zirconium calcine.

Too much sodium can be detrimental. When the sodium content is too high, the particles tend to agglomerate. This effect was observed with simulated LWR commercial (AGNS) calcine that contained

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*Attrition resistance index is a measure of difficulty of wearing particles to an average smaller size. It is determined by measuring the weight percentage of particles of a closely sized product, usually a - 28 + 35 Tyler mesh fraction, that is unchanged in size after undergoing attrition by a jet grinder for a specified period. The apparatus used is a 1-in. ID glass tube with a 1/64-in. diameter orifice drilled in an air distributor plate. In the procedure a 50-g sample is subjected to the grinding action of an air stream from the orifice at sonic velocity for 1 hr. The weight percent of solids remaining unchanged in size is reported as the attrition resistance index.

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TABLE 4.8.1 Typical Calciner Feed and Product Compositions

Type	Al	Zr	SBW	Zr-SBW 3:1 Blend	Al-SBW 8.5:1 Blend	Simulated AGNS LWR HLLW
			Feed Composition (molar)			
Al	1.6	0.7	0.56	0.47	1.5	-
Zr	-	0.45	-	0.25	-	0.06
F	-	3.2	-	1.8	-	-
Na	0.05	0.003	1.59	0.35	0.21	0.26
K	-	-	0.24	0.04	0.03	0.08
NO_3^-	ca. 5	2.4	4.4	2.2	5	2.0
Ca	-	1.8	0.13	0.82	0.015	-
Ba	-	-	-	-	-	0.02
Hg	0.01	-	-	-	-	0.01
Fe	-	0.005	0.01	0.01	-	0.26
H_3BO_3	0.01	0.20	-	0.12	0.01	-
H^+	0.5-1.5	1.6	1.06	1.5	1	0.5
Sr	-	-	-	-	-	0.01
Co	-	-	-	-	-	0.01
Ni	-	-	-	-	-	0.03
PO_4^{3-}	-	-	-	-	-	0.11
Gd	-	-	-	-	-	0.07
Ce	-	-	-	-	-	0.12
La	-	-	-	-	-	0.03
Nd	-	-	-	-	-	0.03
Pr	-	-	-	-	-	0.01
			Calcine Product Composition (wt%)			
Al	47	8.8		7.2		-
Zr	-	9.1		15		5.2
F	-	25		10		-
Na	1.0- 1.5	-		4.2		5.7
K	-	-				-
NO_3^-	2.2	0.9		11		1.9
Ca	-	30		25		-
Ba	-	-				0.9
Hg	2.7	-				1.5
Fe	-	-				14.0
H_2O	0.6	2.0				-
Sr	-	-				0.9
Co	-	-				0.6
Ni	-	-				1.7
P	-	-				2.2
Gd	-	-				10.7
Ce	-	-				16.4
La	-	-				4.4
Nd	-	-				4.5
Pr	-	-				1.4
Product/fines (w/w)	6	4		7		0.63
ARI[a]	60- 80	12[b]	[c]	85[d]	74	20- 30

[a] Attrition resistance index.

[b] Soft, low density product.

[c] Agglomerates and forms very friable calcine.

[d] Calcine was noduled; agglomeration and clinker formation occurred after 90 hr. Increasing Ca concentration can reduce nodule formation.

sodium nitrate. The AGNS waste has a sodium concentration slightly less than the blended zirconium-SBW; however, the AGNS waste is more dilute and, thus the calcined product contains a relatively high weight percentage of sodium. Consequently, the AGNS feed solution cannot be calcined without agglomeration unless iron is added to "tie up" the sodium. (An optimization of ARI for AGNS calcine might be achieved by decreasing the amount of iron additive so that $NaNO_3$ in the product is about 4 wt%. This concept has not been tested.) Also, SBW cannot be calcined alone because the high sodium nitrate content causes agglomeration.

A series of mixtures of zirconium waste and SBW were calcined at 500°C and the product ARI measured. The results are shown in Figure 4.8.3. All values are for blends with Ca:F mole ratios of 0.5, except where noted. Note that when the Ca:F ratio is lower than stoichiometric for CaF_2, the ARI is decreased. Along the abscissa, sodium content decreases as percent zirconium feed increases. Apparently, the ARI goes through a maximum as sodium content is changed. The ARI should not be allowed to attain too high a value because control of particle size becomes poor and clinker formation can occur.

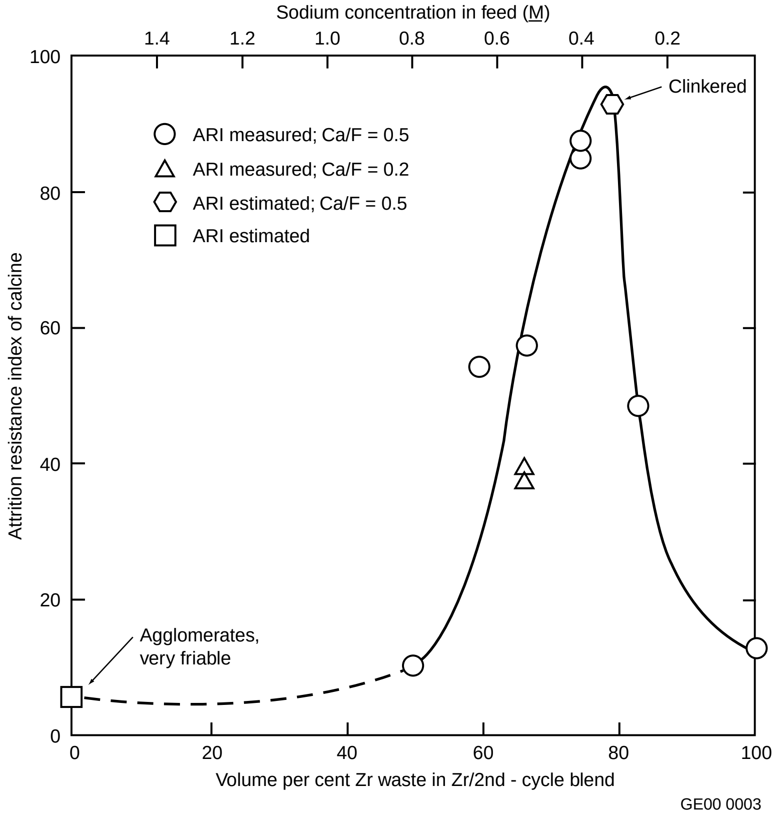

FIGURE 4.8.3 Effect of sodium concentration in blends of zirconium-second cycle HLLW on attrition resistance index (ARI) of calcine.

A similar plot for the same data of ARI vs. the Na:Al mole ratio shows a peak with the clinkered calcine occurring at a mole ratio of 0.55. The optimal ARI of around 60 to 80 occurs on either side of the peak at Na:Al mole ratios of about 0.03 to 0.35 and 0.78 to 0.92. The dependence of ARI on the lower side of the Na:Al ratio is a gradual function. On the high side, at 0.78 Na:Al, the function is steep. Therefore, more careful control of the ratio would be required in that region. Another consideration regarding use of a high Na:Al ratio is that calcine produced from this composition may be more difficult to retrieve from a bin if further processing for final disposal is needed. Therefore, retrieval tests should be conducted.

SBW calcine produced at 600°C in the INTEC 10-cm and 15-cm diameter calciner pilot plants from synthetic wastes calcined with alkali:aluminum atom ratios ranging from 0.56 to 0.74 was subjected to retrievability tests (Nenni and Marshall, 1998). For the highest alkali:aluminum ratio, the alkali metal mole percent in the calcine was 17. The tests followed simulated worst-case bin set conditions of 300°C and compression loading of 15.3 psig for a period of 3 days. The retrieval rates with a vibratory-assisted vacuum recovery nozzle were all greater than the acceptance criteria of 1.5 kg calcine per kilogram air. The researchers caution that when both the high-temperature calcine (with increased alkali-to-aluminum ratio) and the baseline 500°C calcine (with alkali:aluminum mole ratio of 0.32) are exposed to moist air at low temperatures, they can form hard cakes. Therefore, it is possible that any SBW calcine exposed to bin set conditions for many years might not be retrievable. However, there appears to be no additional detriment for the high alkali content.

Cresap, (1980) reported results of shearing strength and retrievability tests on calcine with alkali contents ranging from 2.2 to 11.3 mole%. The tests were performed as a function of storage temperature. All calcines tested with up to 7.0 mole% alkali were retrievable with vibration at temperatures up to 650°C, above the maximum temperature of 600°C expected in the bins. Tests with 11.3 mole% alkali resulted in agglomerated calcine that was too hard to test with the shearing strength test equipment.

An additional factor that affects the ARI is temperature of calcination. Experiments with simulated AGNS feeds at 500 and 600°C indicate that a more porous, friable product is formed at the higher calcination temperature.

Now that fuel dissolution raffinates are no longer available to blend with SBW for calcining, the SBW remaining in the underground liquid high-activity waste tanks at the INTEC is being calcined by blending it with 2.2 *M* $Al(NO_3)_3$ solution. When calcining at 500°C, a (Na + K):Al mole ratio of 0.25:1 has been used. Recent operations are converting to 600°C, where a higher (Na + K):Al ratio can be utilized (when working on the low ratio side of the graphs discussed above). This reduces the bed agglomeration problem while significantly reducing the amount of nonradioactive chemical additions required to calcine SBW and increasing the net processing rate. When the (Na + K):Al mole ratio was 0.5, bed building difficulties were experienced while calcining WM-185 waste. Tests with a 15-cm diameter pilot plant calciner were successful at a ratio of 0.67. The last NWCF campaign recently completed with WM-189 waste started with a 0.27 (Na + K):Al mole ratio at 600°C (that produced calcine with 8.6 mole% Na + K) and gradually increased it to 0.33 (10.6 mole% Na + K in calcine) while maintaining bed stability. The 600°C operation may convert some of the sodium nitrate to NaCl (Boardman, 2000). This may be correlated with the observation that chloride scrubbed from the off gas decreased during the 600°C Campaign (see discussion in subsection entitled "Off-gas Characteristics").

During the first three campaigns of the original Waste Calcining Facility (WCF), the fluidized bed was indirectly heated to 400°C by circulating hot NaK alloy through a tube bundle in the bed. These conditions resulted in virtually 100% volatilization of the ruthenium in the feed and required specific unit operations in the off-gas system for its removal. Starting with the fourth campaign, the heating system was converted to one of internal combustion of kerosene (in-bed combustion - IBC); this required an operating temperature of 500°C to maintain smooth combustion. The heating method change that increased heat transfer rate also enabled an increase in throughput rate by about 65%. The nominal net throughput rates were 230 L/hr with indirect heating, and 380 L/hr with IBC (Berreth and Dickey, 1982); the overall operating range experienced for the WCF was 200 to 420 L/hr. The IBC mode of operation was also designed into the New Waste Calcining Facility (NWCF) that began operating in 1982, replacing the WCF. The combination of higher temperature and partially reducing conditions in the off-gas resulted in some reduction in volatilization of the ruthenium from the bed; more significantly, that which did volatilize was quickly reduced by unburned hydrocarbons in the off-gas to particulate RuO_2 and was effectively removed by the scrubber.

The WCF calciner vessel was constructed of Type 347 stainless steel and the aqueous scrub system components were Type 304-L stainless steel. The NWCF calciner vessel, cyclone, and associated off-gas and fluidizing air piping were constructed of Type 347 stainless steel and the aqueous fluoride-handling portions of the NWCF were constructed of Nitronic 50, which is more resistant to fluoride corrosion and to chloride stress corrosion cracking than the WCF material (Thomas et al., 1977). Chloride concentration in the liquid waste increased over time as a result of recycling of calciner off-gas scrub solution to the tanks, to as high as 875 ppm_w (1100 mg/L).

Zimmerman has compiled and reviewed corrosion data reported in the literature from 1957 to 1977 during the development and operation of the waste calcination process, including the selection of Nitronic 50 for the NWCF aqueous liquid sections (Zimmerman, 1978; 1980). Operating history of the WCF indicates that the Type 347 and Type 304L stainless steels were good choices for construction materials, even after changing from aluminum nitrate to zirconium fluoride-containing wastes and modification to replace the NaK indirect heating system with in-bed combustion of kerosene.

Operating data for the WCF have been reported for Campaigns 1 through 5 (Commander et al., 1966; Lohse and Hales, 1970; Bendixsen et al., 1971; Wielang et al., 1972; Wielang and Freeby, 1973) and 9 (Childs et al., 1982). No campaign reports are available for the NWCF, except for the description of the most recent experience operating at the increased temperature of 600°C provided by Swenson (2000). Newby and O'Brien (2000) have recently published a summary of calcine operating experiences at the ICPP/INTEC. The report describes the calcinability of the different compositions of feed blends and additives processed and is an excellent source for such detailed information and history.

Off-Gas Characteristics

The calciner is used to calcine HLLWs that are either nitric acid solutions or acidic fluoride-nitrate solutions. When fluoride-nitrate wastes are calcined, $Ca(NO_3)_2$ is added to the liquid feed and reacts with the fluorides to form stable, nonvolatile CaF_2. Thus, the primary off-gas constituents are fluidizing air, combustion products of kerosene, water vapor, oxides of nitrogen, and calcine fines, with small amounts of hydrocarbons. Radionuclides in the waste that can volatilize to varying degrees, depending on the operating conditions, are ruthenium, technetium, iodine, and cesium. Mercury, present as a processing chemical from dissolution of aluminum fuels, is another partially volatile species.

Approximately 8 to 20% of the solids content of the calcine solids formed were entrained as fines from the bed and through the cyclone into the off-gas treatment system (OGTS) of the WCF (Christian and Rhodes, 1977).

Cesium volatilization is not a problem at calcination temperatures of 400°C. It may very slightly volatilize at 500 to 600°C, but has not been characterized in the calciner. Any small amount that may volatilize would be quantitatively removed in the scrubber. Technetium-99, while a concern because of its long half-life (2.13×10^5 years) and its relative mobility in the environment, does not represent a regulatory issue because of the relatively low concentrations in wastes processed in the WCF and NWCF. Even for the more concentrated technetium in LWR wastes, NRC effluent concentration limits could be met with virtually complete release of the technetium (Christian and Thomas, 1996). For quantities in LWR wastes, as-low-as-reasonably-achievable (ALARA) considerations may warrant attention to technetium behavior and releases.

While volatile Tc_2O_7 forms under oxidizing conditions, stable alkali and alkaline-earth pertechnetates can form in high level waste (HLW). Thus, the volatility of technetium is low at calcination temperatures and becomes significant only as the temperature increases above about 550 to 600°C. Rimshaw and coworkers (Rimshaw et al., 1980; Rimshaw and Case, 1981) studied the volatility of technetium during the flash evaporation of HLLW solutions in a laboratory pot calciner as a function of temperature. For wastes from the reprocessing of aluminum fuels in nitric acid (Rimshaw and Case, 1981), the technetium volatility was less than 1.1% from 250 to 600°C. The authors attribute the low volatilities to formation of alkaline-earth pertechnetates. For zirconium fuel wastes containing fluoride and nitric acid with aluminum ions, but with no $Ca(NO_3)_2$ added to hold the fluoride from evaporating as is done in the INTEC fluidized-bed calciner, the technetium volatility at temperatures up to 350°C was similarly small, but ranged from 9.2% at 450°C to 21% at 600°C (Rimshaw and Case, 1981). It is evident that the presence of fluoride may result in formation of volatile technetium species. It is unknown what the effect of added $Ca(NO_3)_2$ to the calciner feed would be. For nitric acid PUREX wastes, the volatility was 0.2 to 1.4% at temperatures from 250 to 600°C (Rimshaw et al., 1980), similar to that for the nitric acid aluminum fuel wastes.

Halaszovich, Dix, and Merz (1986) report volatilization of technetium as a drum-dried waste is heated up to 1150°C. Volatilization did not occur below 550°C.

Concentrations of ^{106}Ru and total ruthenium in reprocessing wastes from DOE fuels (e.g., at the INTEC) are sufficiently small that simple technologies enable removal of any volatilized material from the off-gas stream. The concentrations of ^{106}Ru and total ruthenium in INTEC wastes were approximately 0.6 Ci/gal (0.16 Ci/L) and 2×10^{-4} M, respectively (Christian, 1976). In 1-year-cooled, first-cycle raffinate HLLW from the processing of commercial LWR fuels that have been irradiated to 35,000 MWd/MTIHM[*], ^{106}Ru is present at a concentration of 1.7×10^3 Ci/gal (2.5×10^5 Ci/MTIHM) and constitutes 3.7% of total ruthenium present. The total ruthenium concentration is 0.04 M.

Laboratory studies (Christian, 1976) have shown that during fluidized-bed calcination using in-bed combustion heating, 20 to 62% of the ruthenium is volatilized, the higher value occurring during smooth burning of the kerosene, as is characteristic of the full-scale WCF and NWCF. The volatile form is most likely a nitrato or oxyfluoride species.

With in-bed combustion heating at 500°C and a ruthenium volatility from the bed of approximately 60% during calcination of zirconium wastes with fluoride and nitrate, the partial pressure of ruthenium vapors entering the OGTS is approximately 5×10^{-6} atm (Christian, 1976). However, as discussed in the summary of operating experience of the WCF and NWCF, the reducing conditions in the off-gas results in rapid reduction of the ruthenium vapor species to particulate RuO_2 that is removed by the venturi scrubber in the OGTS. In-bed combustion calcination of commercial LWR-type wastes would result in 0.002% volatilization of the ruthenium from the bed and a partial pressure of approximately 4×10^{-8} atm.

The percent volatility of ruthenium from evaporating nitric acid solutions increases as temperature is increased to a maximum at *ca.* 300°C. Above this temperature, it decreases (Igarashi et al., 1993). Similarly, the percent volatility during fluidized-bed calcination using indirect heating can be near 100 up to 350 to 380°C, above which temperature the volatility decreases. When the temperature is increased above about 600°C, the volatility begins to increase from the minimum as a result of the increasing formation of RuO_4(g) above RuO_2 in the presence of O_2.

The mechanism of the decrease of ruthenium volatility with increasing calcination temperature above 300°C is not clearly understood. It might be attributed to dissociation of the nitrosyl complex vapor species as temperature is increased. Spectral observations on the complex species formed between RuO_4(g) and NO_2(g) from 25 to 55°C show that the complex formation increases reversibly as temperature is increased (Christian, 1976). However, at 400°C, the ruthenium species dissociated to RuO_2. Another possible mechanism might involve the formation of nitronium ions, NO_2^+, as the nitric acid concentration is increased during the flash evaporation process. Ortins de Bettencourt and Jouan (1976) observed a decrease in ruthenium volatility from distilling nitric acid solutions, from the maximum in the range of 8 to 12 M HNO_3, at the nitric acid azeotrope concentration of 14.8 M. This may be related to the formation of NO_2^+, which Fletcher (1955) believes causes reduction of RuO_4 to Ru(VI). A similar process may be occurring during calcination, in which the nitronium ion formation rate, and subsequent reduction of Ru(VIII), may increase relative to the evaporation rate of ruthenium with increasing temperature.

When a fluidized-bed calciner is heated internally by the burning of kerosene, the ruthenium volatility is greatly decreased (Christian, 1976). Partially unburned hydrocarbons or CO probably reduce the oxidation potential of the system and reduce the ruthenium volatility.

Thorough discussions of the volatilization mechanisms, behavior, and control of ruthenium, and off-gas treatment technologies for capturing volatilized ruthenium are presented elsewhere (Christian, 1976; IAEA, 1982; Klein, 1991; Christian, 1991; Christian and Thomas, 1996).

Analysis of the calcine and wet scrubbing system during the first processing campaign in the WCF (Commander et al., 1966), which utilized indirect heating at 400°C, indicated that about 95% of the mercury

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[*] MWd/MTIHM = megawatt days (thermal) per metric ton of initial heavy metal. Heavy metal refers to total uranium and plutonium in the nuclear fuels at the beginning-of-life (i.e., before irradiation).

in the feed remained in the product and was transferred to bin storage. Therefore, about 5% was present in the off-gas exiting the calciner bed. The HLLW feed likely had a very low chloride concentration relative to mercury, which was present in the feed solution at 0.01 *M* concentration. Data on chloride concentrations is not currently available to confirm this, however. In later testing, when the WCF was heated by in-bed combustion to 500°C, 96% of the mercury volatilized from the bed (Herbst, 1979). In the NWCF Campaign H-4 in 1997, where in-bed combustion heating at 500°C was used, 84% of the feed mercury was found in the off-gas scrub solution (Schindler, 1997). Some samples of the NWCF bed solids (calcined at 500°C) have had mercury concentrations below detection limits (Garcia, 1997).

A model of the NWCF emissions was developed by Schindler using the Aspen Plus™ software (Schindler, 1995). When the feed Cl:Hg atom ratio exceeds 2, it predicts that the mercury volatilizes from the bed as $HgCl_2$(g). The chloride molar concentration in the feed solution of Campaign H-4 was about twice the mercury concentration, so that volatile mercuric chloride was formed. However, the chloride:mercury atom ratio in the off-gas scrub solution was less than 1. Application of the model indicates that the mercuric chloride vapor partially reacted with metal oxide fines (such as CaO) in the off-gas to form metal chlorides (that were transferred to the calcine bins via the cyclone in front of the scrubber) and elemental mercury that dissolved in the nitric acid scrub solution.

Normally, when operating at 500°C, the chloride has increased to concentrations exceeding that in the feed solution as the quench solution absorbs the chloride volatilized from the feed in the calciner bed. Typically, 5000 mg/L chloride is reached in the scrub solution. During the recent 600°C Campaign, however, it averaged 1240 mg/L (Swenson, 2000). In addition to increased reaction of vaporized chlorides with the oxide fines, some $NaNO_3$ may be converted to NaCl (Boardman, 2000).

Approximately 8 to 20% of the solids content of the calcine solids formed were entrained as fines from the bed and through the cyclone into the OGTS of the WCF (Christian and Rhodes, 1977; Berreth and Dickey, 1982). For the NWCF, improvements in design result in approximately 2% carry-over of particulate materials through the cyclone (IAEA, 1988).

Integrated Off-Gas Treatment System

Introduction

The off-gas from the fluidized-bed calciner is unique in terms of gas flow rate, solids loading, volatile radionuclides, and mercury. Because of the importance of the integral system design and performance for the fluidized-bed calciner off-gas treatment system (OGTS), it is described here. The description provides information on actual performance data during operation.

System Design and Performance

The OGTS for the NWCF was designed as state-of-the-art when it was built and is described here. It is essentially similar to that of the WCF, with some improvements, and is a combination of a wet-dry system consisting of a series of unit operations designed for progressively smaller particles. Operational data is presented for the similar WCF off-gas system because more information has been compiled and because effects of indirect heating vs. in-bed combustion of kerosene can be shown. Improvements in the NWCF individual component designs generally result in a better performance. Data during cold testing of the NWCF and early operational data are also provided. Schindler (1978) discusses the specific design details of the individual off-gas components of the WCF and improvements for the NWCF that resulted from the WCF experience.

The NWCF off-gas treatment system is depicted in Figure 4.8.1. Off-gas clean-up is primarily directed at removing particulate matter from the calciner off-gas (Freeby, 1978). During initial operation (1963 to 1970) of the WCF, volatile ruthenium was present in the calciner off-gas in sufficient quantities to require use of silica gel adsorbers. The nominal gross feed rate is 570 L/hr, the limit being established by particle entrainment and, in recent years, constraints on NO_x release rates imposed by agreement with the State of Idaho. The NWCF has operated, when conditions permit, at up to 900 L/hr, the limit being the ability of the OGTS, primarily the blowers, to handle the flow. To minimize carry-over of fine particles from the fluidized bed, the 1.5-m (5-ft) diameter bed section has a 2.1-m (7-ft) diameter expanded deentrainnment section above it as high as permitted by cell dimensions (3.0 m). The top of the deentrainment section has a double venetian-blind baffle for deflecting particles. A majority of entrained fine particulate material is removed from the 500°C off-gas by a high-efficiency cyclone fines separator at the exit of the calciner and transported pneumatically to the product storage bins. The off-gas is then cooled to 70 to 75°C and saturated in a spray quench tower prior to passing through a high-energy venturi scrubber where most of the remaining particles are removed along with some of the volatilized ruthenium. The scrub solution is typically 2 to 4 *M* HNO_3; this dissolves the scrubbed solids. Some condensation of water occurs in this step, generating a liquid recycle to the feed system of some 10 to 15% of the gross feed rate. The off-gas then passes through a venturi scrubber knockout drum, where removed water aerosols are returned to the scrub hold tank for the quench tower, then a condenser, and a mist eliminator.

The scrubber off-gas exiting the mist eliminator passes through the adsorber superheater and three parallel silica gel ruthenium adsorber beds. The adsorbers each contain a lower and upper bed of silica gel. The lower bed acts primarily as a prefilter to remove residual entrained particles and hydrocarbons. The dry upper bed will remove any remaining ruthenium vapor species. The final off-gas clean-up step consists of four parallel banks of three series HEPA filters. Two banks are online during normal processing; one bank is online during shutdown periods. Two off-gas compressors in parallel (one online during normal processing) maintain the entire off-gas system under a slight negative pressure; a third parallel, auxiliary blower is used to maintain the system under negative pressure during shutdown periods.

The silica gel beds are periodically washed to reduce the pressure drop from accumulation of particles and condensed hydrocarbons. This will also regenerate the silica gel for capacity of adsorbing ruthenium, although it is never challenged with in-bed combustion heating of the calciner.

The NWCF process off-gas is combined with other plant gases, and is finally treated with the Atmospheric Protection System (APS) HEPA filters.

The stack gases are sampled at the 27-m (90-ft) level. During routine operations in the earlier years of NWCF operation, the sampling system consisted of a particulate filter and three gas monitoring beds in series: charcoal, silver zeolite, and silica gel. The particulate filter was pulled daily for counting. It had a detection limit for ^{106}Ru of 0.63 µCi for the 24-hr sample. The gas sample adsorber beds were pulled biweekly and had a detection limit of 0.41 µCi ^{106}Ru, equivalent to 0.029 µCi/24 hr average. No ^{106}Ru gas species has ever been detected since operation of the NWCF began in 1982.

In recent years, as fuel and waste processing operations have decreased, the main stack monitoring system and its operation have been modified. The particulate filter is pulled weekly for gamma scanning. However, an online NaI scintillation counter will detect any instantaneous increase in gamma nuclides collected on the filter and set off an alarm. A monthly composite is counted for americium, plutonium, and strontium. Only a charcoal gas sampler is used for iodine. (The charcoal is only changed out for counting when requested; there is no regulatory requirement for it.)

The NO_x, normally present in the approximately 2000 scfm (3400 Nm^3/hr[*]) process off-gas at 1.5 to 3 vol% during processing of HLLW, is diluted by a factor of 50 in the stack by plant ventilation air and released. The concentration at the site boundary is generally two orders of magnitude below the clean air standard of 0.05 ppm. Nevertheless, as mentioned earlier, the State of Idaho has recently imposed limits on NO_x emission rates, agreed to by the Department of Energy, that sometimes restrict the processing rate. The above operating conditions correspond to between 97 and 194 kg NO_2 equivalent/hr. The current permitted NO_x emission rate is 472 lb/hr (214 kg/hr). NWCF flowrates are held to limit the rate to 95% of the permitted value, or 203 kg/hr. Because the remaining sodium-bearing wastes can only be calcined now by blending in aluminum nitrate with the feed stream, the nitrate concentration will increase. To limit the NO_x emissions to 90% of the current limit, the feed rate to the NWCF will have to be decreased to between 570 and 680 L/hr, the range depending on the ratio of $Al(NO_3)_3$-to-SBW

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[*] Refers to cubic meters of gas per hour at normal (N) condition (i.e., standard temperature [70°F] and pressure).

volumes required. When processing HLLW, the feed rate was typically 680 L/hr, but occasionally reached 760 L/hr.

Iodine-129 quantities in the processed fuels were sufficiently small that the site boundary doses resulting from releases during fuel dissolution and calcination of HLLW have been on the order of 0.1 mrem/year EDE, well within the 10 mrem/year DOE INEEL limit. Thus, iodine removal technology has not been necessary.

Schindler (1978) summarized the performance of the WCF OGTS for removal of ^{137}Cs and ^{90}Sr for eight campaigns; the report discusses the basis for the design of the NWCF OGTS in light of the WCF design and performance. Christian and Rhodes (1977) tabulated the performance of the WCF OGTS components for ruthenium and particle removal during the first five campaigns. The results of these two compilations are summarized in Table 4.8.2. The waste feed types are aluminum fuel dissolution first-cycle extraction raffinate, which is a nitric acid solution, and Zircaloy fuel dissolution first-cycle extraction raffinate, which is an acidic fluoride-nitrate solution. In the first three campaigns, the WCF was operated at 400°C with indirect heating (by circulating hot NaK through a tube bundle in the fluidized bed). In subsequent campaigns, the bed was heated by in-bed combustion of kerosene at 500°C, which is the mode of operation for the NWCF.

TABLE 4.8.2 Component Decontamination Factors for the WCF

Campaign No.	Waste Feed Type	Nuclide Removed	DF Calciner & Cyclone	 Scrubber System	 Feed thru Scrubber	 Silica Gel Adsorbers	 HEPA Filters	 Overall (feed-to-stack)[a]
1	Al	^{90}Sr	6.6	600	3900	12	160	1×10^7
		^{137}Cs	5.9	690	4100	9	280	1.3×10^7
		^{106}Ru	2.1	10.8	23	240	1	$(2\text{-}5) \times 10^3$
1	Al	^{90}Sr			1000	10	1000-2000	$1 \times 10^7\text{-}5 \times 10^8$
		^{106}Ru			13	400-2000	1	$10^3\text{-}10^5$
	Zr	^{90}Sr			2750	10	3000	1.7×10^8
		^{106}Ru			100	1000	1	10^5
4	Zr	^{90}Sr			2800	8.0	630	1.4×10^7
		^{106}Ru			80	12.4	850	8×10^5
5	Zr	^{137}Cs	12	25	300	3 (wet)	1300	1.2×10^6
		^{106}Ru	1.4	30	42	3	1030	1×10^5
6	Zr	^{90}Sr			2300	3 (est)	75	5×10^5
		^{137}Cs			400	3 (est)	75	9×10^4
8	Zr	^{137}Cs				2-6 (wet)	10-30	

[a] The overall DF is usually an independent measurement from the individual DFs and may be larger than the combined component DFs.

Data from Christian and Rhodes, (1977); Schindler, (1978).

During the first three campaigns, the WCF used a “multiclone” with six elements operating and ten elements plugged. Then the multiclone was replaced with a cyclone.

In Campaign 2, the efficiency of the scrubber system for removing ruthenium and particles was greater for the Zr-type waste than for the Al waste. The latter is representative of a commercial fuel dissolution HLW. In later campaigns, the pressure drop across the scrubber was decreased from 13-17.5 kPa to 5-7.5 kPa, resulting in decreased efficiency for particle removal.

The behavior of cesium changed when the calciner was converted from NaK indirect heating at 400°C to in-bed combustion heating at 500°C. In Campaign 1, the DFs (decontamination factors) for ^{137}Cs and ^{90}Sr were essentially the same, indicating that cesium and strontium were both particulate solids. In Campaign 6 at 500°C, the DF for cesium was a factor of six smaller than that for strontium and other particulate species. The cesium may be partially volatilized at the higher temperature and then condensed in the quench tower to form fine particles. In-bed combustion of kerosene may have an effect.

The conversion to in-bed combustion heating resulted in reducing the volatile form of ruthenium to particulate RuO_2 by the time it reached the scrubbers. Thus, after the third campaign, its removal efficiencies by the silica gel adsorbers and HEPA filters were the same as for other particulate species. In earlier campaigns, ruthenium was in the form of a vapor species and the silica gel provided a high DF for it while the HEPA filters provided no removal.

In the first four campaigns, separator-type HEPA filters were used and provided an average DF of greater than 1000. During Campaign 5, the filter type was changed to a separatorless filter that provided greater flow and solids capacities. However, they deteriorated rapidly in service from moisture, acid fumes, and pressure stresses. When freshly installed, DFs of 42,000 were measured. However, failed filter elements in a bank during the course of a campaign resulted in DFs decreasing to 75.

Specific conditions and details of the WCF off-gas equipment operation and performance may be found in Schindler's report (Schindler, 1978).

The WCF was replaced by the NWCF operations in 1982. Improvements in the design of specific off-gas treatment components, such as the cyclone and venturi scrubber, resulted in more efficient particulate removal. Provisions were incorporated to keep the HEPA filters dry.

Unpublished results of measurements of particle decontamination factors show a feed-to-filter DF of 1.0×10^5, based on filter leach analyses during hot operation (Donovan and O'Brien, 1984), and 0.83×10^5, based on extensive off-gas sampling during initial cold (nonradioactive) operation of the NWCF (Swenson, 1982). Also, cold tests of particle removal by the silica gel adsorbers showed an average DF of 13 (range 9.1 to 19; because of measurement uncertainties downstream of the adsorbers, an average DF of 10 is claimed) (Swenson, 1982). Measurements of the off-gas particle loading just ahead of the HEPA filters showed average and maximum values of 0.29 and 0.43 mg/Nm^3, respectively (a normal cubic meter of off-gas corresponds to feeding of 0.33 L aqueous waste to the calciner).

Additional limited performance data for the NWCF OGTS for particles during cold testing and early hot operations were tabulated by the International Atomic Energy Agency (IAEA) (IAEA, 1988). DFs are: calciner and cyclone, approximately 50; quench tower and venturi scrubber, approximately 200; calciner through venturi scrubber, 10^4; silica gel adsorber bed, 10. The DF from feed through the adsorber bed is 1×10^5, consistent with the unpublished results reported above for feed-to-filter DFs. If one assumes 1000 for the HEPA filter DF, the calculated feed-to-stack DF is 10^8.

In the first WCF fluidized-bed calciner campaign at the ICPP (400°C, indirect heating), about 95% of the mercury feed appeared in the product transferred to storage (Commander et al., 1966). The wet scrubbing system removed about 80% of the mercury in the calciner off-gas and the silica gel adsorbers and HEPA filters efficiently trapped the remainder. In a later mass balance study for mercury in the WCF, when it was operating with in-bed combustion at 500°C, 96% of the feed mercury was volatilized from the calciner bed (Herbst, 1979). The venturi acidic scrub system removed 98% of the volatilized mercury. The scrub solution was recycled to the calciner feed inlet. At the end of a campaign, the loaded scrub solution was returned to the HLW tanks. Silica gel adsorber beds downstream of the scrubber collected 92.5% of the mercury entering the beds, or 1.4% of the feed mercury. These beds were periodically regenerated by washing; the washings were recycled to evaporators or routed to the HLW tank farm and then calcined with the HLLW. Provisions were in place for the silica gel to be changed out and the spent material placed in the calcine storage bins; however, this was never necessary. HEPA filters beyond the adsorbers removed 83% of the mercury reaching them, collecting 0.1% of feed mercury; 0.02% of the feed mercury, ca. 6 g/day, was vented to the main stack.

When chloride was present in the waste of NWCF Campaign H-4, the mercury was completely volatilized. Over a 3-month sampling period, 84% was found in the scrub solution and 0.75% was discharged to the atmosphere. The 15% not found was likely distributed as residuals in unrinsed process vessels and piping, sorbed on the silica gel beds, and, possibly, in the calcined solids fines (Schindler, 1997). As mentioned above, WCF studies showed that the silica gel beds adsorb most of the mercury that exits the scrubber. Pilot plant calcining tests with mercury have shown higher mercury concentrations on the fines samples than in the calcine bed particles (Newby, 1980). The atmospheric discharges from the NWCF resulted in an average stack gas mercury concentration of 15 μg/Nm^3. For a stack gas flowrate of about 100,000 scfm (170,000 Nm^3/hr), this corresponds to a daily release rate of 60 g mercury.

The Cl:Hg atom ratio in the scrub solution started at 1:1 and decreased over time to 0.7:1, below the stoichiometric ratio of the expected $HgCl_2$. As noted in the subsection entitled on "Off-gas Characteristics," thermodynamic modeling led to the conclusion that about half of the $HgCl_2$ vapor formed during calcination of the feed reacted with metal oxides to form metal chlorides that were retained with the calcine and removed by the cyclone (Schindler, 1997).

The stack emission rate of mercury from operation of the NWCF observed by Schindler was confirmed by extensive sampling results reported and evaluated for environmental risk assessments (Young et al., 2000).

The concentration of mercury in the NWCF (and WCF) off-gas probably depends more on the $HgCl_2$ concentration in the scrub solution than on the mercury concentration in the feed. Downstream of the scrubber, of the dissolved mercury species, only the $HgCl_2$ would be evolved as a vapor. The partial pressure of mercury in the NWCF off-gas corresponding to the 15 μg/m^3 observed in the stack is many orders of magnitude less than the vapor pressure of $HgCl_2$ at the scrubber temperature. In the absence of a Henry's law constant for it, Raoult's law was assumed for $HgCl_2$ in the scrub solution. The calculated vapor pressure is within an order of magnitude of the observed partial pressure, indicating some possibility of vapor transport through the scrubber.

Another significant observation is that mercury was found on the HEPA filters in the WCF study (Herbst, 1979). Mercury has also been observed on NWCF filters (Brewer, 1993). This indicates transport of the nonvolatile (at near ambient temperature) HgO. The partial pressure of mercury-containing gas (presumably as $HgCl_2$) downstream of the scrubber is insufficient to result in desublimation of $HgCl_2$ on the filters. Because the off-gas exiting the scrubber is warmer than the scrub solution temperature, equilibrium is not established, and some of the oxide may simply pass through. Aerosol formation from evaporation of some 15% of the scrub solution may carry some of the mercury, as $Hg(NO_3)_2$.

Defining Terms

ALARA: As-Low-as-Reasonably-Achievable. The principle established by the U.S. Nuclear Regulatory Commission that a licensee "shall establish, implement, and maintain procedures designed to maintain doses of radiation as low as reasonably achievable, social and economic factors being taken into account."

ARI: Attrition Resistance Index. A measure of difficulty of wearing particles to an average smaller size. It is determined by measuring the weight percentage of particles of a closely sized product, usually a - 28 + 35 Tyler mesh fraction, that is unchanged in size after undergoing attrition by a jet grinder for a specified period. The apparatus used is a 1-in. ID glass tube with a 1/64-in. diameter orifice drilled in an air distributor plate. In the procedure, a 50-g sample is subjected to the grinding action of an air stream from the orifice at sonic velocity for 1 hr. The weight percent of solids remaining unchanged in size is reported as the attrition resistance index.

DF: Decontamination Factor. The ratio of entering-to-exiting concentration of the species for the unit operation. Percent removal is 100(1- 1/DF).

Fluidized-bed calcination: Thermal process for converting HLLW and SBW into solid granules. The acidic, high-activity aqueous waste is sprayed through an atomizing nozzle into a fluidized bed of particles heated to 400 to 600°C. The particles are fluidized by a flow of air through a distributor plate with holes at the bottom of the bed. The water and nitric acid are flash evaporated, and the residual salts and oxides are deposited on the surface of the bed particles.

HEPA filter: High-Efficiency Particulate Air Filter. Tested to remove 99.97% of dioctyl phthalate (DOP) particles of 0.3 μm diameter.

HLLW: High-Level Liquid Waste. The first-cycle extraction raffinate from processing irradiated nuclear fuels for solvent extraction separation of uranium. It contains the radionuclides and processing chemicals after having separated out the uranium.

ICPP: Idaho Chemical Processing Plant; name changed to INTEC in 1998. U.S. Department of Energy facility where spent naval nuclear fuels were received, stored, and processed for recovery of enriched uranium from 1953 to 1992.

INEEL: Idaho National Engineering and Environmental Laboratory. U.S. Department of Energy site where the INTEC is located.

INTEC: Idaho Nuclear Technology and Engineering Center, location of NWCF and WCF.

LWR: Light-Water Reactor. Commercial nuclear power plants used in the United States for producing electricity.

Nitronic 50: A nitrogen-strengthened modification of austenitic Type 316 stainless steel developed by Armco Steel Corporation. Its higher chromium and molybdenum content results in improved corrosion resistance to aqueous fluoride solutions encountered in NWCF operation.

NWCF: New Waste Calcining Facility. Replacement fluidized-bed calciner, with 5-ft diameter bed, for the WCF. Began operation September 1992.

OGTS: Off-Gas Treatment System. Comprised of all components for treating the flowing off-gas from the calciner to cool it and remove radioactive particles and volatilized radioactive ruthenium prior to discharge to a stack.

P/F: Mass ratio of calcine product particles to powdery fine particles that are entrained out of the bed of the fluidized-bed calciner.

PUREX: Plutonium-Uranium Extraction solvent extraction process developed to separate uranium and plutonium from dissolved irradiated nuclear fuel elements.

SBW: Sodium-Bearing Waste. The remaining high-activity liquid waste at the INTEC that must be removed from the underground storage tanks and stabilized into a solid form. It was generated from sodium carbonate scrubbing of the tributyl phosphate extractant used in the separations process and from decontamination solutions.

WCF: Waste Calcining Facility. Original fluidized-bed calciner, with 4-ft diameter bed, for converting HLLW into solid granules. Operated from December 1963 to March 1981.

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For Further Information

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Chapter Five

Non-Thermal Treatment Technologies

5.1

Supercritical Fluid Extraction Technology for Nuclear Waste Management

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Introduction

Solvent extraction is one of the most widely used techniques for concentration, separation, and cleaning of a variety of substances in industrial operations. Conventional solvent extraction processes usually require using organic liquids, acidic or alkaline solutions, or a combination of these, generating environmental problems for handling and disposal of used solvents. In the past two decades, there has been considerable interest in developing techniques utilizing supercritical fluids as solvents for chemical extraction, separation, synthesis, and cleaning.[1,2] The reasons for developing supercritical fluid extraction (SFE) technologies are mostly due to the changing environmental regulations and increasing costs for disposal of conventional liquid solvents. Supercritical fluids exhibit gas-like mass transfer rates and yet have liquid-like solvating capability. The high diffusivity and low viscosity of supercritical fluids enable them to penetrate and transport solutes from porous solid matrixes. Furthermore, the solvation power of a supercritical fluid depends on density; thus, one can achieve the optimum conditions for a particular separation process by manipulating the temperature and pressure of the fluid phase.

Carbon dioxide (CO_2) is widely used in SFE because of its moderate critical constants (T_c = 31.1°C, P_c = 72.8 atm, φ_c = 0.471 g/mL), inertness, low cost, and availability in pure form (Figure 5.1.1). In SFE processes, compounds dissolved in supercritical CO_2 are separated by reducing the pressure of the fluid phase, causing precipitation of the solutes. The fluid phase is usually expanded into a collection vessel to remove the solutes and the gas is recycled for repeated use. The unique properties of supercritical CO_2 have found many new applications in industrial operations. Typical examples of large-scale industrial applications of the SFE technology using supercritical CO_2 include the preparation of decaffeinated coffee and hop extracts.[1]

Direct extraction of metal ions by supercritical CO_2 is highly inefficient because of the charge neutralization requirement and the weak solute-solvent interactions. However, when metal ions are chelated with organic ligands, they may become quite soluble in supercritical CO_2.[3] Quantitative measurements of metal chelate solubilities in supercritical CO_2 were first made by Wai and co-workers in 1991 using a high-pressure view cell and UV/VIS spectroscopy.[4] In this study, the authors noted that fluorine substitution in the chelating agent could greatly enhance (by 2 to 3 orders of magnitude) the solubility of metal chelates in supercritical CO_2 (Table 5.1.1). The demonstration of copper extraction from solid and liquid materials using supercritical CO_2 containing a fluorinated chelating agent bis(trifluoroethyl)dithiocarbamate was

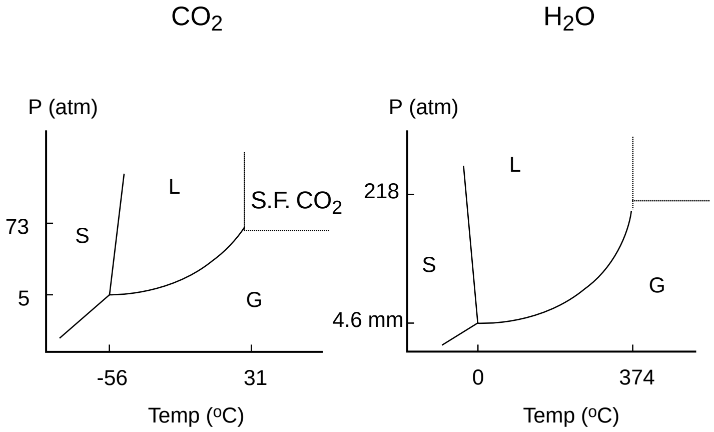


FIGURE 5.1.1 Phase diagrams of CO_2 and H_2O.

TABLE 5.1.1 Solubility of Some Fluorinated Metal Dithiocarbamates Relative to their Non-fluorinated Analogues in Supercritical CO_2

Metal Dithiocarbamate[a]	Solubility at 50°C and 100 atm
$Cu(DDC)_2$	1.1×10^{-6} *M*
$Cu(FDDC)_2$	9.1×10^{-4} *M*
Ni(DDC)	8.5×10^{-7} *M*
NiFDDC)	7.2×10^{-4} *M*
$Co(DDC)_3$	2.4×10^{-6} *M*
$Co(FDDC)_3$	8.0×10^{-4} *M*

[a] DDC = $(CH_3CH_2)_2NCS_2^-$; FDDC = $(CF_3CH_2)_2NCS_2^-$.

Date from Reference 4.

reported in 1992.[5] Since then, over 50 papers regarding SFE of metals from different systems have been published in the literature. A variety of chelating agents, including dithiocarbamates, β-diketones, organophosphorus reagents, and macrocyclic ligands, have been tested for metal extraction in supercritical fluid CO_2.[6] These studies provide a basis for understanding the nature of metal chelation and extraction in supercritical fluids. According to the literature, the important parameters controlling SFE of metal species appear to be:

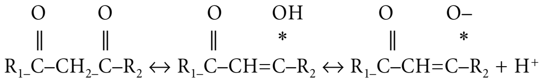
1. Solubility and stability of chelating agents
2. Solubility and stability of metal chelates
3. Water and pH
4. Temperature and pressure
5. Chemical form of metal species
6. Matrix

This *in situ* chelation-SFE technique may have a wide range of applications to metal related problems, including toxic metal decontamination and mineral processing. The new SFE technology appears attractive for nuclear waste treatment because it can greatly reduce the secondary waste generation compared with the conventional processes involving liquid solvents. Other potential advantages of using the SFE technology for nuclear waste management include fast extraction rate, capability of penetration of solid matrixes, and rapid separation of solutes by depressurization. The tunable solvation power of supercritical fluid CO_2 also allows potential separation of metal complexes based on their difference in solubility in the fluid phase or difference in partition coefficient between the fluid phase and the matrix. This unique property of supercritical CO_2 may be very useful for separating uranium and plutonium complexes without requiring chemical redox reactions as in the traditional PUREX process. This section summarizes the information regarding SFE of lanthanides, actinides, strontium, and cesium currently available in the literature to illustrate the capability of the SFE technology for removing long-lived radioisotopes from contaminated wastes. The possibility of utilizing the SFE techniques for treating mixed wastes and for reprocessing spent nuclear fuels is also discussed.

Supercritical Fluid Extraction of Lanthanides and Actinides

Lanthanides and actinides in solid and liquid materials can be extracted using a chelating agent such as a β-diketone dissolved in supercritical CO_2.[6-10] Fluorine-containing β-diketones such as hexafluoroacetylacetone (HFA) and thenoyltrifluoroacetone (TTA) are more effective than the nonfluorinated acetylacetone (acac) for SFE of the f-block elements. In several reported SFE studies for lanthanide and uranium, TTA was used as the chelating agent. One reason for using TTA is that it is a solid at room temperature (m.p. 42°C) and is easy to handle experimentally. Other commercially available fluorinated β-diketones, often in liquid form at room temperature, have also been used for SFE of lanthanides and actinides (Table 5.1.2). A strong synergistic effect was observed for the extraction of lanthanides from solid samples when a mixture of TBP and a fluorinated β-diketone was used in supercritical CO_2.[7,8] Tributylphosphate alone is ineffective for SFE of lanthanides from solids. This is expected because TBP is neutral and trivalent lanthanide ions are not extractable by supercritical CO_2 without counteranions. However, when TBP is mixed with TTA, the extraction efficiencies of the mixed ligands for the lanthanides are drastically increased with respect to each individual ligands (Table 5.1.3). This is probably due to adduct formation, with TBP replacing a coordinated water molecule in the lanthanide-TTA complex, thus increasing the solubility of the adduct complex.

TABLE 5.1.2 Properties of Some Commercially Available β-Diketone



$$R_1\text{–}\overset{\overset{O}{\|}}{C}\text{–}CH_2\text{–}\overset{\overset{O}{\|}}{C}\text{–}R_2 \leftrightarrow R_1\text{–}\overset{\overset{O}{\|}}{C}\text{–}CH=\overset{\overset{OH}{*}}{C}\text{–}R_2 \leftrightarrow R_1\text{–}\overset{\overset{O}{\|}}{C}\text{–}CH=\overset{\overset{O-}{*}}{C}\text{–}R_2 + H^+$$

β-Diketone	Abbrev.	R_1	R_2	Mol. Wt.	B.P. (°C)
Acetylacetone	AA	CH_3	CH_3	100.12	139 (760 Torr)
Trifluoroacetylacetone	TAA	CH_3	CF_3	154.09	107
Hexafluoroacetylacetone	HFA	CF_3	CF_3	208.06	70–71
Thenoyltrifluoroacetone	TTA		CF_3	222.18	103–104 (9 Torr)
Heptafluorobutanoylpivaroylmethane	FOD	$C(CH_3)_3$	C_3F_7	296.18	33 (2.7 Torr)

Uranium and thorium in solids and aqueous solutions can also be extracted by supercritical CO_2 containing fluorinated β-diketones. For example, spiked UO_2^{2+} and Th^{4+} in sand can be extracted by supercritical CO_2 containing TTA with efficiencies around 70 to 75% at 60°C and 150 atm with 10 minutes of static and 20 minutes of dynamic extraction.[10] Using a mixture of TTA and TBP, the extraction efficiencies of UO_2^{2+} and Th^{4+} are increased to >93%.[10] The feasibility of extracting uranyl ions from natural samples was tested using mine wastes collected from an abandoned uranium mine in the Northwest region, (United States). The uranium concentrations in two mine waters tested were 9.6 μg/mL and 18 μg/mL, respectively. The mine waters were extracted with a 1:1 mixture of TTA and TBP in neat CO_2

TABLE 5.1.3 Synergistic Extraction of Uranyl, Thorium, and Lanthanide Ions with TTA and TBP in Supercritical CO_2 (60°C and 150 atm)

Uranyl and Thorium Ions in Water[a]

	Percent Extraction (%)	
Extractant	$(UO_2)^{2+}$	Th^{4+}
TTA	38 ± 4	70 ± 5
TBP	5 ± 2	6 ± 2
TTA + TBP	70 ± 5	87 ± 5

Lanthanide Ions Spiked on Filter Paper[b,c]

		Percent Extraction (%)		
Extractant	Amount (µmole)	La^{3+}	Eu^{3+}	Lu^{3+}
TBP	80	2 ± 1	3 ± 1	4 ± 1
TTA	80	14 ± 2	16 ± 3	20 ± 3
TTA+TBP	40 + 40	92 ± 3	94 ± 4	95 ± 4

[a] From Ref. 10. [b] From Ref. 9.

[c] Filter paper sample contained 10 µg of each lanthanide.

at 60°C and 150 atm for a static time of 10 minutes followed by 20 minutes of dynamic extraction. Under the specific experimental conditions, the percent extraction of uranium from these samples was 81 ± 4% and 78 ± 5%, respectively. The mine waters were also added to a soil sample collected from northern Idaho. The contaminated soil samples were dried at room temperature for the SFE study. The results of extraction of uranium from the contaminated soil samples with a 1:1 mixture of TTA/TBP or HFA/TBP in supercritical CO_2 at 60°C and 150 atm are given in Table 5.1.4.[11] The percent extraction of uranium with HFA/TBP for both soil samples A and B is about 90%, whereas TTA/TBP shows lower percent extractions (77 to 82%) of uranium under the same conditions.

TABLE 5.1.4 Extraction of Uranium from Mine Water and from Contaminated Soil with Supercritical CO_2 (60°C and 150 atm)

Sample	Uranium Conc. (µg/mL)	Extractant	% Extraction
Mine water A	9.6	TTA+TBP	81 ± 4
Mine water B	18.0	TTA+TBP	78 ± 5
Soil A	6.3	TTA+TBP	82 ± 5
		HFA+TBP	91 ± 4
Soil B	15.4	TTA+TBP	77 ± 4
		HFA+TBP	89 ± 5

Note: Mine water: 4-mL sample, 200 µmole each of TTA and TBP; soil sample:100-mg sample, 200 µmole each of TTA and TBP or HFA and TBP. HFA = hexafluoroacetylacetone; TTA = thenoyl-trifluoroacetone.

Data from Reference 11.

The efficiency of extracting uranium from a standard uranium tailings sample obtained from CANMET (Canada Centre for Mineral and Energy Technology, Ottawa, Canada) with supercritical CO_2 and TTA was also evaluated.[8] The tailings sample contained 1010 ppm uranium. Repeated extraction with supercritical CO_2 containing TTA resulted in 80% of the total uranium originally present in the tailings. A fraction of the uranium in the tailings apparently could not be removed by TTA in supercritical CO_2.

The residue after the SFE and the original tailings were treated by the EPA Toxicity Characteristics Leaching Procedure (TCLP). The TCPL test indicated that after the SFE, most of the leachable uranium (>97%) in the tailings was removed by supercritical CO_2.

Tributylphosphate-modified CO_2 containing TTA was used by Laintz et al.[12] to extract lanthanides from an acidic aqueous matrix. Near-quantitative extraction of the trivalent Sm, Eu, Gd, Dy, Yb, Ho, and La ions from aqueous solutions using TBP-modified CO_2 was observed. Furton et al.[13] evaluated the extraction and spectrophotometric determination of $UO_2(NO_3)_2 \cdot 6H_2O$ from different solid matrices by liquid ethanol and by supercritical CO_2 using FOD and TBP as extractants. The highest recoveries were observed with supercritical CO_2 modified with FOD (0.1 *M*), TBP (0.1 *M*), and ethanol (5% v/v). In a comparison with liquid ethanol extraction, the SFE method required a shorter extraction time and produced higher recoveries and greater precision.

In highly acidic solutions (1 to 6 *M* HNO_3), organophosphorus reagents such as TBP and TBPO dissolved in supercritical CO_2 can extract uranyl ions (UO_2^{2+}) and thorium ions (Th^{4+}) effectively (Figure 5.1.2).[14] Uranyl nitrate does not show an appreciable solubility in supercritical CO_2. However, when it is coordinated with TBP, the uranyl nitrate TBP complex becomes very soluble in supercritical CO_2.[15] The extraction efficiencies for UO_2^{2+} and Th^{4+} using TBP-saturated supercritical CO_2 are comparable to those observed in solvent extraction with kerosene containing 19% v/v TBP.[14] Uranyl in nitric acid solutions is extracted as $(UO_2)(NO_3)_2 \cdot 2TBP$ in supercritical CO_2 containing TBP.[8] This is similar to the form of the uranyl complex extracted from nitric acid solutions using kerosene and TBP.[16] The extraction was found to follow first-order kinetics with a rate constant close to that reported for the solvent extraction. Meguro et al.[17] reported the equilibrium relations involved in supercritical CO_2 extraction of uranyl ions from nitric acid solutions with TBP. These results suggest that supercritical CO_2 can be used to replace the organic solvents conventionally utilized in the PUREX process.[18]

Solubility of Uranyl Complexes

Solubility Measurement Using Spectroscopic Techniques

The solubility of a uranium complex in supercritical CO_2 is an important factor in determining its efficiency of extraction by supercritical CO_2. Therefore, accurate measurement of the solubility of uranium complexes in supercritical CO_2 is important for developing supercritical fluid-based extraction processes. There are three traditional methods of determining solubility in supercritical fluids: gravimetric, chromatographic, and spectroscopic. Spectroscopic methods generally offer more rapid determination of solubility, with increased sensitivity, and require small amounts of compounds. If a metal complex has characteristic absorption bands in the ultraviolet-visible (UV-VIS) region, a spectroscopic method is a good choice for determining its solubility in supercritical CO_2. A stainless steel, high-pressure view cell with quartz windows was used originally by Laintz et al.[4] in 1991 for determining the solubilities of a number of metal dithiocarbamate complexes in supercritical CO_2. One drawback of using the high-pressure view cell for solubility measurement is its fixed pathlength (e.g., about 5 cm in the case of Laintz's original work), which limits the concentration range of the measurement. For highly soluble metal complexes, the absorbance may be out of the linear range of the Beer-Lambert law. In addition, the high-pressure view cells are expensive to fabricate, usually costing several thousand dollars each. Recently, the use of a high-pressure fiber-optic system for measurement of solubility of a uranyl complex $UO_2(NO_3)_2 \cdot 2TBP$ in supercritical CO_2 was reported.[19] The fiber-optic system, consisting of three fiber-optic cells with pathlengths ranging from 38 µm to 1 cm, enables compounds of high or low solubility to be measured over a concentration range of several orders of magnitude. The system is capable of withstanding pressure in excess of 300 atm, and spectra over the entire UV-VIS range (200 to 900 nm) can be obtained. The cost of manufacturing the fiber-optic system is about one tenth that for a typical high-pressure, stainless steel view cell.

The structure of the fiber-optic system reported by Carrot and Wai[19] is illustrated in Figure 5.1.3. An ISCO syringe pump, model 260D (ISCO, Lincoln, Nebraska), was used to supply CO_2 at the desired pressure. Supercritical CO_2 was introduced to the saturation cell containing the test compound via a 1.5-m (1/16-in. OD × 0.03-in. ID) stainless steel equilibration coil to ensure the CO_2 was at the correct

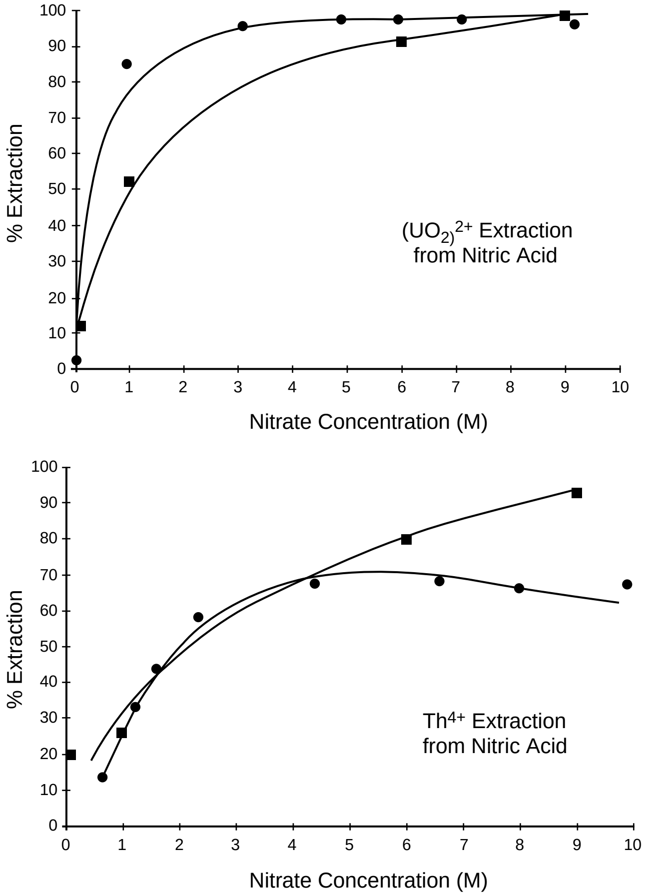


FIGURE 5.1.2 A high-pressure fiber-optic reactor with CCR array UV/VIS spectrometer. (From Ref. 20.)

temperature prior to entering the cell. Either a 3.5-mL saturation vessel or a 14.9-mL view cell (5-cm pathlength) was connected to a Rheodyne 6-port valve to contain the sample. Using the view cell allowed the phase behavior of the uranyl complex under supercritical conditions to be observed. The switching valve enabled the sample cell to be switched in or out of the flow path without the need for depressurizing the entire system and also facilitated the cleaning and flushing of the fiber-optic cells. Three high-pressure UV-VIS cells, with pathlengths of 38 μm, 733 μm, and 1 cm were used for the solubility measurements. Flow of the saturated supercritical solution through the cell was controlled via a high-pressure valve connected to the outlet of the optical cell manifold. Pressure was maintained in the system using a crimped stainless steel restrictor manufactured from 1/16-in.× 0.01-in. ID tubing to give a flow of 100 mL/min at 300 atm and room temperature. The tip of the restrictor was housed in a heated aluminum block to minimize plugging during depressurization. All components of the apparatus, except the view cell, were housed in an Eldex HPLC oven to allow precise control of the temperature (±0.1°C). Heating of the external view cell was maintained by a digital temperature controller. A Cary 1E UV-VIS spectrometer and fiber-optic interface (Varian Instruments) was used for spectroscopic measurements in the work of Carrott and Wai.[19]

To determine the solubilities of metal chelates in supercritical CO_2, both the pathlength of the fiber-optic cells and the molar absorptivity of the complex must be known. First the pathlength of each of the optical cells was determined. The 1-cm pathlength cell was constructed by simply measuring the distance between the fibers during assembly; however, this is impossible for the cells with a pathlength less than 1 mm. The pathlength of these cells was determined using a series of standard anthracene solutions with

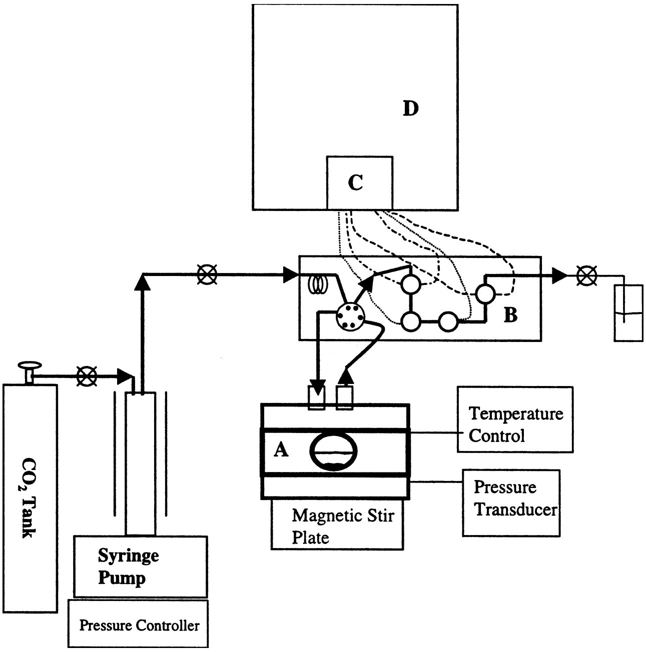


FIGURE 5.1.3 Extraction of uranyl and thorium ions from nitric acid solutions with supercritical CO_2 containing TBP. (l) Solvent extraction with 19% TBP in kerosene; (n) SFE. (Data from Ref. 14.)

a known molar absorptivity. The molar absorptivity of anthracene at 359 nm was calculated using the Beer-Lambert law where the pathlength was 1 cm. The pathlengths for the two remaining cells were calculated from the slope of linear calibration curve of absorbance (at 359 nm) vs. concentration using the calculated molar absorptivity. The molar absorptivity for each complex was determined using standards of the metal chelate in hexane in the 1-cm pathlength cell. Hexane was used because it has a similar polarity to CO_2 and because solutes exhibit similar extinction coefficients and negligible wavelength shifts in absorption maxima.[19] The molar absorptivities for all complexes measured were calculated from the slope of a linear calibration curve of absorbance (at one wavelength) vs. concentration.

Recently, a high-pressure fiber-optic reactor was used by Hunt et al.[20] to measure the dissolution rate of some organic compounds in supercritical CO_2. The basic structure of this reactor (Figure 5.1.4) is similar to the fiber-optic solubility cell reported by Carrott and Wai.[19] The fiber-optic system can be connected to a CCD array UV/VIS spectrometer to obtain absorption spectra rapidly. The high-pressure fiber-optic system reported by Hunt et al.[20] is capable of obtaining one UV/VIS spectrum per second over the entire UV-VIS range. This type of fiber-optic reactor system will be very useful for studying the rates of fast dissolution processes and chemical reactions in supercritical fluids.

Solubility Data and Modeling

The solubilities of $(UO_2)(NO_3)_2 \cdot 2TBP$ in supercritical CO_2 in the temperature range 40 to 60°C and pressure range 100 to 300 atm are shown in Figure 5.1.5.[15] This important uranyl complex is highly soluble in supercritical CO_2, reaching a solubility of approximately 0.4 mol/L at 40°C and 300 atm. This solute concentration range is similar to those found in the PUREX process. The leveling off at pressures above 200 atm at 40°C was due to the complete dissolution of the $UO_2(NO_3)_2 \cdot 2TBP$ solid placed in the reaction cell. At higher temperatures, the density decreases at a given pressure, correlating with decreased solubility of $UO_2(NO_3)_2 \cdot 2TBP$ as the temperature is increased. The solubilities of several uranyl-TTA-X complexes at 40°C and various pressures are given in Figure 5.1.6, where X = TBP, TEP (triethyl phosphate), TOPO (trioctylphosphine oxide), TBPO (tributylphosphine oxide), and H_2O. In this group of uranyl-TTA adduct complexes, $UO_2(TTA)_2 \cdot TBP$ is the most soluble in supercritical CO_2 at each

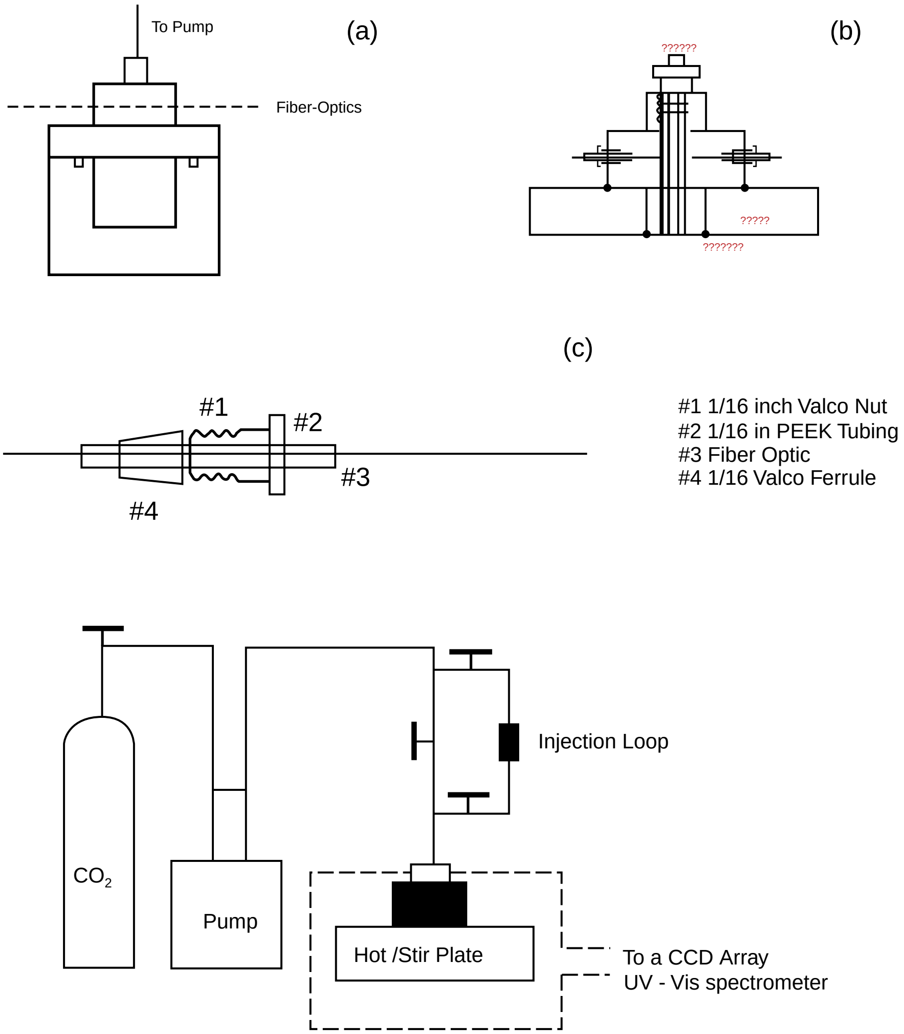


FIGURE 5.1.4 A high-pressure fiber-optic system for solubility measurements in supercritical CO_2. (From Ref. 19.)

pressure, followed by $UO_2(TTA)_2{\cdot}TEP$ and $UO_2(TTA)_2{\cdot}TOPO$. All of these compounds showed an increase in solubility in CO_2 with increasing pressure. The solubilities of $UO_2(TTA)_2{\cdot}TBPO$, and $UO_2(TTA)_2{\cdot}H_2O$ are significantly less than those of the other three complexes. $UO_2(TTA)_2{\cdot}H_2O$, the least soluble uranyl-TTA complex in this series, was used as the starting material to synthesize the remaining $UO_2(TTA)_2{\cdot}X$ adduct complexes. Replacing the coordinated water molecule with an organophosphorus ligand would significantly increase the solubility of the resulting complex. The most soluble adduct complex studied, $UO_2(TTA)_2{\cdot}TBP$, is 2 orders of magnitude more soluble than the maximum concentration of $UO_2(TTA)_2{\cdot}H_2O$. In comparison with $UO_2(NO_3)_2{\cdot}2TBP$, the solubility of $UO_2(TTA)_2{\cdot}TBP$ in supercritical CO_2 is approximately an order of magnitude lower.

A simple model, which relates the solubility of a compound to the solvent's density and the absolute temperature, was used by Waller et al.[21] to predict the solubility of the uranyl complexes in supercritical CO_2. According to this model, the molecules of the solute and those of the solvent would associate with one another to form a solvato complex. The presence of this complex in the supercritical fluid at equilibrium is represented by the following reaction:

$$A + kB \leftrightarrow AB_k \tag{5.1.1}$$

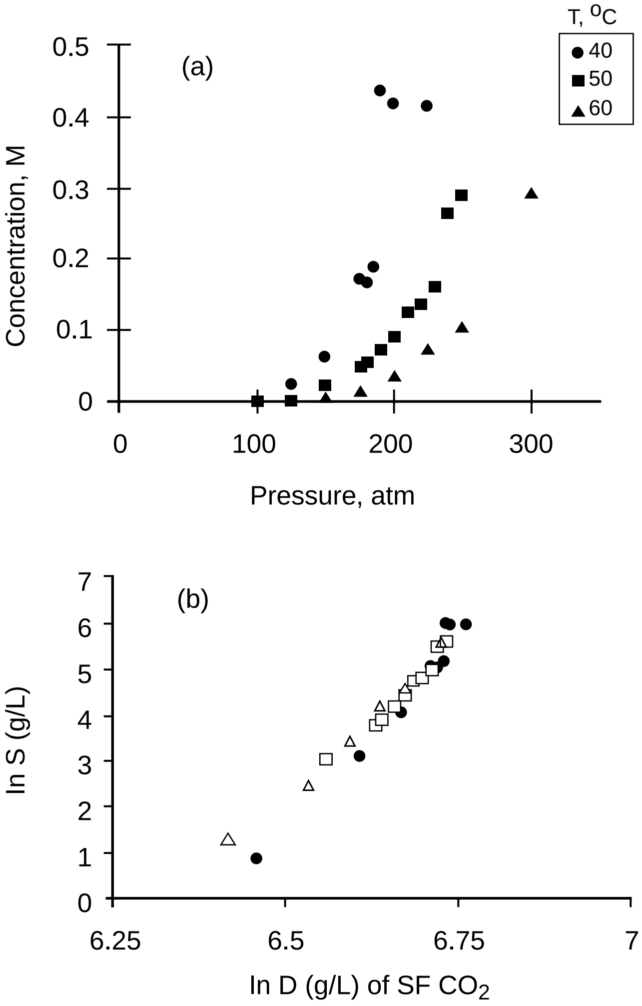


FIGURE 5.1.5 (a) Solubility of $UO_2(NO_3)_2 \cdot 2TBP$ in supercritical CO_2 ; (b) ln S vs. ln D plot for the solubility data. (Data from Ref. 15.)

Equation (5.1.1) is interpreted as one molecule of solute A associating with k molecules of a solvent B to form one molecule of a solvato complex AB_k. The equilibrium constant, K, is represented by Equation (5.1.2):

$$K = \frac{[AB_k]}{[A][B]^k} \tag{5.1.2}$$

Equation (5.1.2) can be expressed in logarithmic form as:

$$\ln[AB_k] = k \ln[B] + \ln[A] + \ln K \tag{5.1.3}$$

The equilibrium constant (K) can be expressed as a function of the enthalpy of solvation (ΔH_{solv}):

$$\ln K = \frac{\Delta H_{solv}}{RT} + q_s \tag{5.1.4}$$

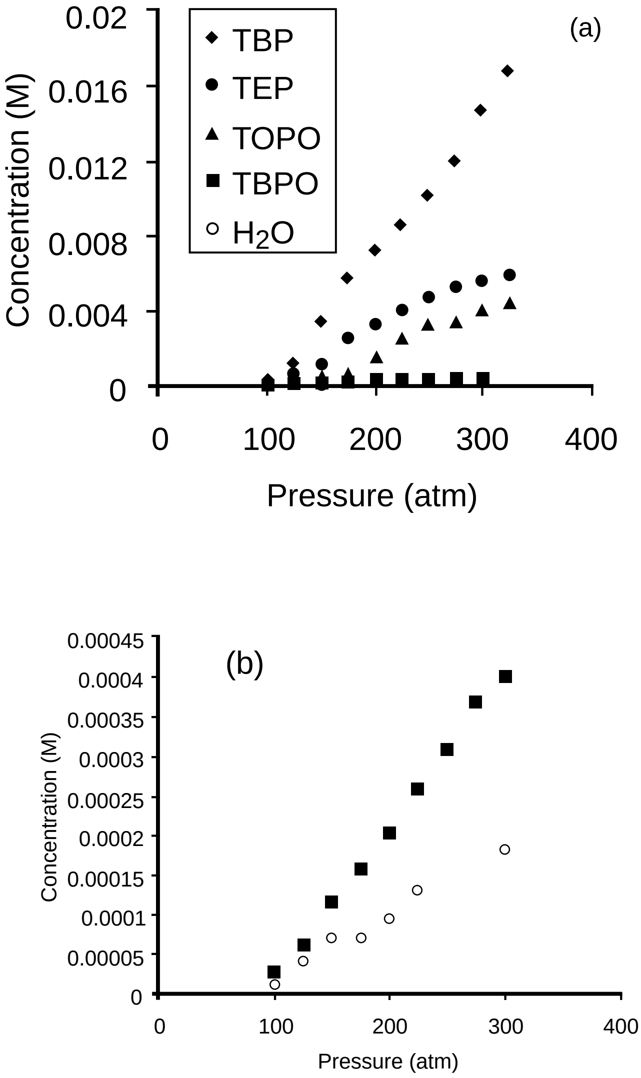


FIGURE 5.1.6 Solubility of $UO_2(TTA)_2{\cdot}X$ in supercritical CO_2, where X = TBP (tributyl phosphate), TEP (triethyl phosphate), TOPO (trioctyl phosphine oxide), TBPO (tributyl phosphine oxide), and H_2O.

where R is the ideal gas constant, T is the temperature, and q_s is a constant.

The concentration of the solvato complex can be related to the density of the fluid phase by:

$$\ln S = k \ln D + C \tag{5.1.5}$$

where S represents the solubility of the solute in g/L, k is a constant for the solute-solvent system which indicates the degree of solvation of the solute in a supercritical fluid, D is the density of the supercritical fluid in g/L, and C is a constant related to the ΔH_{solv} and volatility of the solute. Equation (5.1.5) predicts a linear relationship between ln D and ln S, with the slope and intercept determining k and C, respectively.

When the $UO_2(NO_3)_2{\cdot}2TBP$ data shown in Figure 5.1.5 is plotted in terms of as ln S vs. ln D as shown in Figure 5.1.7, all the experimental data falls on a straight line. The five $UO_2(TTA)_2{\cdot}X$ compounds also exhibit the linear relationship between ln S and ln D expected by the solvato-complex model (Figure

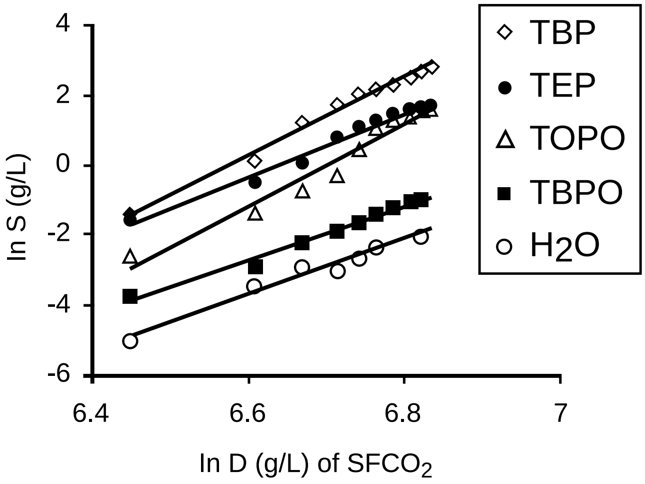


FIGURE 5.1.7 ln *S* vs. ln *D* plot of $UO_2(TTA)_2 \cdot X$ complexes in supercritical CO_2.

TABLE 5.1.5 Values of *k* and *C* Obtained from ln *S* vs. ln *D* Plot for Some Uranium Complexes Dissolved in Supercritical CO_2

Uranium Complex	*k*	*C*
$UO_2(NO_3)_2 \cdot 2TBP$	16.7	–107
$UO_2(TTA)_2 \cdot TBP$	11.1	–73.3
$UO_2(TTA)_2 \cdot TEP$	9.0	–59.8
$UO_2(TTA)_2 \cdot TOPO$	11.8	–79.0
$UO_2(TTA)_2 \cdot TBPO$	7.6	–53.1
$UO_2(TTA)_2 \cdot H_2O$	7.9	–56.3

Data from Reference 21.

5.1.7). The slope (*k*) and intercept (*C*), calculated using Equation (5.1.5), are shown in Table 5.1.5 for each compound at 40°C. All complexes studied gave a positive value for *k* and a negative value for *C*. According to the solvato-complex model, the *k* value should be related to the average number of solvent molecules associated with the metal complex. The most highly soluble complexes appear to be most highly solvated; for example, the *k* value for $UO_2(NO_3)_2 \cdot 2TBP$ is about 17. For the $UO_2(TTA)_2 \cdot X$ complexes, the phosphate adducts are more soluble than the phosphine oxide adducts. For the phosphate adducts, the one with the higher *k* value ($UO_2(TTA)_2 \cdot TBP$, $k = 11$) is more soluble than the one with the lower *k* value ($UO_2(TTA)_2 \cdot TEP$, $k = 9$). This is also true for the phosphine oxide adducts; $UO_2(TTA)_2 \cdot TOPO$, having a *k* value of 11.8, is more soluble than $UO_2(TTA)_2 \cdot TBPO$ with a *k* value of 7.6. The results obtained from this study suggest that it is the nature of the adduct and the *k* value that determine the solubility of these uranyl-TTA adduct complexes in supercritical CO_2. The large *k* values in general suggest that the supercritical fluid CO_2 interacts strongly with these soluble complexes. The solvato-complex approach appears satisfactory for modeling all the uranyl complexes solubility data in supercritical fluid CO_2 reported in the literature. Smart et al.[3,18] also showed that Equation (5.1.5) could be used to model the solubilities of a number of other metal chelates in supercritical CO_2. Using the solvato-complex model, the solubilities of uranium complexes in supercritical CO_2 can be predicted over a wide density range based on a few experimental measurements.

SFE of Strontium and Cesium

Selective extraction of alkali metal and alkaline-earth metal ions from aqueous solutions to organic solvents with crown ethers as extractants is well established in the literature.[22] Extraction of these hard metal ions with crown ethers in supercritical CO_2 is expected to be difficult because of limited solubilities of the resulting metal complexes in CO_2. It is known that fluorinated metal chelates are CO_2-philic.[4] Thus, fluorination of ligands is one method of increasing the solubility of metal complexes in CO_2. This approach requires the design and synthesis of specific fluorinated macrocyclic compounds. Another method is to extract crown ether-metal complexes as ion-pairs into supercritical CO_2 utilizing fluorinated counteranions.[23] It is known that 18-membered crown ethers with cavity diameters in the range of 2.6 to 2.8 Å are the most suitable hosts for Sr^{2+} (2.2 Å).[24] For example, ^{90}Sr can be selectively extracted from nitric acid solutions with dicyclohexano-18-crown-6 (DC18C6) dissolved in a paraffinic or halogenated solvent, where nitrate serves as the counteranion.[25] This macrocyclic system is currently being evaluated for removing ^{90}Sr ($t_{1/2}$ = 30 years), a major uranium fission product, from the high-level acidic nuclear wastes stored at the Idaho DOE site.[26]

DC18C6 is quite soluble in supercritical CO_2, with a solubility estimated to be $>10^{-2}$ mol/L at 60°C and 100 atm. Direct extraction of Sr^{2+} (5.6×10^{-5} *M*) with an excess amount of DC18C6 (5.4×10^{-4} *M*) in supercritical CO_2 showed virtually no detectable extraction of Sr^{2+} from water (Table 5.1.6) or from a 1.3 *M* nitric acid solution. With the addition of a fluorinated carboxylic acid such as pentadecafluoro-n-octanoic acid (PFOAH), extraction of Sr^{2+} from water with DC18C6 in SF CO_2 became significant. The pH of water in equilibrium with supercritical CO_2 under the experimental conditions should be around 2.9 according to a previous study.[27] Because of the inductive effect of the fluorinated group in PFOAH, the pK_a value of this perfluorinated acid is around 1. Therefore, PFOAH is expected to exist as the anionic form $PFOA^-$ under the specified experimental conditions of the water/supercritical fluid CO_2 system. With a concentration of $Sr^{2+} = 5.6 \times 10^{-5}$ *M* and a mole ratio of Sr^{2+}: DC18C6:$PFOA^-$ = 1:10:50, nearly quantitative extraction (98%) of Sr^{2+} from water into supercritical CO_2 was observed at 60°C and 100 atm. Under these conditions, Ca^{2+} and Mg^{2+} were extracted at 7% and 1%, respectively. Selective transport of Sr^{2+} in the presence of Ca^{2+} and Mg^{2+} from an aqueous solution to the supercritical CO_2 phase apparently can be achieved using DC18C6 and PFOA– according to the results shown in Table 5.1.6. Based on the extraction data, it was also estimated that the Sr^{2+} complex extracted by supercritical CO_2 had a ratio of Sr:DC18C6:$PFOA^-$ = 1:1:2. The rate of extraction of Sr^{2+} from aqueous phase into SF CO_2 with DC18C6 and PFOAH is reasonably fast, requiring about 20 minutes of static and 20 minutes of dynamic extraction to complete the extraction of Sr.

Selective extraction of Sr^{2+} by supercritical CO_2 with DC18C6 and perfluoro-1-octanesulfonic acid tetraethylammonium salt (PFOSA-$N(C_2H_5)_4$) or its potassium salt (PFOSA-K) was observed in 1.3 *M* HNO_3 (Table 5.1.7).[23] The extraction of Sr^{2+} in the acid solution with a Sr^{2+}:DC18C6:PFOSA-K ratio of 1:10:50 was 60%, whereas Ca^{2+} and Mg^{2+} were extracted at about 8% and 2%, respectively. The extraction efficiency of Sr^{2+} increased to 76% when the crown ether concentration was doubled. The fluorinated carboxylic acid PFOAH is less effective than the fluorinated sulfonic acid for Sr^{2+} extraction in the acid solution. In general, a high selectivity of extracting Sr^{2+} over Ca^{2+} and Mg^{2+} was observed in all acid solution experiments. It should be pointed out that the high level acidic nuclear wastes stored at the Idaho DOE site are in 1.3 *M* HNO_3.

Extraction of cesium (Cs) from aqueous solutions into supercritical CO_2 was reported recently using different macrocyclic compounds and PFOAH.[28] Under conventional liquid-liquid extraction conditions, the 21-crown-7 host with a cavity diameter in the range of 3.4 to 4.3 Å was found selective for Cs^+, which has a cationic diameter of 3.34 Å. In the SFE experiments, dicyclohexano-21-crown-7 (DC21C7) was found more effective than 18C6, DC18C6, and DB24C8 (dibenzo-24-crown-8) for Cs^+ extraction from aqueous solutions. The efficiency of SFE of cesium from water (pH 2.9) using DC21C7 and a fluorinated counteranion such as PFOA or PFOSA-$N(C_2H_5)_4$ depends on temperature, the initial concentration of cesium, and the amount of the counteranion. Table 5.1.7 shows some SFE results at 100 atm and in the temperature range 21 to 60°C with DC21C7 as the ligand and an initial cesium concentration of

TABLE 5.1.6 Extraction of Sr^{2+}, Ca^{2+}, and Mg^{2+} from Water by Supercritical Fluid CO_2 Containing DC18C6 and a Perfluorinated Counteranion PFOA- or PFOSA- at 60°C and 100 atm

Mole Ratio			% Extraction		
Sr^{2+}:DC18C6:PFOA–H			Sr^{2+}	Ca^{2+}	Mg^{2+}
1	10	0	1	0	0
1	0	10	4 ± 1	1 ± 1	1 ± 1
1	5	10	36 ± 2	1 ± 1	1 ± 1
1	10	10	52 ± 2	2 ± 1	1 ± 1
1	10	50	98 ± 2	7 ± 2	2 ± 1
Sr^{2+}:DC18C6:PFOSA-K					
1	10	10	97 ± 2	8 ± 2	2 ± 1

Note: The aqueous solution contained a mixture of Sr^{2+}, Ca^{2+}, and Mg^{2+} with a concentration of 5.6×10^{-5} M each; pH of water under equilibrium with SF CO_2 = 2.9; 20 min static followed by 20 min dynamic flushing at a flow rate of 2 mL/min. PFOA-H = $CF_3(CF_2)_6COOH$; PFOSA-$N(C_2H_5)_4$ = $CF_3(CF_2)_6CF_2SO_3[N(C_2H_5)_4]$; PFOSA-K = $CF_3(CF_2)_6CF_2SO_3K$.

Data from Reference 23.

TABLE 5.1.7 Extraction of Sr^{2+}, Ca^{2+}, and Mg^{2+} from 1.3 *M* HNO_3 by Supercritical Fluid CO_2 Containing DC18C6 and PFOAH or PFOSA Salt at 35°C and 200 atm

Mole Ratio			% Extraction		
Sr^{2+}:DC18C6:PFOA-H			Sr^{2+}	Ca^{2+}	Mg^{2+}
1	10	0	1	0	0
1	10	50	18 ± 2	2 ± 1	1 ± 1
Sr^{2+}:DC18C6:PFOSA-K					
1	10	50	60 ± 3	8 ± 2	2 ± 1
1	20	50	76 ± 3	8 ± 2	1 ± 1
Sr^{2+}:DC18C6:PFOSA-$N(C_2H_5)_4$					
1	10	50	61 ± 3	7 ± 2	2 ± 1

Note: The acid solution contained a mixture of Sr^{2+}, Ca^{2+}, and Mg^{2+} with a concentration of 5.6×10^{-5} M each; 20 min static followed by 20 min dynamic flushing at a flow rate of 2 mL/min. PFOA-H = $CF_3(CF_2)_6COOH$; PFOSA-$N(C_2H_5)_4$ = $CF_3(CF_2)_6CF_2SO_3[N(C_2H_5)_4]$; PFOSA-K = $CF_3(CF_2)_6CF_2SO_3K$.

Data from Reference 23.

1.57×10^{-4} *M* (mole ratio of [Cs^+]:[DC21C7]:[Counteranion] = 1:100:100). The water sample also contained about an equal concentration of K^+ and Na^+. Up to 63% of the cesium in the water sample was extracted by supercritical CO_2 at 40°C when PFOAS-$N(C_2H_5)_4$ was used as the counteranion. Potassium was also extracted with about the same efficiency as Cs. The results at 20°C is for the liquid CO_2. According to Table 5.1.8, liquid CO_2 is more efficient than supercritical CO_2 for the extraction of cesium under these conditions. Increasing the temperature from 40 to 60°C resulted in a decrease of cesium extraction efficiency. This is likely due to the decrease in supercritical CO_2 density with increasing temperature at a fixed pressure. More research is apparently needed to find better conditions for the

TABLE 5.1.8 Effect of Temperature on the Extraction Efficiency of Cs^+, K^+, and Na^+ in the Presence of DC21C7 and a Fluorinated Counteranion PFOA or PFOSA-N(C_2H_5)$_4$

		% Extraction		
Counteranion	T/°C	Cs^+	K^+	Na^+
PFOA–H	21	60	72	0
	40	43	53	0
	60	16	19	0
PFOSA-N(C_2H_5)$_4$	21	67	73	0
	40	63	69	0
	60	55	39	0

Note: The mole ratio [Cs^+]:[DC21C7]:[Counteranion] = 1:100:100. P = 100 atm, 20 min static extraction and 25 min dynamic flushing at a flow rate of about 2 mL/min.

Data from Reference 28.

extraction of cesium using CO_2 as a solvent. The possibility of extracting cesium and strontium directly from solid materials using supercritical CO_2 as a solvent has not yet been reported.

Extraction of Mixed Wastes

Supercritical CO_2 extraction of organic pollutants such as polychlorinated biphenyls (PCBs) and polyaromatic hydrocarbons (PAHs) from solid materials is a well-established technique for environmental analysis.[29] Many reports have shown that supercritical CO_2 and methanol-modified supercritical CO_2 are capable of extracting PCBs and PAHs from soil with efficiencies often comparable to that of the conventional Sohxlet method. It is also well established now that metal species can be extracted from solid materials using the *in situ* chelation/SFE method.[6] For a system containing both organic compounds and metal species, a sequential SFE procedure can be used to remove the organic components and the metal species separately from the mixed waste. For example, the mixed waste can be first extracted with neat supercritical CO_2 to remove the organic compounds. This is followed by a second extraction with the addition of a suitable chelating agent to the supercritical fluid phase to remove the metal species from the system. Using the sequential extraction approach, organic pollutants, toxic metals, and radioisotopes can, in principle, be separately removed from a mixed waste. Real wastes often contain toxic organic compounds and metal species. Some of the wastes existing at various DOE sites are known to contain organic compounds, toxic metals, and radioisotopes, including uranium and transuranic elements. For example, the storm sewer sediment at Oak Ridge National Laboratory is known to contain uranium, PCBs, mercury, and other metals.[30] The sequential SFE technique may provide an effective means of treating mixed wastes, particularly mixed solid wastes with porous matrices.

The sequential extraction technique is illustrated by the following examples involving the extraction of PCBs, PAHs, and uranium from solid materials. Table 5.1.9 shows the results of sequential extraction of PCB and uranium from a spiked filter paper sample. The sample was first extracted with neat supercritical CO_2 to remove the PCB, followed by the addition of TTA and TBP to extract uranium.[31] Near-quantitative recovery of the PCB and over 90% of the spiked uranium were extracted from the paper according to the conditions specified in Table 5.1.9. Another example is the extraction of PAHs and some common metal species (Cd, Pb, and Zn) from filter paper and from sand.[32] Again, good recoveries were observed using the sequential extraction method. The chelating agent used in the metal extraction in this case was LiFDDC or Cyanex-302. The latter is a commercially available, phosphorus-containing extractant with a chemical name of bis(2,4,4-trimethlphenyl)monothiophosphinic acid.

In principle, the sequential SFE technique is capable of removing organic pollutants, toxic metals, and radioactive elements from mixed solid wastes without involving any acid or organic solvent. This approach

TABLE 5.1.9 Sequential Extraction of Mixed Wastes (PCB(BZ#54) + Uranium) with Supercritical CO_2

Sample	First Extraction Neat CO_2 for PCB	Second Extraction CO_2+TTA+TBP for Uranium
Sand	98	94
Idaho soil	97	75
UTS-4 tailings	98	86

Note: 200 μg BZ#54 (2,2′,6,6′-tetrachlorobiphenyl), 200 μg U, 300 mg TTA, and 200 μL TBP; UTS-4 tailings contained 1010 μg uranium/g tailings (from CANMET). 150°C and 200 atm for PCB extraction, 80°C and 200 atm for uranium extraction; 30 min static followed by 30 min dynamic extraction at a flow rate of 1.5 mL/min.

Data from Reference 31.

should result in significant reduction of secondary waste generation compared with conventional acid dissolution/solvent extraction processes. The matrix effect for the SFE of metals from solid materials such as soil appears more complicated than that of organic compounds. This is probably due to the fact that metals can usually present in different oxidation states and chemical forms in various mineral phases of soil.

Potential Applications

The most successful process for reprocessing spent nuclear fuel has been the PUREX process. In this process, the entire fuel rod with exception of the cladding is dissolved in 6 M HNO_3, with subsequent extraction of uranium and plutonium into an organic solvent through the formation of nonpolar complexes with TBP. Although the PUREX process has been extensively studied, the process has the inherent disadvantage of liquid-liquid separation. Disposal of the high level liquid waste produced from the PUREX process is expensive. The nuclear industry has been paying attention to the applications of supercritical fluid for utilization at the process chemistry level.[18] The suggested applications can be grouped into two categories: (1) for recycle of spent fuel, and (2) for treatment of nuclear wastes.

As described in the subsection entitled "Solubility of Uranyl Complexes," uranyl nitrate in conjunction with TBP is the most soluble complex formed in supercritical fluid CO_2. This suggests that supercritical CO_2 may be an effective substitute for the organic phases commonly used in the PUREX process for the extraction of uranium from nitric acid solutions. The proposed flowsheet for a supercritical fluid system containing TBP (Super Purex Process) is illustrated in Figure 5.1.8. It was shown that some main fission products (including La^{3+}, Cs^{+}, Sr^{2+}, Ba^{2+}, Zr^{4+}, Mo^{6+}, and Pd^{2+}) and some stainless steel corrosion products (such as Fe^{3+}, Ni^{2+}, and Cr^{3+}) were not significantly extracted in the supercritical fluid extraction system. Further, the distribution coefficients for U(VI)/Pu(IV) in the SFE process were found to vary with temperature and pressure, suggesting that separation of uranium and plutonium might be achieved by manipulating the conditions of the extraction.

Alternatively, a dry process may be possible, wherein the acid dissolution step is eliminated by direct dissolution of the uranium oxide in supercritical fluid CO_2 containing suitable ligands. Direct dissolution of uranium oxides (UO_3 and U_3O_8) in supercritical CO_2 containing TTA and TBP has been demonstrated.[33] Other fluorinated β-diketones and organophosphorus reagents may also form soluble uranyl complexes in supercritical CO_2. The solubility of the uranyl-β-diketone adduct complexes is important for the development of a dry extraction process that may entirely eliminate the need for acid and other organic solvents from the extraction procedure. Of the limited number of $UO_2(TTA)_2 \cdot X$ complexes studied (see "Solubility of Uranyl Complexes" subsection), the most soluble one is $UO_2(TTA)_2 \cdot TBP$. While less soluble than $UO_2(NO_3)_2 \cdot 2TBP$, $UO_2(TTA)_2 \cdot TBP$ is still sufficiently soluble to be potentially useful, thus making reprocessing of spent nuclear fuels by a dry process a realistic proposition.

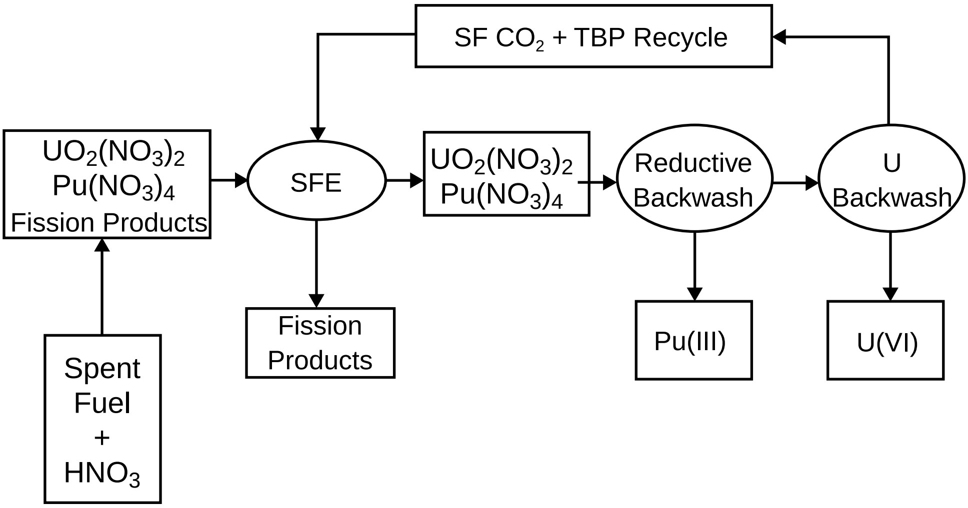


FIGURE 5.1.8 Flowsheet of a proposed Supercritical Fluid PUREX Process. (From Ref. 18.)

One area where SFE technology may find important applications is the clean-up of low-level radioisotope-contaminated materials generated by a wide range of facilities, including nuclear power plants, government and defense laboratories and reactors, hospitals, and industrial plants. The waste takes a variety of forms, such as medical treatment and research materials, contaminated wiping rags and paper towels, used filters and filter sludge, protective clothing, hand tools, equipment, parts of decommissioned nuclear power plants, etc. The matrices of such wastes often consist of porous materials. The low viscosity and surface tension of supercritical fluid CO_2 allows it to enter a porous matrix, dissolve a given compound, and exit without any of the problems normally associated with liquids. Mixed wastes usually are referred to as wastes containing both hazardous chemical components, subject to the requirement of the Resource Conservation and Recovery Act (RCRA), and radioactive components, subject to the requirements of the Atomic Energy Act. The DOE is the source of about 90% of all mixed waste in this the United States. The sequential extraction technique described in the previous subsection enables separation of toxic organic compounds, metals, and radioisotopes from a mixed waste into individual constituents, enormously simplifying disposal of such wastes.

Another area where supercritical fluid CO_2 technology may prove valuable is for stabilization of cement-based matrices. Cement is a common material for encapsulating nuclear waste materials. Usually, mixtures of cement form a solid material rather rapidly. However, in the interior of the cement, reaction continues to take place over a long period of time as the calcium hydroxide reacts with the CO_2 in the atmosphere to form the more stable calcium carbonate. The carbonation process is slow because water blocks the pores and stops CO_2 penetration. Supercritical fluid CO_2 can speed up this natural conversion by dissolving and transporting water from the microporous cement structure, leaving the calcium hydroxide to react with the CO_2 of the fluid.[34] Research is currently underway at the Los Alamos National Laboratory to study the potential of supercritical-treated cements for encapsulating nuclear wastes.[35]

Commercialization of these supercritical fluid technologies, although still years away, should offer many benefits for the 21st century nuclear industry. Such benefits should be realized in terms of improved efficiency of chemical processes, reducing secondary waste generation, and cost-savings associated with waste disposal. Research in developing more effective chelating agents and in understanding the factors controlling the extractability of fission products, uranium and transuranic elements in various waste matrices by supercritical fluid CO_2 is needed to develop practical processes for nuclear waste management.

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5.2

Electrochemical or Direct Chemical Oxidation

5.2.1 Mediated Electrochemical Oxidation Using Silver and Cobalt Based Systems

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Introduction

Mediated Electrochemical Oxidation (MEO) is a promising technology for the treatment of hazardous and mixed wastes such as those produced in commercial applications, biomedical research, and from defense operations involving the U.S. DOE and DOD. The combination of a powerful oxidant and an acid solution in the MEO system allows the conversion of nearly all organics, whether present in hazardous or in mixed waste, to carbon dioxide and water. The degree of decomposition of the organic(s) depends on such as factors as time allowed for the reaction, fluid transport, temperature, and other factors associated with the particular system. In properly designed systems, insoluble transuranics can be simultaneously dissolved through this process for subsequent separation and recovery. The oxidant, or mediator, is a multivalent transition metal ion that can be cleanly recycled in a number of charge-transfer steps in an electrochemical cell.

Although the oxidation of organics and the dissolution of transuranics by higher valency metal ions have been known for some time, applying the MEO technology to waste treatment is a relatively recent development. Numerous groups, in both the United States and Europe, have made substantial progress in the last decade toward understanding the mechanistic pathways, kinetics, and engineering aspects of the process. Over the past 20 years, several high-valency metal ions have been investigated as mediators, including Ag(II),[1-7] Ce(IV),[6,13-17] Co(III),[6,8-10] and Fe(III).[10,11] Each of these shows different kinetics with respect to oxidative chemistry and optimal waste streams differ slightly for each system.

At Lawrence Livermore National Laboratory (LLNL), substantial contributions have been made to this knowledge base in these and other areas. Conceptual design and engineering development have been completed for a pilot plant-scale MEO system, and numerous data have been gathered on the efficacy of the process for a wide variety of anticipated waste components. In addition, LLNL has completed a 3-year, multi-million dollar Cooperative Research and Development Agreement (CRADA) with EOSystems (now known as CerOx Corporation[18]) toward the development of this technology for the commercial sector. Some of the expertise acquired during this CRADA is reviewed in another section of this book. This section reviews the data obtained at LLNL on the chemical, electrochemical, and engineering aspects for the systems Ag(II)/HNO_3 and Co(III)/H_2SO_4, with both laboratory- and bench-scale systems, and covers the topics of organics destruction, transuranic recovery, and some of the ancillary systems.

Process Chemistry Fundamentals

Organics Destruction

MEO is based on the oxidation of the organic components of a waste stream to carbon dioxide through a series of charge-transfer steps involving a mediator. This mediator, typically a transition metal in its highest valency state, is generated at the anode of an electrochemical cell and dispersed throughout the anolyte solution. Upon oxidation of the organic species by the mediator, the reduced mediator is reoxidized at the anode and the cycle repeats until all oxidizable material in the cell is depleted. Equation (5.2.1.1) is a representative stoichiometric reaction for the oxidation of ethylene glycol.

$$(CH_2OH)_2 + 10\ (Ag^{2+} \text{ or } Co^{3+}) + 2\ H_2O \Leftrightarrow {}_2CO_2 + 10\ (Ag^{+} \text{ or } Co^{2+}) + 10\ H^{+} \tag{5.2.1.1}$$

The electrochemical current loop is completed by the cathode reaction, which is typically the reduction of the electrolyte or of protons. The representative cathodic reactions for the Ag/HNO_3 and Co/H_2SO_4 systems are shown in Equations (5.2.1.2) and (5.2.1.3), respectively.

$$HNO_3 + 2H^{+} + 2e- \Leftrightarrow\ HNO_2 + H_2O \tag{5.2.1.2}$$

$$2H^{+} + 2\ e- \Leftrightarrow\ H_2 \tag{5.2.1.3}$$

Note that Equation (5.2.1.2) is the dominant reaction for the silver system when the concentration of nitric acid is greater than 2*M*; when this is not the case, Equation (5.2.1.3) becomes more important.

Although the organic oxidation process chemistry for the Ag/HNO_3 and Co/H_2SO_4 systems is similar, significant differences exist between them. For example, in the Ag/HNO_3 system, the cathodic reaction is the reduction of nitrate ions, which can result in the formation of NOx. To prevent this, HNO_2 can be converted back to HNO_3 by reacting it with oxygen; this method is described in more detail in a later subsection. Also, this cathodic reaction is electrochemically reversible and a cationic exchange membrane must be employed to prevent the reoxidation of nitrite ion at the anode and consequent loss of current efficiency. In the Co/H_2SO_4 system, the cathodic reaction is the reduction of protons [Equation (5.2.1.3)], resulting in the release of hydrogen gas from the catholyte. Because this reaction is irreversible, no membrane is required in this system.

Another difference between the cobalt and silver systems is in the relative rates of the reaction of the oxidized form of the mediator with water. This reaction is parasitic because it leads to a reduction of the mediator, although there may be some benefits due to the production of radical species (e.g., hydroxy radicals) that are also oxidants.[19] The rate of reaction of Ag(II) with water is relatively rapid,[19] whereas Co(III) is somewhat more stable in water, especially at low pH.[20-23]

In both the Ag(II) and Co(III) processes, the anodic process for the generation of the higher valency mediator is mass transport limited, and the limiting current is thus based on this characteristic. Cell design and electrolyte flow parameters must be optimized for the maximum production efficiency of the mediator species in order to maximize the economics of the process. Operation of the system beyond the limiting current for mediator generation results in the production of oxygen from water oxidation; this conceivably could assist in the oxidative pathways for certain organics but more likely would result in a decrease in overall system efficiency.

Laboratory-Scale Experiments

The typical experimental setup was a flat plate cell with 0.5 L (each) anolyte and catholyte loops, a platinum anode (coated on either titanium or niobium) of about 35 cm^2 with a nickel or titanium or niobium cathode, and a Nafion membrane. The destruction efficiencies for a variety of organic substrates are shown in Table 5.2.1.1. These results were obtained by Total Organic Carbon (TOC) analyses of the remaining electrolyte (both anolyte and catholyte) following a particular run or by an integrated measurement of the amount of CO_2 produced during the run using a dedicated CO_2 analyzer and computer

TABLE 5.2.1.1 Summary of Organics Destruction Data for Laboratory-Scale MEO Systems

Organic Compound	Mediators Tested	Acid Conc. (*M*)	Destruction Efficiency (%)
Alcohols			
Ethylene glycol	Ag/Co	4–12/2–6	100
2-Propanol	Co	2–4	65[a]
1-Chloro-2-propanol	Co	2–4	>99
1,3-Dichloro-2-propanol	Co	2–4	>99
Aromatics			
Benzene	Ag	3	88[a]
2,4-Diaminotoluene	Ag	4–12	100
CH3-X			
Nitromethane	Ag	4	0
Aliphatic			
Dodecane	Ag	6	99
Organic materials			
Trimsol (cutting oil)	Ag/Co	8–12/4–6	>99/60
Cellulose	Ag/Co	4-12/2–6	>99.9/>99.9
Biomass	Ag	8, 10	97
Latex	Ag	8, 10	98
Tyvek	Ag	8, 10	98
Polyvinylchloride	Ag/Co	8/4	21/0

Note: Solid materials were shredded to approx. 1/8 inch. The times required to achieve the stated destruction efficiencies were generally 15 min to 1 hr.

[a] Organic volatilization partially accounted for efficiencies of <100%.

data acquisition. It was judged that TOC measurements provided the most accurate determination of destruction efficacy, although destruction efficiencies listed as being greater than 99% may in fact be higher but limited by the analytical technique. In some cases, the amount of evolved CO_2 was insufficient to account for complete destruction although a TOC analysis indicated no remaining organic material in either the anolyte or catholyte solution. Thus, it appeared that either the original organic substrate, or its intermediate oxidation products, volatilized before complete oxidation could occur. This effect was especially pronounced with extremely volatile organics (e.g., acetone). In Table 5.2.1.1, a note is made of those organic substrates in which volatilization appeared to be a significant factor in nonquantitative conversion to CO_2. A properly designed off-gas system (with perhaps a condenser) would do much toward alleviating this volatilization problem.

In general, the Ag/HNO_3 system performed more effectively than the Co/H_2SO_4 system. This is due to three factors: (1) the oxidation potential of Ag(II) is higher than that of Co(III), (2) the Ag/HNO_3 system is believed to involve OH radical species due to the oxidation of water by Ag(II),[20] and (3) nitric acid is itself a more powerful oxidant than sulfuric acid. A limited number of experiments were performed on systems using Fe(III)[10] and Ce (IV) (also reported on in a separate section) as mediators, but the effectiveness of these for organics destruction under ambient conditions was judged to be less than either Ag(II) or Co(III).

It should be noted at this point that the oxidation of any organic is a series of charge-transfer steps: oxidation occurs as a cascade of one-electron steps resulting from the collision of the organic species with the oxidized form of the mediator. Mechanistic pathways can become exceedingly complex for large organics and intermediate species can be more or less reactive than the original compound. *A priori* predictions of a particular compound's ease of oxidative destruction are difficult, but empirically it was noted that the more oxidizable functional groups that an organic substrate has, the more facile the oxidation by MEO. Thus, a diol would result in faster oxidation than a single alcohol group. The only functional group that exhibited no detectable oxidation was the C-F bond, such as contained in polytetrafluoroethylene (Teflon) and polyvinylidenefluoride (Kynar). In fact, both of these polymers make excellent materials of construction for MEO systems due to their inertness. One other notable exception was that the silver system was totally ineffective in destroying nitromethane, while scoping studies showed that it was possible with the cobalt system. This phenomenon is not understood at this point but would perhaps make an interesting future study.

Even if thermodynamic predictions would indicate that a given organic might be oxidizable by Co(III) or Ag(II), little oxidation will occur if few collisions between mediator and organic occur. That is, the surface area of contact should be maximized to achieve optimal rates of destruction. For soluble organics, this is not a problem because the organic is dispersed homogeneously throughout the electrolyte. However, with insoluble or immiscible compounds, this contact issue can be a significant factor. In tests with these types of substrates, the organic simply floated on top of the electrolyte solution (or sank to the bottom), and destruction was exceedingly slow. This was the case with organics such as benzene, dodecane, and trimsol. It is believed that the formation of an emulsion with a surfactant might be one way of attacking this problem.

Bench-Scale Experiments

A diagram of the bench-scale MEO system at LLNL is shown in Figure 5.2.1.1. The heart of the system is, of course, the electrochemical cell, but the system also contains several ancillary units for off-gas treatment and electrolyte recycling, which are described in more detail below (see also Figure 5.2.1.4). The bench-scale organics destruction experiments were performed on a commercial plate and frame cell (Imperial Chemical Industries, Model FM-21). This two-channel cell contained three niobium cathodes and two platinum-coated niobium anodes, each with an active surface area of 0.85 m^2; the anode and cathode compartments were separated by a Nafion 117 membrane. This system has a capability of up to 3000 A, with a flow rate of 4 gpm per cell channel and anolyte and catholyte fluid volumes of 20 and 40 L, respectively. The electrolyte used in this system was 0.5 M $AgNO_3$ in 8–10 M HNO_3, at operating temperatures of 50 to 70°C. Organic compounds were introduced into the cell in continuous feed mode, and destruction efficiencies were calculated solely by the method of TOC analysis described in the laboratory-scale experiments above. When the organic to be tested was a solid, it was shredded to a size of about 1/8 in.

The oxidized form of the mediator in the nitric acid electrolyte has a dark blue or almost black appearance, while the reduced mediator/electrolyte is a red or maroon color. Spectroscopic techniques can thus be used to monitor the relative amounts of the Ag(II) and Ag(I) species and can provide valuable clues as to the efficiency of mediator generation, limiting current/mass transfer regime, rate of organics destruction, etc. A limited number of such spectroscopic investigations were performed on the Ag/HNO_3 bench-scale system at LLNL but the data are not reported here.

Destruction data for several organics obtained with this Ag/HNO_3 MEO unit is given in Table 5.2.1.2, and also in References 24 and 25. Figures 5.2.1.2 and 5.2.1.3 illustrate the relationship between destruction efficiency and current efficiency observed with this bench-scale system for trimsol and cellulosic materials, respectively. This current efficiency is defined as the ratio of the amount of current *theoretically* required to completely oxidize a given quantity of organic to carbon dioxide to that amount of current required *in an actual test*. As can be seen in Figures 5.2.1.2 and 5.2.1.3, gains in destruction efficiencies are obtained at the expense of current, or coulombic, efficiency. In batch-mode tests, as the concentration of readily available organic substrate decreases at the completion of a particular run, inordinately long time periods are required to oxidize the few organic fragments that remain. Hence, efficiency is "lost" as parasitic reactions such as the oxidation of water become increasingly important.

Ancillary Systems

Several associated systems have been designed and tested in association with this bench-scale Ag/HNO_3 MEO system, including the recycling of the electrolyte, off-gas treatment, and final electrolyte disposal. A schematic of these systems is shown in Figure 5.2.1.4, and each is described in more detail below. Because the development of the Co/H_2SO_4 system was limited to laboratory-scale experiments, similar system engineering studies were not completed.

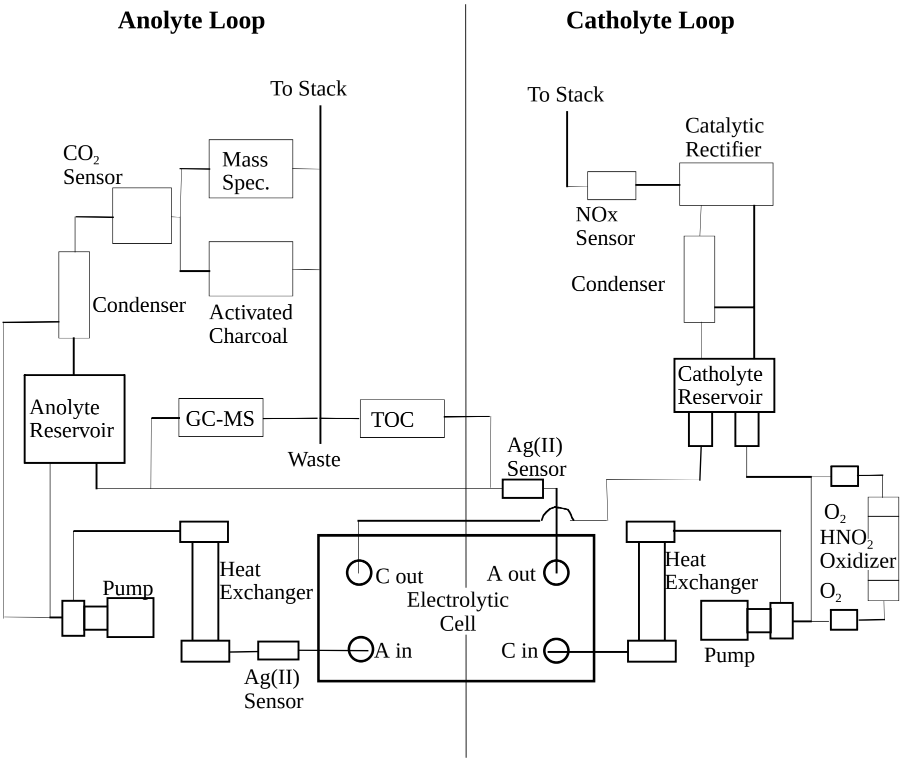

FIGURE 5.2.1.1 Diagram of bench-scale MEO system at LLNL.

TABLE 5.2.1.2 Summary of Organics Destruction Data for Bench-Scale MEO System

Organic Compound	Mediator	Acid Conc. (*M*)	Destruction Efficiency (%)
Trimsol	Ag	10–12	>99.9
Cellulosic materials	Ag	8–10	>99.9

Note: Solid materials were shredded to approximately 1/8 in.

Silver Chloride Recovery. In the destruction of chloride-containing organics in the Ag/HNO_3 system, the chlorine released upon oxidation of the organic is immediately precipitated as insoluble silver chloride. To prevent the loss of the mediator when treating chloro-organics, a method has been developed to recover this mediator.[26] This method is based on the reduction of silver chloride to silver:

$$2AgCl + 2NaOH + H_2O_2 \Leftrightarrow 2Ag^0 + 2NaCl + 2H_2O + O_2 \qquad (5.2.1.4)$$

and subsequent separation and redissolving of silver in nitric acid for reuse:

$$4Ag^0 + 6HNO_3 \Leftrightarrow 4AgNO_3 + NO + NO_2 + 3H_2O \qquad (5.2.1.5)$$

The advantages of this method are that the chemicals are relatively inexpensive and the only waste generated will be sodium chloride, which can be dried and disposed of via polymer encapsulation; this waste quantity is minimal if a low stoichiometry of sodium hydroxide is used. Despite these advantages,

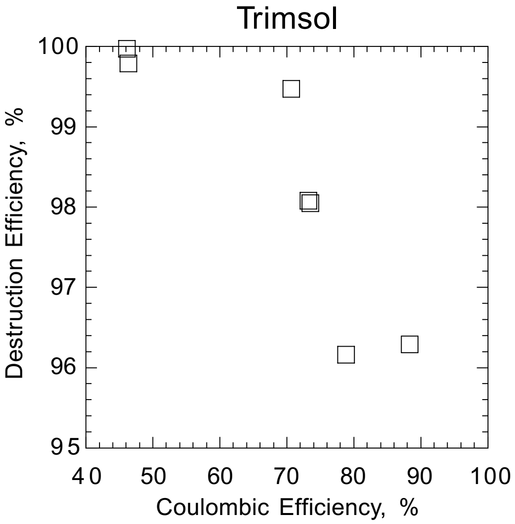

FIGURE 5.2.1.2 Relationship between current and destruction efficiencies for bench-scale tests of trimsol.

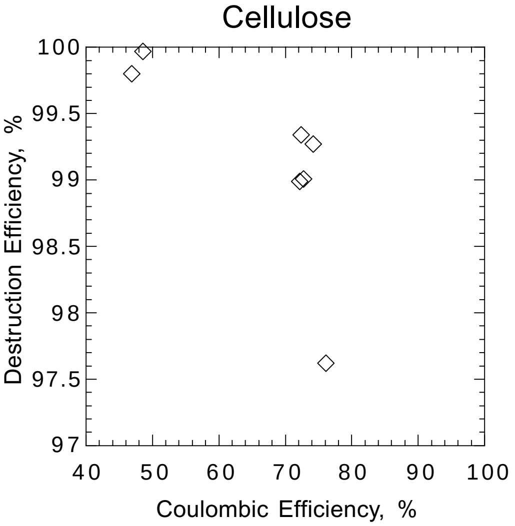

FIGURE 5.2.1.3 Relationship between current and destruction efficiencies for bench-scale tests of cellulose.

there is no quantitative information available in the literature and therefore pilot plant-scale tests were conducted at LLNL to study this process.

Optimal results were obtained when using an excess of sodium hydroxide and hydrogen peroxide, with 98% conversion of silver chloride obtained for stoichiometries of 1.25X NaOH and 10.32X H_2O_2 at 80°C. The excess H_2O_2 is unstable and breaks down into water and oxygen, which are not undesirable additions to the waste stream. Because this decomposition occurs quickly in alkaline solutions at high temperatures, the conversion efficiency decreases as the reaction time increases and careful control of reaction time is required.

Silver Removal. A system has been designed and tested to recover the silver mediator from the anolyte before final disposal/treatment of the used electrolyte in the Ag/HNO_3 system.[27] This process is based on the reaction of Ag(I) with hydrochloric acid to form insoluble silver chloride, which is then separated

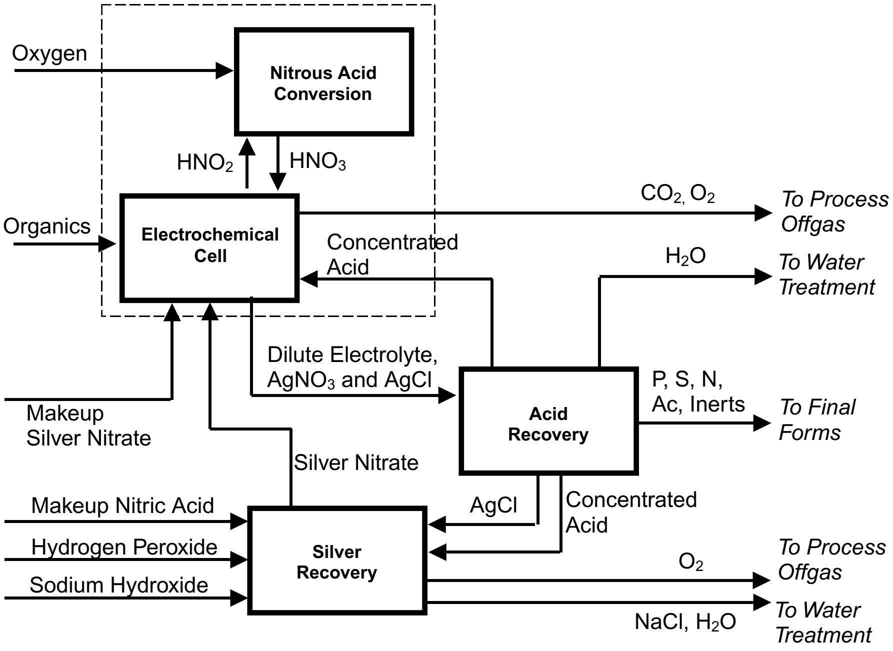

FIGURE 5.2.1.4 Flow diagram for MEO system, including ancillary components.

by centrifuging. Tests with this system at the bench scale yielded silver removal efficiencies of 99.999% with HCl in 5% excess, 99.990% with HCl in 0.5% excess, and >99.5% with HCl added in stoichiometric quantities. After removal of the silver, the electrolyte is boiled off until almost dry by passing it through a thin-film evaporator. The evaporator bottoms are carried out and if desired, any radionuclides present can be recovered by ion exchange. If recovery is not desired or feasible, the radioactive material is disposed of via grouting or ceramicization.

Nitrite Oxidation/NOx Reduction. As mentioned, the reduction of nitrate is the dominant cathodic reaction when the concentration of nitrate is greater than 2 *M* [Equation (5.2.1.2)]. The nitrous acid generated must be converted back to nitric acid; otherwise, the nitrous acid in the liquid phase will eventually decompose:

$$3HNO_2 \Leftrightarrow 2NO(g) + NO_2^- + H_3O^+ \tag{5.2.1.6}$$

Reacting the nitric oxide with oxygen regenerates the nitric acid and prevents this decomposition:

$$2NO + O_2 \Leftrightarrow 2NO_2 \tag{5.2.1.7}$$

$$3NO_2 + H_2O \Leftrightarrow 2HNO_3 + NO \tag{5.2.1.8}$$

In practice, these mechanistic pathways can become more complex, combining a mixture of gas- and liquid-phase reactions.

However, because oxygen is only very sparingly soluble in the solution, typical reactors in the form of packed-bed columns would have to be very tall to attain reasonable nitric acid regeneration efficiencies. A turbo-aerator was developed at LLNL that achieves very high efficiencies in a small volume.[28] The turbo-aerator draws the gas and the fluid together, and passes them through a row of stator blades that disperses the gas into very small bubbles. This device is installed in the catholyte flow loop, and the advantages of intimate mixing and high surface area contribute to measured efficiencies of 95 to 99%.

Plutonium Oxide Dissolution

Insoluble transuranic oxides can be dissolved and separated out in a specialized MEO system known as Catalyzed Electrolytic Plutonium Oxide Dissolution, or CEPOD.[13-17,29] In fact, it was for this reason that the Ag/HNO_3 system was originally developed, primarily at Pacific Northwest National Laboratory. In such as system, insoluble plutonium oxide is converted to the water-soluble plutonyl ion as shown in Equation (5.2.1.9).

$$PuO_2 + 2\ Ag^{2+}\ ?\ PuO_2^{2+} + 2\ Ag^+ \qquad (5.2.1.9)$$

A flow diagram of the CEPOD system for transuranic recovery is shown in Figure 5.2.1.5. The chemistry of this system is very similar to the bench-scale Ag(II)/HNO_3 MEO system above, and many of the ancillary systems are also applicable. The main differences include a dissolver loop added in the anolyte flow stream, and an annular cell with a gold anode. Dissolution of transuranic oxides was modeled with Cu(oxalate), as this material is insoluble in nitric acid in the presence of Ag(I) but dissolves in the presence of Ag(II) due to the facile oxidation of oxalate anions by Ag(II). Although modeling studies,[28] engineering design, and construction of this system are complete, insufficient testing has been done at LLNL to report any conclusive data.

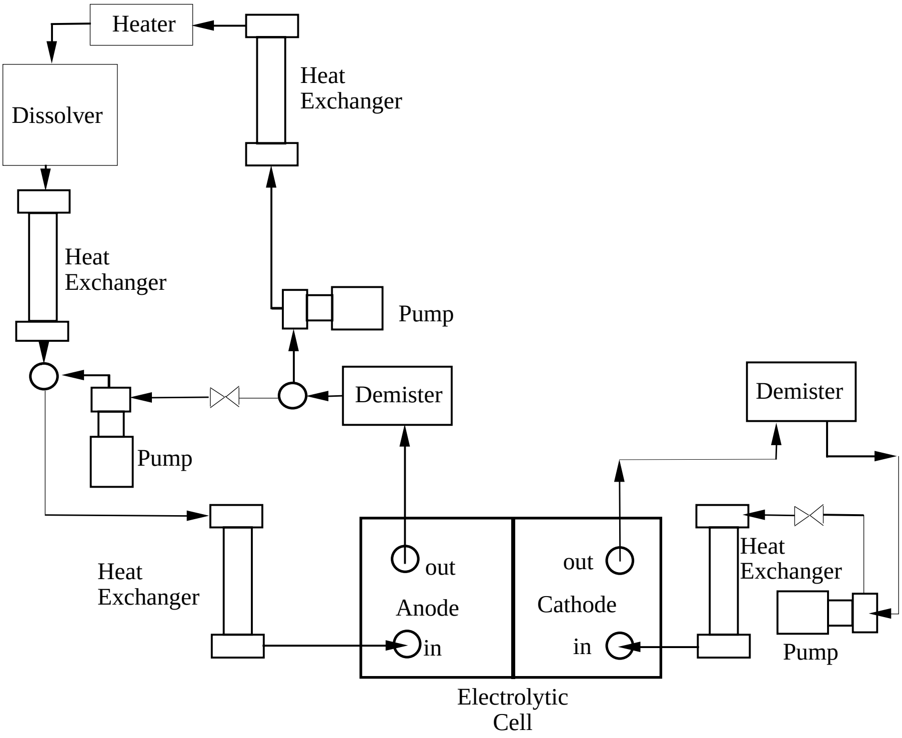

FIGURE 5.2.1.5 Flow diagram of CEPOD system.

Advantages of MEO

Due to the political and regulatory difficulties encountered in the remediation of mixed wastes, few traditional techniques have demonstrated sufficient acceptability. Even if the waste were classified as simply "hazardous," problems still exist if there is the possibility of the formation of harmful species such as dioxins or furans. Typically, these problems arise due to the volatility of radionuclide species or to the reactivity of certain organics when treating waste at elevated temperatures; because MEO operates at near ambient conditions in an aqueous system, it provides a more acceptable alternative. Questions have arisen as to the economics of this process. While these issues must certainly be addressed when selecting a waste treatment technology, it is outside of the scope of this chapter section.

The advantages offered by MEO technology are inherent in the system. As mentioned, the oxidation/dissolution processes are accomplished at near-ambient pressures and temperatures (room temperature to 70°C). In addition, all waste stream components and oxidation products (with the exception of evolved gases) are contained in an aqueous environment. This electrolyte acts as an accumulator for inorganics that were present in the original waste stream, and the large volume of electrolyte provides a thermal buffer for the energy released during oxidation of the organics. Also, the generation of secondary waste is minimal, as the active oxidant is self-regenerating and the system does not require periodic addition of reagents. Finally, as the destruction is electrochemically driven, the entire process can be shut down by simply turning off the power, affording a level of control unavailable in some other techniques.

Conclusions

The Ag(II)/HNO_3 and Co(III)/H_2SO_4 MEO systems described herein demonstrate the ability to completely oxidize a wide variety of organic compounds and no doubt would prove useful in specific commercial or government waste treatment applications. For the organic substrates studied, the silver system proved much more potent than the cobalt system, and this advantage is further bolstered if one is considering treatment of plutonium-contaminated mixed wastes. However, each combination of mediator and electrolyte offers a unique mix of treatable waste streams, and the selection of one over the other (or of other systems not considered in this work) will likely depend on the target waste stream.

It was noted that the functionalities present on the organic play a significant role in the ease of oxidation; at one extreme, alcohol, double-bond, and carboxylic acid groups greatly facilitated the process; while at the other extreme, aliphatic hydrocarbons exhibit little or no evidence of oxidation. In practice, no oxidation occurs if no favorable functionalities are present. Most organics fall somewhere in between, with more –OH groups and fewer C–H or C–C bonds accelerating the oxidation. Although an all-encompassing maxim for the destruction efficacies of organic functional groups is not possible, a general rule-of-thumb is that the ease of oxidation of a particular species follows the general order:

Alcohols > Chloro/Amino/Nitro/Phospho > Aromatic > Ketones/Aldehydes > Aliphatic

These results demonstrate that mediated electrochemical oxidation (MEO) is a viable alternative for the low-temperature destruction of the organic components of waste streams and for the dissolution/separation of transuranic oxides. Because of system operating parameters, several advantages over other techniques are offered in the area of substrate range and form, off-gas composition, secondary waste generation, and volatile species containment.

Acknowledgments

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5.2.2 Mixed Acid Oxidation

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Introduction

Several *nonthermal* processes have been developed to destroy organic waste compounds using chemicals with high oxidation potentials. These efforts have focused on developing technologies that work at low temperatures, relative to incineration, to overcome many of the regulatory issues associated with obtaining permits for waste incinerators. One such technique with great flexibility is mixed-acid oxidation. Mixed-acid oxidation, developed at the Savannah River Site, uses a mixture of an oxidant (nitric acid) and a carrier acid (phosphoric acid). The carrier acid acts as a nonvolatile holding medium for the somewhat volatile oxidant. The combination of acids allows appreciable amounts of the concentrated oxidant to remain in the carrier acid well above the oxidant's normal boiling point.

In the process, 70 wt% nitric acid (boiling point = 121°C) remains in solution at 150 to 200°C even when the system is at or near atmospheric pressure. The nitric acid converts hazardous organic molecules to the associated oxidation products, CO_2, CO, H_2O, and inorganic acids. Hazardous metals in the incoming waste stream dissolve into the mixed acid matrix. Nitric acid in the range of 150 to 200°C can effectively oxidize a wide range of stable organic materials, including paper, oils, polyvinylchloride (PVC), polyethylene, neoprene rubber, and polystyrene (Pierce et al., 1995).

Nitric acid is reduced primarily to NO, NO_2, and water; the NOx can be recycled. Phosphoric acid, contaminated with hazardous metals, is not consumed in the oxidation process and is disposed. The mixed-acid oxidation concept has been combined with simple nitric acid recycle techniques and phosphoric acid immobilization techniques to produce a closed-loop process for treating both hazardous and radioactive organic wastes.

The mixed-acid technology was originally developed to address the specific needs of the Savannah River Site, other DOE facilities, and commercial nuclear operations. Of particular interest was the treatment of solid contaminated *job-control waste*, a heterogeneous mixture of plastics, cellulose, lead, rubber, resins, absorbed solvents and oils, steel, ceramics, HEPA filters, etc., contaminated with transuranic (TRU) elements. As a result of its process capabilities, the technology can also be applied to other hazardous and radioactive waste streams.

Fundamentals of Mixed-Acid Oxidation

Oxidation

Mixed-acid oxidation is a simple process that uses oxygen from air or another readily available oxidant as the net oxidizer. Nitric acid (HNO_3) is used as the oxidant because it can be regenerated in an acid recovery system and, to some extent, in the reaction solution. Because the oxidation occurs in the liquid phase and converts organic molecules to gaseous compounds, the process does not produce organic ash by-products.

Liquid-phase oxidation of organic molecules should be easier than gas-phase oxidation at a given temperature. This is due to the ability to produce high concentrations of the reactants and to reduce termination reactions because radicals have a more difficult time diffusing to the walls (Seminov, 1958). Direct oxidation of most organic compounds by HNO_3 can be energetically favorable [Equation (5.2.2.1)], but very slow due to the inability to break the carbon-hydrogen bond. Other oxidation pathways are not energetically favorable, as shown in Equations (5.2.2.2) and (5.2.2.3). The heat of reaction, ΔH, values are in kcal/mole. (Seminov, 1958; Dickerson, 1969).

$$RCH_3 + HNO_3 \rightarrow RCH_2OH + HNO_2 \qquad \Delta H \cong -25 \qquad (5.2.2.1)$$

$$RCH_3 + HNO_3 \rightarrow RCH_2\cdot + H_2O + NO_2\cdot \qquad \Delta H \cong 35 \qquad (5.2.2.2)$$

$$RCH_3 + HNO_2 \rightarrow RCH_2\cdot + H_2O + NO\cdot \qquad \Delta H \cong 28 \qquad (5.2.2.3)$$

R denotes an organic group that does not affect the ΔH for the shown reaction. The oxidation of organic compounds is usually initiated by the production of organic radicals generated by dissolved $NO_2\cdot$ and $NO\cdot$ in solution. For many types of organic compounds, the attack by $NO_2\cdot$ can be first order (Smith, 1993).

$$CH_3(OH)CH_2 + NO_2\cdot \rightarrow CH_3(OH)CH\cdot + HNO_2 \qquad \Delta H \cong 0 \qquad (5.2.2.4)$$

$$CH_3CHO + NO_2\cdot \rightarrow CH_3(O)C\cdot + HNO_2 \qquad \Delta H = -7 \qquad (5.2.2.5)$$

For aliphatic compounds, higher concentrations of $NO_2\cdot$ and $NO\cdot$ are needed to initiate the reaction. At the same time, because of the apparent reaction order of three [Equations (5.2.2.6) and (5.2.2.7)], these reactions should be significantly accelerated under conditions of elevated pressure.

$$RCH_3 + H_2O + 3NO_2\cdot \rightarrow RCH_2\cdot + 2HNO_2 + HNO_3 \qquad \Delta H \cong -15 \qquad (5.2.2.6)$$

$$RCH_3 + H_2O + 2NO_2\cdot + NO\cdot \rightarrow RCH_2\cdot + 3HNO_2 \qquad \Delta H \cong -8 \qquad (5.2.2.7)$$

A typical aliphatic carbon-hydrogen bond strength of 99 kcal/mole was used in the calculations (Smith, 1993). The organic radicals are then either oxidized by nitric and nitrous acids or nitrated by $NO_2\cdot$. When this occurs, hydrogen-carbon bonds on carbon atoms that are also bonded to oxygen are weakened, thereby allowing much quicker hydrogen abstraction and further oxidation. As the organic molecules gain more oxygen atoms, the organic molecules become increasingly soluble in the oxidation solution. Once in solution, the molecules are quickly oxidized to CO_2, CO, and H_2O. If the original organic compound contains chlorine then HCl (hydrochloric acid) and NOCl can be formed; chlorine gas has not been observed.

Along with oxidation, there is likely a dehydration reaction aiding in the decomposition of the organic oxidation products. This occurs due to the presence of 14.8 *M* (or higher) H_3PO_4, which is a strong dehydrating agent. For example, due to the strong dehydrating ability of the reaction solution, cellulose can be carbonized in concentrated H_3PO_4 near 140°C through a series of intermediate compounds to form carbon and water. The carbon is readily attacked by nitric acid, with CO as one of the reaction products. The fraction of CO released can be as high as 60%. It is possible that the relative production of CO and CO_2 is determined to some extent by competing mechanisms; the CO by way of a dehydration mechanism and the CO_2 from oxidation with HNO_3 and $NO_2\cdot$ (Smith, 1993). The presence of large amounts of CO in the off-gas led to the addition of dissolved palladium (0.0010 to 0.0015 *M*) in the phosphoric acid to reduce the CO levels to below 2.5%.

Implementation of the technology is made possible by the limited, but sufficient, solubility of nitric acid in concentrated phosphoric acid. Concentrated nitric acid (70 wt%) boils at 121°C, which is well below the temperature range (150 to 200°C) needed for vigorous reaction rates. At atmospheric pressure, phosphoric acid can retain up to 148 g/L HNO_3 at 155°C and 20 g/L HNO_3 at 185°C. The solubility of

TABLE 5.2.2.1 HNO_3 Solubility in Concentrated H_3PO_4

	Temperature		
Pressure	155°C	170°C	185°C
0 psig	148 g/L	64 g/L	20 g/L
10 psig	195 g/L	107 g/L	46 g/L
20 psig	252 g/L	147 g/L	73 g/L
	190°C	205°C	220°C
15 psig	40 g/L	15 g/L	1.3 g/L

HNO_3 in H_3PO_4 increases with increasing pressure (Table 5.2.2.1). While pressurization of HNO_3 to raise its boiling point has been used in the oxidation of small organic samples, safety concerns about elevated pressures and runaway nitric acid reactions inhibit further development.

An important process-related issue exists with regard to safety when considering the reaction of organic molecules with nitric acid. The common concern is that stable nitrated organics can form explosive mixtures. While nitration of organic molecules is a common industrial method, the conditions existing in the mixed-acid oxidation system do not provide the appropriate matrix for stable nitrated organic molecule formation (Olah et al., 1989). Two conditions work together and rapidly hydrolyze any potential nitrated compounds. First, the presence of water readily strips nitro groups to form the corresponding alcohol. If moisture is not removed from the reaction, explosive compounds are difficult to form. A second reaction involves the reaction of hot, concentrated mineral acids with nitroparaffins to produce a hydroxylamine and organic acid (Fuson, 1950) As a result, nitrated organics do not build up during mixed-acid oxidation and the process can be safely operated.

Off-Gas Handling

Several approaches exist for handling the off-gas, but the most attractive involve the recycle of nitric acid. Some options employ proprietary technology, of which little is known aside from vendor claims. The best-known approach is the one used in nitric acid manufacturing. Nitrous oxide (NO) is combined with air (to form NO_2 gas) and then contacted with water in a distillation column. The downsides of this approach — high operating pressures (6 to 12 atm) and large reaction columns — make this approach impractical for small-scale operations.

The most attractive alternative for most situations is hydrogen peroxide absorption. Hydrogen peroxide readily absorbs both NO and NO_2 to produce nitric acid. Calculations of the maximum theoretical nitric acid concentration expected for absorption of NO_2 using hydrogen peroxide indicate that nitric acid concentrations in excess of 60 wt% could be obtained using 30% hydrogen peroxide. Using the equation

$$2\ NO_2 + H_2O_2 \rightarrow 2\ HNO_3 \tag{5.2.2.8}$$

it was determined that a maximum concentration of 61.3 wt% could be obtained with 30% H_2O_2 and 78.7 wt% with 50% H_2O_2. These calculations do not account for any acid formation that may occur due to NO_2 absorption by the balance of water in the hydrogen peroxide solution.

It is important to note that the presence of NO gas in the stream reduces the maximum theoretical concentration. The reaction of NO with H_2O_2 is as follows:

$$2\ NO + 3\ H_2O_2 \rightarrow 2\ HNO_3 + 2\ H_2O \tag{5.2.2.9}$$

Not only is peroxide efficiency reduced, but there is also dilution from water in the reaction products. The stoichiometry yields theoretical maximum acid concentrations of 47.0 wt% for 30% H_2O_2 and 60.8 wt% for 50% H_2O_2. (Pierce et al., 1998).

Hazardous Metal Immobilization

The ideal process should remove metals from the acid stream and recycle the phosphoric acid. Several techniques were evaluated, including ion exchange, solvent extraction, and precipitation. In each case, the presence of many metals together in a viscous acid solution limits the metal recovery, in addition to making the overall process more complex. As a result, techniques were sought to immobilize the hazardous constituents within the acid matrix. Two approaches were identified that simplify the process while providing a chemically stable final waste form.

The first approach uses an iron phosphate (FeP) glass to immobilize the phosphoric acid along with residual metal contaminants. The Fe_2O_3/P_2O_5 system offers many benefits over traditional borosilicate glasses which make it well suited for this need (Ramsey et al., 1995); the benefits include:

- FeP has a low melting point for a waste glass (1050 to 1100°C) and low viscosity, which permit short process cycle times at relatively low temperatures.
- The FeP system can incorporate high concentrations of metal ions, especially iron. This is important because it is expected that metal corrosion products will be a primary source of metals in the acid (carbon and stainless steels are major components of job control waste, and both exhibit high corrosion rates in the HNO_3/H_3PO_4 solution).
- A glass waste form reduces the volume of the waste stream by approximately 40% when compared with phosphoric acid.
- The FeP glass is extremely resistant to leaching of metals from the matrix, thereby providing a waste form that is at least as stable as the current borosilicate high-level waste glasses.

Another immobilization alternative uses the chemically bonded ceramic waste forms advanced at Argonne National Laboratory (ANL) (Singh et al., 1994). Two variations of the waste form were developed: magnesium phosphate (MgP) and potassium magnesium phosphate (KMgP). Of the two, KMgP shows more promise for incorporation into the acid oxidation process. The ceramic forms have the advantages of being made at room temperature using low-tech equipment. ANL has demonstrated the immobilization process at the 55-gallon scale. Furthermore, KMgP waste forms are chemically stable and have been shown to pass the Toxicity Characteristic Leach Procedure (TCLP), ASTM C1220-92, for hazardous metals.

The ceramic is valuable for immobilizing RCRA metals and short-lived radioisotopes such as ^{137}Cs and ^{90}Sr. The iron phosphate glass, which has the stability of a high-level waste glass, is preferable for immobilizing actinide metals. In comparison, the ceramic is easier to make, while the glass provides a greater volume reduction and a more stable form.

Technology Application

Oxidation

Application of the technology strongly depends on the waste matrix. For example, oxygenated hydrocarbons are more susceptible to attack than long-chain aliphatics, and acid-soluble compounds react faster than insoluble ones. Regardless, in the range of 140 to 210°C and 0 to 15 psig, most compounds can be quantitatively oxidized to CO_2, CO, H_2O, and inorganic acids. Compounds that have been quantitatively oxidized as measured by CO_2 release, within experimental error (±2%), include cellulose, tributylphosphate, nitromethane, neoprene, benzoic acid, polyethylene, polypropylene, polyvinylchloride (PVC), and both aliphatic and naphthenic oils. Any CO released was contacted with palladium metal at 150°C in air to convert it to CO_2.

Experiments reveal the onset of oxidation for the soluble, oxygenated hydrocarbons at about 120°C (e.g., cellulose, nitromethane). At 140°C, the oxidation of these compounds is essentially complete in less than 15 min (no NO_2 gas being released from solution). The result for nitromethane is important because it confirms Fuson's observations that nitrated compounds can be quickly hydrolyzed in strong mineral acids at this temperature (Fuson, 1950). Representative reactions include (Smith, 1993):

$$CH_3NO_2 + H_2O + H_3PO_4 \rightarrow HCO_2H + H_2NOH{\cdot}H_3PO_4 \qquad \Delta H \cong -44 \quad (5.2.2.10)$$

$$H_2NOH{\cdot}H_3PO_4 + HNO_2 \rightarrow N_2O + 2H_2O + H_3PO_4 \qquad \Delta H = -66 \quad (5.2.2.11)$$

The surface oxidation of neoprene [poly (2-chloro-1,3-butadiene)] was found to be uniform, allowing measurement of the surface area and weight loss during its destruction. The release of chloride formed during the oxidation of neoprene had no observable effect on reaction rates at concentrations up to 0.1 *M*. The effect of concentrations above 0.1 *M* was not evaluated. Oxidation of neoprene is relatively rapid (compared to polyethylene and PVC) due to carbon-carbon double bond weakening of carbon-hydrogen bonds in α positions relative to the double bond.

The oxidation rate of aliphatic compounds such as polyethylene, PVC, and *n*-dodecane was found to be unmeasureably slow in an air-sparged reaction solution below 180°C. In an air-sparged system, the concentrations of NO· and NO_2· are too low for reactions (5.2.2.6) and (5.2.2.7) to have any appreciable effect. Complete oxidation was achieved by increasing the system pressure and eliminating the air sparge to facilitate higher NO· and NO_2· concentrations in solution. Data reflecting the oxidation behavior of polyethylene is shown in Figure 5.2.2.1.

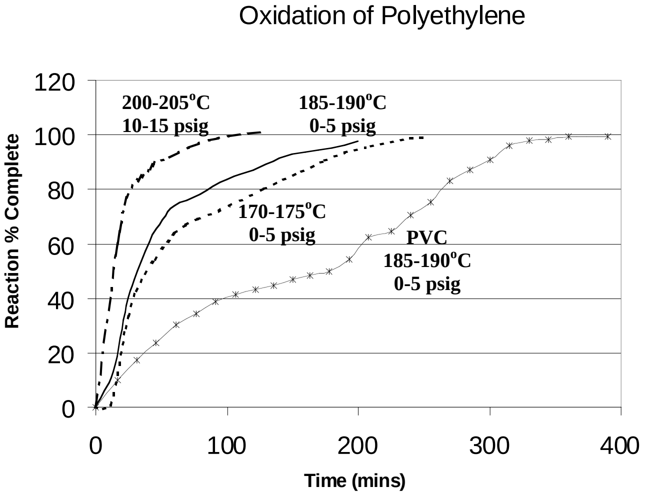

FIGURE 5.2.2.1 Oxidation behavior of polyethylene. (From Pierce, R.A., Smith, J.R., and Poprik, D.C. 1995. Nitric-phosphoric oxidation of solid and liquid organic materials, *WM95 Proceedings.* WM Symposia, Inc., Tucson, AZ. With permission.)

The reaction rate dependence of aliphatic compounds on NO· and NO_2· levels is demonstrated in a more pronounced manner when using microwave-based sample dissolution techniques. These are well-developed methods that use mineral acids and oxidants (e.g., H_2O_2 and HNO_3) at elevated pressure (100 to 150 psig) and temperature (150 to 200°C) to digest organic samples. When 0.1-g samples of aliphatic compounds and 5 mL 70% nitric acid are placed in a 100-mL digestion vessel, the samples dissolve in 5 to 10 min. Rapid dissolution was demonstrated on PVC, low- and high-density polyethylene, polypropylene, and Tygon®. The role of the microwave energy, other than heating, is expected to be small because it is of insufficient energy to cause bond breakage. Reactions (5.2.2.6) and (5.2.2.7) are very likely the initiating oxidation steps because the pressure vessel makes it possible for NO· and NO_2· to exist at much higher concentrations. Upon completing the digestion, process solutions were blue, indicating the presence of nitrous acid.

During rapid oxidation reactions, the ratio of CO to CO_2 in the off-gas tends to increase. Under certain conditions, the CO percentage can be quite high. For compounds such as cellulose, ethylenediaminetetraacetic acid (EDTA), tributylphosphate (TBP), and nitromethane, CO percentages were measured as high as 20, 25, 43, and 60%, respectively. Because of the high CO fractions, palladium was added to the phosphoric acid as a catalyst for converting CO to CO_2. Concentrations of 0.0010 to 0.0015 *M* palladium were used. The palladium reduced the CO for cellulose, EDTA, TBP, and nitromethane by a factor of 20 to 25 to 0.9, 0.9, 1.3, and 2.3%, respectively (Smith, 1993).

The selection of reaction conditions is very important when balancing reaction rates with process safety (i.e., limited acid concentrations, pressures, and temperatures). At the same time, conditions must be identified that will produce complete oxidation. Because increases in both temperature and acid concentration increase reaction rates, which is more important? Is it better to reduce the acid concentration for higher temperatures, or vice versa? Experience indicates that more stable organic compounds (aliphatics) will require higher temperatures for complete oxidation than those needed for oxygenated molecules (e.g., cellulose).

The stability of the oxidation by-products of aliphatic molecules was demonstrated during the destruction of water-soluble oils. Starting solutions were prepared at 155, 170, and 185°C with the maximum soluble nitric acid concentrations: 0.148, 0.0645, and 0.0195 g/mL, respectively. The data is listed in Figure 5.2.2.2. At each temperature, the initial reaction rate was essentially the same. However, the oxidation characteristics of stable intermediate compounds become apparent as the reaction at 155°C stops abruptly before completion. Seminov has also demonstrated this principle. He showed that organic hydroperoxides, a type of compound that has great potential for forming in this system, would decompose to release water and carbon dioxide above 130 to 150°C. However, below 130°C, the formation of stable intermediates is common (Seminov, 1958).

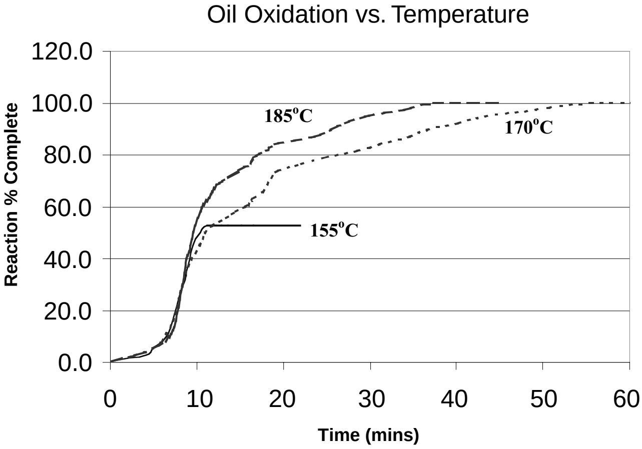

FIGURE 5.2.2.2 Oil oxidation vs. temperature. (From Pierce, R.A., Smith, J.R, and Poprik, D.C. Nitric-phosphoric oxidation of solid and liquid organic materials, *WM95 Proceedings*. WM Symposia, Inc., Tucson, AZ. With permission.)

Conversely, when oxygenated compounds such as cellulose are oxidized above 165°C, they produce very rapid reactions and high volumes of gas by-products. As a result, optimum reaction conditions for easily oxidized compounds (i.e., cellulose) include lower temperatures with higher acid concentrations to offset rapid reactions and a corresponding rapid decrease in acid concentration. Optimum conditions for PVC, polyethylene, and other long-chain aliphatics will use elevated temperatures where the destruction of long-chain intermediates is necessary (Pierce et al., 1995).

The application of this principle was demonstrated on a mixture of cellulose, latex rubber, polyethylene, and Tyvek®. When heated slowly, the cellulose dissolves at <90°C, latex at 140 to 145°C, polyethylene at 160 to 170°C, and Tyvek® at 180 to 185°C. When the waste mixture is added to the process at 160°C, all material dissolves within 15 min except for Tyvek®. Tyvek® does not dissolve until the temperature is raised to 180 or 190°C. When the waste mixture is added and processed at 180 to 190°C, all materials except Tyvek® dissolve within 10 min. Under these conditions, the Tyvek® dissolves within 45 min.

Batch tests were also conducted with a mixture of cellulose, neoprene, polyethylene, and PVC at 170°C/1.0 M HNO_3/8–10 psig and at 185°C/0.5 M HNO_3/8–10 psig. The oxidation of cellulose, neoprene, and polyethylene at 170°C and 1.0 M HNO_3 occurred at rates similar to those at 185°C and 0.5 M HNO_3. In both cases, the neoprene and polyethylene dissolved within 15 min, and at rates somewhat higher than anticipated. The PVC sample dissolved in 60 min at 185°C, and in 85 min at 170°C. It is expected that the accelerated rates for neoprene and polyethylene are caused by the oxidation of cellulose, which by its reaction produces $NO\cdot$ and $NO_2\cdot$ for an increase in initiation reactions (5.2.2.6) and (5.2.2.7). Based on the experiments conducted over the range of conditions, typical oxidation rates have been identified, and these rates are listed in Table 5.2.2.2.

TABLE 5.2.2.2 Typical Oxidation Rates (g/hr) per Liter of Reaction Solution

Compound	155°C 0–5 psig	170°C 0–5 psig	185°C 0–5 psig	170°C 12–15 psig	185°C 12–15 psig	205°C 12–15 psig
Cellulose	95	150	>150	>150	—	—
Neoprene	—	40	—	70	—	—
LDPE	2	5	13	14	40	90
HDPE	—	—	—	—	—	25
PVC	<1	1	4	4	15	35
Benzoic acid	—	—	—	—	45	—
Styrene resin	—	30	—	65	—	—

Differences between materials are not the only issue to be considered in applying the technology. Variations in thickness, density, and melting point of similar materials must also be addressed. Tests were run in a semi-continuous mode in which similar samples were added over a 3-hr period. Low-density polyethylene (LDPE) from bags (thickness = 0.004 in.) was added to the reaction vessel at 185°C and 10 to 12 psig. The samples dissolved within 15 min throughout the experiment and were subsequently oxidized. The rate of addition corresponded to a throughput rate of 20 g/L of solution per hour. Next, the experiment was repeated using a thicker (nominal thickness = 0.05 in.), higher density LDPE from bottles. Overall dissolution was 3 to 5 times slower because of the increase in thickness and density; the material required 50 min to dissolve, instead of 10 to 15 min. However, the continuous oxidation rate eventually stabilized and was only about one half that of the polyethylene bag.

Comparable behavior has not been observed when material properties vary more significantly. For example, PVC bag samples can be oxidized in approximately 1 hr at 205°C and 8 to 10 psig. Dense PVC pipe samples under the same conditions are essentially nonreactive. As a result, scouting studies should be run on representative waste material to assess the suitability of mixed-acid oxidation as a treatment method.

While oxidation rates are important, it is equally important to know how much waste can be processed through a known volume of phosphoric acid before the acid must be immobilized. Because phosphoric acid is not consumed in the process, inorganic material solubility determines its useful life. Based on typical job control waste streams, the inorganic compounds of greatest concern are iron, aluminum, and silicon. Iron is present as carbon and stainless steel, aluminum is present as the metal, and silicon is often a major component in cellulose. Each component has a solubility limit, and its behavior at that limit can be critical.

In practice, the greatest concern is with iron precipitation because (1) it is the most prominent metal in the waste streams, and (2) iron phosphate hydrate precipitates as a continuous gelatinous mass. The precipitate does not dissolve in water; in fact, precipitation is even worse if water is added because it increases the amount of water available to form a network of hydrates. Experimental work dissolving Fe_2O_3 into 85% phosphoric acid shows the following iron solubility: 187 g/L at 141°C, 165 g/L at 165°C, and 144 g/L at 183°C.

Work with silica coming from paper oxidation shows that precipitation of dissolved silica does not present immediate processing problems. Silica precipitates as an anhydrous silicon phosphate that is well divided and dispersible. At 165°C, the solubility limit for silicon in 85% H_3PO_4 is approximately 40 g/L. Experiments with aluminum also show that its precipitate might cause a need for additional processing. Additions of aluminum nitrate to 85% phosphoric acid at 190°C show an aluminum solubility limit of 75 g/L. Furthermore, when the precipitate forms, it forms as a gelatinous mass, similar to that observed for iron. On the other hand, experiments indicate that the precipitate is water soluble.

Off-Gas Handling

In situations where HCl is generated as a by-product of oxidation, it must be removed prior to nitric acid recovery and recycle. Experiments show that no detectable HCl remains in the oxidation vessel after the oxidation cycle. If not removed separately, the HCl will end up in the acid recycle system and, subsequently, build up throughout the system. The use of water as a scrubber for HCl was tested. While the scrubber was effective in removing HCl quantitatively up to 2000 ppm, the water also absorbs essentially all NO_2 present to form HNO_3. As the acid absorption limit for water was approached, absorption of HCl was proportional to the total acid concentration ($[HCl] + [HNO_3]$) (Pierce et al., 1998). The data clearly shows that a water scrubber does not separate HCl from NO_2.

A secondary approach evaluated a simple condenser for the removal of HCl and water vapor without significant NOx absorption. The first experiments with a low surface area condenser yielded a retention of approximately 50% of the HCl, while allowing 99% of the NOx to pass through the system. NOx losses come from water absorption of NO_2 to produce HNO_3. The condenser arrangement was modified for improved condensation of both HCl and H_2O. The modified arrangement yielded somewhat better results at 67% HCl retention with 3% NOx loss. Improved designs should yield results that will meet most process requirements. It is anticipated that removal of 75% of the HCl with less than 5% NOx loss should be sufficient.

After HCl and excess water vapors are removed, the remaining NOx stream is recovered as nitric acid by contacting it with oxygen and reacting it with hydrogen peroxide. To optimize the process, four key parameters were evaluated:

1. $NO:O_2$ ratio
2. Residence time to convert NO to NO_2 prior to absorption
3. % H_2O_2
4. Use of oxygen vs. air to convert NO to NO_2

The studies (Pierce et al., 1998) revealed the following:

1. Tests with pure NO yield a nitric acid concentration of 23 wt% (4.1 *M*, well below the theoretical of 47 wt%) as compared to 61 wt% (13.2 *M* at theoretical yield) when NO is mixed with air prior to absorption.
2. Controlled absorption conditions have consistently shown conversion of 30% H_2O_2 to 13.0–13.4 *M* HNO_3, which is at the theoretical yield.
3. 50% H_2O_2 absorbs to 67 wt% (compared to 79% theoretical, which is above the 70 wt% HNO_3 azeotrope) and does not offer an advantage over 30% H_2O_2 commensurate with the higher cost, concentration, and chemical instability.
4. Oxygen does not seem to provide any significant benefit over air.
5. The optimum residence time required for maximum use of H_2O_2 is 60–90 s, although times as little as 30 s can be effectively used.
6. The optimum $NO:O_2$ ratio is 1:1, but ratios as low as 1:2 reduce NOx absorption by less than 10%.

Table 5.2.2.3 provides the data.

In conjunction with optimization testing, analyses were also conducted on the NOx concentration emitted after being passed through three absorption vessels in series. Continuous monitoring of NOx emissions from the third peroxide vessel always showed 30 ppm or less, and was primarily below 5 ppm. This is within the clean air standard limit of 200 ppm. Although absorption efficiency is largely a function

TABLE 5.2.23 NOx Absorption into 30% H_2O_2

O_2:NO	0	1:2	2:2	5:2	1:2	1:2	1:2	1:2
Oxidant	n/a	Air	Air	Air	O_2	Air	O_2	Air
Residence Time	60	60	60	60	60	30	30	120
NOx Fed (moles)	Acid Conc. Measured Using Titration (M)							
0.000	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.016	1.35	2.04	2.11	1.74	1.16	1.02	0.86	0.62
0.032	2.75	4.70	5.63	3.87	2.83	3.33	3.13	2.40
0.065	4.10	8.44	9.20	7.24	6.54	6.54	7.90	6.19
0.098	4.14	10.34	11.64	9.26	9.21	8.59	10.42	9.13
0.114		11.10	12.32	9.79	10.26	9.58	11.33	9.41
0.146		12.25	12.77	10.89	11.67	10.87	12.40	10.77
0.179		12.78	13.31	11.60	12.58	11.26	12.85	12.30
0.211		12.83	13.39	11.67	13.03		12.93	13.26
0.228					13.10			13.34

of geometry and gas/liquid contacting, the data is indicative of what can be expected from nitric acid recycle operations.

A separate series of tests was devised to identify hazardous and volatile components in the off-gas, with the ultimate objective of being able to evaluate dioxin production potential. On the bench scale, tests were run with surrogate waste streams and dioxin precursors to address the range of temperature, pressure, and nitric acid compositions anticipated. Cellulose, polyethylene, neoprene, and PVC samples were used as the bulk waste. Pentachlorophenol (PCP) and trichlorophenol (TCP) were added as dioxin precursors. Water scrubbers and charcoal filters were placed in series in the off-gas stream to collect organic emissions.

The water scrub for the oxidation of the above surrogate waste was found to contain no chlorinated or aromatic compounds. There were trace quantities (<1 mg/L) of mixed ketones — ketones are generally thought of as neutral, mobile volatile liquids that are the second step in the oxidation of a hydrocarbon. Trace quantities of alkyl nitrates and short-chain chlorinated hydrocarbons were also identified in the scrubber. No organic compounds were found in the activated carbon filter downstream of the liquid scrubber. The residual concentrated phosphoric acid was also analyzed following a series of eight tests; it contained trace quantities of both chlorinated pyridine and nitrochlorobenzene, but no other related compounds. These findings demonstrate that nitrated organics, although present in trace quantities, do not build up in solution. Furthermore, there were no phenols or dioxins identified in solution above the detection limit of 1 mg/L.

Off-gas tests were replicated using a 40-L pilot system. These tests employed much larger quantities of surrogate waste stream, but still used the same charcoal tubes for final emissions testing. The water wash for the tests had an organic mix of 2 to 4 ppm alkyl nitrates and other trace chlorinated hydrocarbons. In is unclear whether the alkyl nitrates were absorbed as alkyl nitrates, or whether they had been absorbed as a different compound and then nitrated by the stream of NOx passing through the water. Throughout pilot testing, there were no dioxins or phenols detected. This combination of bench-scale and pilot-scale tests indicates that no detectable organic emissions should pass through the nitric acid recycle system — an extremely important characteristic for an incineration alternative.

Hazardous Metal Immobilization

Although relevant immobilization techniques are well-represented in the literature, they do not directly address the specific needs as they relate to mixed-acid oxidation. In evaluating the ceramic forms, both MgP and KMgP were tested. MgP is produced by gradually mixing an appropriate mixture of MgO and H_3BO_3 to diluted phosphoric acid (<60 wt%). During the addition of MgO and H_3BO_3, a large heat spike occurs due to the neutralization of the acid, and, if not managed correctly, can lead to premature curing of the ceramic. The KMgP process first neutralizes the H_3PO_4 stream with KOH and the optimum amount of water to produce a solution with KH_2PO_4 crystals present. Next, a mixture of MgO and additional KH_2PO_4 is added and the slurry is stirred until it begins to thicken. With KMgP, because the heat of neutralization occurs with KOH addition, the solid components can be added much more liberally without premature curing.

A primary issue associated with producing the KMgP is optimizing the formulation to minimize the waste volume. Two different compositions were made: one formulation recommended by Argonne National Lab and the other with 15% less water (as water dampens the curing reactions). The first sample was stirred for 9 min before it began to set up. The reduced-water sample reached a higher temperature than the first sample, and it was stirred for only 4 min. The samples were allowed to cure for 2 weeks before being submitted for leach testing.

The samples were leach tested using a modified TCLP method. The results showed that Si^{4+}, PO_4^{3-}, and $NO_{3\_}$ leach from the second sample at 2 to 3 times the rates observed in the first sample. Furthermore, the first sample showed less that 0.007 mg/L Mg leached vs. 309 mg/L Mg for the second sample. The variations in leach rates, particularly with the Mg, are caused by the insufficient curing brought about by rapid solidification. Argonne National Lab has performed a wide range of TCLP tests under varying conditions to characterize the leach rates of both MgP and KMgP waste forms. The ANL studies have shown that both phosphate-bonded ceramics consistently meet the RCRA limits (Singh et al., 1994).

Nonradioactive and radioactive work was also conducted on iron phosphate glass to identify the preferred glass composition for immobilizing radioactive solutions. Testing examined the range of primary components: Fe_2O_3, 15–45 wt%; Na_2O, 0–6 wt%; SrO, 0–3 wt%; balance is P_2O_5. Glasses were consistently produced for formulations containing 20 to 40% Fe_2O_3, 4 to 6% Na_2O, 2 to 3% SrO, and 51 to 74% P_2O_5. Based on the quality of glasses formed, the preferred formulation is 33% Fe_2O_3, 5.5% Na_2O, 2.5% SrO, and 59% P_2O_5. This composition allows fluctuation in the composition without jeopardizing glass formation.

As a follow-up, glasses were made with the preferred formulation using radioactive and nonradioactive mixed-acid oxidation process solutions with the exception that barium (Ba) was used instead of strontium. Samples were submitted for leach testing using the Product Consistency Test (PCT), ASTM C-1285. The leachability for the primary components of the nonradioactive glass were as follows: P = 0.022 g/L, Ba = 0.001 g/L, Na = 0.087 g/L, and Fe = 0.001 g/L. Results for the radioactive glass were P = 0.031 g/L, Ba = 0.002 g/L, Na = 0.104 g/L, and Fe = 0.000 g/L. Comparing this to the Environmental Assessment (EA) glass standard for borosilicate glass is difficult because the major components differ. However, both the EA and FeP glasses contain comparable amounts of sodium: 12.1% for the EA glass vs. 5.5% for the FeP. The allowable leachability for sodium from the EA glass is 13 g/L and is approximately 100 times greater than the sodium leach rates observed for FeP. In addition, TCLP results indicated that the RCRA metals present did not leach at detectable limits, with the exception of barium (present at 2.5 wt%) which leached at 1.05 mg/L (which is below the RCRA limit of 100 mg/L). Strontium eventually replaced barium to avoid the use of an RCRA hazardous metal in the glass formulation.

Both KMgP and FeP proved to be acceptable final waste forms for the mixed-acid oxidation process. Of particular value is their tolerance of wide ranges of impurities. When combined with the acid oxidation and nitric acid recycle, the three components yield a closed-loop process that can treat a wide range of waste types. All unit operations are based on simple technology and can be easily integrated. Integrated systems have been demonstrated in the laboratory and with an engineering-scale system (40-L oxidation vessel).

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For Further Information

The cited references by Pierce and Smith contain detailed discussions of the technology as it has evolved from its inception to the current state of development. Phosphate-bonded ceramics such as MgP and KMgP are discussed extensively in Section 8 of this handbook.

Defining Terms

Job-control waste: A heterogeneous mixture of plastics, cellulose, lead, rubber, resins, absorbed solvents and oils, steel, ceramics, etc., generated during process operations.

Nitration: A chemical reaction that introduces the NO_2 group into an organic compound.

Non-thermal: A classification established for alternative oxidation technologies that sets maximum operating conditions at 350°C and 200 psig.

Oxidant: The substance that causes the oxidation of another element through the donation of electrons; the electron donation may involve the transfer of oxygen atoms.

Oxidation: The process by which the oxidation number of a substance is increased; the process frequently involves the union of the substance with oxygen.

5.2.3 Mediated Electrochemical Oxidation of Mixed Wastes

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Introduction

Mediated electrochemical oxidation (MEO) is part of the family of technologies that includes all metal-ion-catalyzed electrochemical processes for organic destruction. The underlying chemistry was described in the 1960s and has since been reviewed with a historical perspective describing applications at the Pacific Northwest National Laboratory (PNNL) over a period of 17 years by the early workers (Ryan et al., 1992) at PNNL. The aim of the earliest applications of catalyzed electrochemical processes at PNNL was to accelerate the dissolution of plutonium oxide from solid mixed transuranic oxides recovered from reactors. The CEPOD process (Catalyzed Electrochemical Plutonium Oxide Dissolution), employed either a silver or a cerium metal ion as the electrocatalyst to facilitate the dissolution of plutonium oxide by its oxidation to the PuO_2^{2+} ion (Ryan et al., 1992).

The extension of the CEPOD process to the destruction of organic materials was explored at PNNL where the process was called Catalyzed Electrochemical Oxidation (CEO) (Ryan et al., 1992; Buehler and Surma, 1995). The early work at PNNL looked at destruction of organic materials that were commonly encountered in nuclear processing such as wipes, gloves, and tributyl phosphate kerosene mixtures. The work expanded to other National Laboratories owing to the growing concern concerning the quantities of radioactive processing wastes that had been accumulating since the 1940s. Among the groups that investigated the catalyzed electrochemical oxidation chemistry were the AEA (former Atomic Energy Authority) in Great Britain (Steele, 1989), Lawrence Livermore National Laboratory (LLNL) (Hickman et al., 1991), and Los Alamos National Laboratory (LANL) (Zawodzinski et al., 1993). Each of the laboratories focused on different mediators for the process, as discussed below.

The Process Chemistry Fundamentals

The MEO process involves the reaction of a high oxidation state metal ion with an organic material to convert the organic carbon to carbon dioxide, carbon-bound heteroatoms to their respective oxidized species (e.g., amine nitrogen to nitrate), and hydrogen ultimately to water. The processes operate near room temperature and at atmospheric pressure in an aqueous acid electrolyte. The processes afford virtually complete destruction of the organic materials because the oxidized metal-ion mediators are thermodynamically powerful and kinetically active oxidizing agents and, important for regulatory concerns, the organic materials and reaction intermediates are confined in the electrolyte until conversion of bound carbon to carbon dioxide is complete.

It is the containment of the destruction reaction and by-products including, for example, all accompanying trace quantities of radioactive elements that has been the driving force for the investigation of the MEO processes in the National Laboratories. The MEO processes were developed as one method to destroy the many mixed wastes held in the nuclear complexes that resulted from nuclear fuels and weapons processing. Processing many of these wastes required the use of nitric acid electrolytes (the preferred electrolyte) to keep the traces of transuranic elements soluble in the waste process solutions for ultimate isolation, stabilization, and disposal.

MEO processes rely on the ability of a high oxidation state metal ion to oxidize organic materials to carbon dioxide and water and contained sulfur to sulfuric acid, nitrogen to nitric acid, and phosphorous to phosphoric acid. The fate of the most common and most important heteroatom — chlorine — depends on the mediator, as discussed below. The destruction process, using tributyl phosphate as the example has the reaction stoichiometry shown in Equation (5.2.3.1). The total destruction of 1 mole of tributyl phosphate requires 72 moles of the oxidized mediator, or 72 Faradays:

$$(n\text{-}C_4H_9O)_3PO + 24\ H_2O + 72\ M^{(n+1)+} \rightarrow 12\ CO_2 + H_3PO_4 + 72\ M^{n+} + 72\ H^+ \quad (5.2.3.1)$$

The metal ion mediator is returned to the active state by oxidation at the anode in an electrochemical cell according to Equation (5.2.3.2). A corresponding reaction must occur at the cathode to maintain electrical neutrality and this reaction, in a nitric acid electrolyte is shown in Equation (5.2.3.3).

$$72\ M^{n+} \rightarrow 72\ M^{(n+1)+} + 72\ e^- \quad (5.2.3.2)$$

$$72\ e^- + 72\ H^+ + 36\ HNO_3 \rightarrow 36\ H_2O + 36\ HNO_2 \quad (5.2.3.3)$$

The relative energetics of the dominant mediators are listed in Table 5.2.3.1. As seen in Table 5.2.3.1, Ag(II) is the most powerful (thermodynamic) oxidizing mediator, followed by Co(III) and Ce(IV). These potentials are a measure of the chemical "potency" of the metal ion with respect to the desired destructive reaction with organic materials. The baseline reactivity for the organic materials is represented by the potential for methane (CH_4). All species with potentials above the 0.59-V value listed for CH_4 have no energy barrier for spontaneous reaction with CH_4 and, by inference, all other organic materials.

TABLE 5.2.3.1 Oxidation-Reduction Couples for Selected Metal Ions

Redox Reaction	E^0 (V)[2]
Mediators	
$Ag^{2+} + e^- = Ag^+$	1.98
$Co^{3+} + e^- = Co^{2+}$	1.82
$Ce(NO_3)_6^{2-} + e^- = Ce(NO_3)_6^{3-}$ (in HNO_3)	1.61
Other Reactions of Interest	
$Cl_2 + 2\ e^- = 2\ Cl^-$	1.36
$O_2 + 4\ H^+ + 4\ e^- = 2\ H_2O$	1.23
$HNO_3 + 2\ H^+ + 2\ e^- = HNO_2 + 2\ H_2O$	0.94
$Ag^+ + e^- = Ag^0$	0.80
$H^+ + e^- = 1/2\ H_2$	0.00
$CH_3OH + 2\ H^+ + 2\ e^- = CH_4 + H_2O$	0.59

Potentials from Latimer, 1952.

As implied by Equation (5.2.3.1), the oxygen in the product CO_2 does come from water. This reaction of water produces protons that pass through the membrane (*vide infra*) to react at the cathode according to Equation (5.2.3.3). It should be noted that ions carry the current in solution in electrochemical processes, and electrons carry the current in the external circuit (the wires). In operation, the ion current must equal the electron current.

The fourth chemical transformation involved in the MEO process is the recovery of nitric acid from the nitrous acid cathode reduction product shown in Equation (5.2.3.3). Nitrous acid is unstable at the process temperatures and disproportionates into NO and HNO_3 in aqueous solution according to Equation (5.2.3.4) (Shriver et al., 1994).

$$3\ HNO_2 + H_2O \rightarrow 2\ NO + HNO_3 \tag{5.2.3.4}$$

The recovery/recycle of nitric acid from the nitric oxide decomposition product requires both oxidation and absorption processes. First, the NO must be oxidized to NO_2 with molecular oxygen, as shown in Equation 5.2.3.5a

$$2\ NO + O_2 \rightarrow 2\ NO_2 \tag{5.2.3.5a}$$

which, in turn, is converted to nitric acid upon absorption in water according to Equation (5.2.3.5b).

$$3\ NO_2 + H_2O \rightarrow 2\ HNO_3 + NO \tag{5.2.3.5b}$$

The reactions described in Equations (5.2.3.5a, b) are those of nitric acid manufacture. The reaction of NO with oxygen is a termolecular process and is the rate-determining step in the overall process for nitric acid make. The reaction is favored by elevated gas pressures and does not involve any gas liquid absorption process. The absorption of NO_2 into water, as shown in Equation (5.2.3.5b), is a facile process. The major "hiccup" in the process is the return of NO from the absorption process, which requires a continuous recycle in the process. The $HNO_3/NO_2/NO/H_2O$ chemistry is extremely complex; the equilibria involved make it difficult to exhaust a of gas phase free of NOx components without some type of scrubbing operation (Joshi et al., 1985).

When Equations (5.2.3.1) through (5.2.3.5) are summed (with the correct balancing multipliers), the overall resultant reaction is virtually identical to the combustion reaction. The only variance is associated with chlorine; in incineration (combustion), chlorine appears as hydrogen chloride (HCl). HCl is not the chlorine product in cerium-catalyzed MEO. The individual chemical personalities of each of the common mediators are described in the next subsection.

Mediator Specific Characteristics

Silver

Ag(II) has been the most widely investigated mediator (Steele, 1989; Gray et al., 1992; Chiba et al., 1995; Chiba, 1993). Ag(II) has the highest oxidation potential of the common mediators and, as anticipated, has the highest room temperature reactivity toward organics. The high reactivity of Ag(II) includes a reactivity toward water in which Ag(II) oxidizes water to produce oxygen and Ag(I) [Equation (5.3.2.6)]. This parasitic reaction limits the lifetime of Ag(II) in solution which, in turn, has a profound impact on the design of the process.

$$4\ Ag^{2+} + 2\ H_2O = O_2 + 4H^+ + 4\ Ag^+ \tag{5.2.3.6}$$

In aqueous solution, Ag(II) has a room-temperature half-life of 20 min (Lawrence, 2000) which allowed for its extensive study in the laboratory at benchtop scale. However, maintaining this Ag(II) lifetime in a practical operating system with electrochemical cells using 40 to 80 kW of power, a minimum process level for practical application of the MEO technology would require heroic and impractical cooling efforts.

The expected short lifetime of Ag(II) under practical operating conditions would require that the organic waste materials be processed in the electrochemical cell at the locus of generation of the reactive Ag(II) species. Organic waste materials, particularly some of the "legacy" mixed wastes in government inventories, are typically complex mixtures with some suspended solid components. Their direct injection into the electrochemical cells with their internal manifolding and close spacings can be expected to result in system plugging. This, in turn, would require system disassembly for repair, a very undesirable activity in mixed waste applications.

Another impediment for general application of silver as a mediator is due to its intolerance of chlorine. The processing of chlorine-containing organic materials, major waste components, with silver results in the formation of insoluble silver chloride, which removes active mediator from the process. A major effort has been expended to design processes to separate the insoluble silver chloride (as well as silver phosphate and silver sulfate) from the anolyte to recover and recycle the silver back to the process (Hsu et al., 1996b; Conlin et al., 1999). The design and operation of the silver recovery process is the key factor in the process economics (Hsu et al., 1996a).

Cobalt

Cobalt as a mediator has been investigated almost as much as silver, albeit the investigations were usually more in the way of surveys compared to the Ag(II) efforts (Zawodinski et al., 1993; Farmer et al., 1992; Balazs et al., 1999). Co(III) is a very powerful oxidant and reacts quite readily with many organic materials at room temperature although, apparently it can exhibit a very low reactivity toward some chlorocarbons (Cournoyer and Smith, 1999). In general, cobalt is very similar to silver in that it possesses most of the same disadvantages while offering no distinct advantage of its own.

Since the reduced form of the mediator is a divalent ion, Co^{2+}, its transfer rate through the Nafion® membrane is lower than that of Ag^+ but still significant over time. Therefore, a process for the recovery and recycle of cobalt from the catholyte must be included in the design of the working process. The chlorine tolerance of cobalt-mediated systems is still unsettled. While chlorine materials in solution do not produce an insoluble species with either Co(II) or Co(III), there is evidence that some of the chlorine ends up as perchlorate. In practice, this limits the application of cobalt-mediated processing to non-chlorinated waste materials.

Co(III), like Ag(II), is unstable in aqueous solution with respect to water oxidation at a rate that rapidly increases with temperature such that around 50°C the water oxidation rate greatly exceeds the rate of reaction of organic materials (Cournoyer and Smith, 1999). Again, as noted above, a temperature of 50°C would be difficult to maintain with the 40 to 80 kW of electrochemical processing encountered in the typical small application of the technology. Consequently, like Ag, the use of a Co-mediated process would require the processing of the waste in the electrochemical cell which affords the same plugging consequences as discussed for Ag(II) above.

Cerium

The history of the use of cerium as a mediator has the same beginnings as Ag(II) at PNNL (Ryan et al., 1992). Cerium has the lowest oxidation potential of the three (Ag(II), Co(III), Ce(IV)) and, as a result, is expected to show the lowest reactivity, under the same conditions, of the group. This is the case as established by a comparative study of the trio of mediators; at room temperature, organic destruction was observed in Ag- and Co-mediated reactions, while none was measured for the Ce-mediated examples (Cournoyer and Smith, 1999). However, at elevated temperatures (75 to 100°C), the reactivity of Ce(IV)-mediated processes exceeds that of Ag(II) or Co(III) for tested organic materials (Surma et al., 1998; Cournoyer and Smith, 1999).

The relative paucity of exploratory work using Ce(IV) as a mediator is probably due to the fact that elevated temperatures are required to achieve reasonable reaction rates for the destruction of organic materials with Ce(IV). The heating of relatively small experimental test rigs is fairly complicated and, thus, often avoided by laboratory workers. Larger systems usually have the opposite problem, in that active cooling is required to maintain the desired steady-state temperature. For example, the 80-kW system of Figure 5.2.3.1 operating at a current density of 4000 A/m^2 dumps about 150×10^3 kJ/hr of heat into the process fluids. This is enough heat to maintain the desired reaction temperature and to evaporate the excess water in the process coming from the cathode reaction, [Equation (5.2.3.3), and from the waste material (Nelson et al., 1999)].

Both the reduced and oxidized forms of cerium exist in nitric acid solution as anionic nitrato complexes with similar structures, differing by one unit of negative charge, the Ce(III) complex is given by $Ce(NO_3)_6^{3-}$ and the Ce(IV) is given by $Ce(NO_3)_6^{2-}$. The occurrence of the soluble Ce species as anionic complexes greatly reduces their transport through the Nafion® membrane so there is minimal loss of mediator from the anolyte to the catholyte.

The Ce mediator is also the most chlorine tolerant of the three mediators. The destruction of chlorocarbons with a cerium-mediated process results in the rejection of the chlorine as molecular chlorine which passes out of the system with the carbon dioxide. Thus, chlorine is removed from the process on a continuous basis without interfering with the state of the mediator. The use of the cerium-mediated process for the destruction of chlorocarbon materials, particularly chlorine-containing pesticides and herbicides such as Kelthane™, chlordane, and 2,4-dichlorophenoxy acetic acid, has been recently reported (Nelson et al., 2000).

Finally, unlike Ag(II) and Co(III), the Ce(IV) oxidizing ion can be inventoried in that it does not react with water even at the high process temperatures (100°C) encountered with an 80-kW plant. CerOx' operational experience with systems operating at both 40 and 80 kW has shown that the dc energy required by the electrochemistry provides more than enough process heat to maintain the reaction temperatures in the required 95 to 100°C range for the cerium-mediated systems, with some active cooling still required to keep the solutions under their boiling points. Operation at lower reaction temperatures, required for either Ag or Co-mediated systems, at these power levels would require extensive and expensive cooling efforts to maintain near-ambient process temperatures. For example, the 40-kW operation with two CerOx proprietary bipolar cellpacks operating at 500 A (3800 A/m^2) and approximately 45 V applied potential has Joule heating to a level of 1.13×10^5 kJ/hr.

In addition to the obvious advantage of conservation of electrical energy presented by the absence of the parasitic water oxidation reaction, the stability of the Ce(IV) species permits the use of a separate reactor for organic destruction at the elevated temperature required by the cerium mediator. Thus, with a Ce-mediated system, the processing of the organic waste materials can be made external to and separate from the electrochemical cell (Nelson et al., 1999). This ability offers many advantages in system design while also enhancing cell performance and lifetime and avoids any fouling on the anode surfaces common to direct organic oxidation at the electrode surface.

Other (e.g., Ruthenium)

A new approach describing a two-step mediated process using a combination of ruthenium solution chemistry and chlorine electrochemistry was recently published by the AEA group (Davidson et al., 1999). This double MEO process uses the high reactivity of Ru(VIII) toward organic materials to effect the desired organic destruction. In the course of the destruction reaction, the Ru(VIII) is reduced to Ru(IV). The reactive oxidant is regenerated through reaction with hypochlorite that arises from electrogenerated chlorine.

The electrochemistry involved in this process is the familiar chemistry of chlor-alkali manufacture, the largest and most understood electrochemical application in the world. The anode process is the production of molecular chlorine from soluble chloride and the cathode process is the production of hydrogen. The latter avoids the formation of water that occurs with the reduction of nitric acid [Equation (5.2.3.3)]. In the ruthenium process, the chlorine is produced under conditions that favor its disproportionation to hypochlorite [Equation (5.2.3.6)]. The hypochlorite (or chlorine), in turn, oxidizes the Ru(IV) in a series of steps to the active Ru(VIII).

$$Cl_2 + H_2O = HOCl + HCl \qquad (5.3.2.6)$$

This chemistry is in its infancy; thus, not much information is available about its performance to be able to evaluate the potential of its application to organic waste destruction. It certainly is a chloride-tolerant system, based on the obligatory involvement of chlorine in the overall process. Further work will be necessary to judge the feasibility of this process chemistry for application to a general organic waste destruction.

Implementation of the Process Chemistry

To make a working process from the chemistry, the reactions described in Equations (5.3.2.1) through (5.3.2.5), need to be incorporated into a set of unit operations that work in a predictable and economic manner. A commercial embodiment of the cerium-catalyzed process has been installed at the University of Nevada at Reno for on-site processing of the University's organic hazardous wastes. A schematic of this system is presented in Figure 5.2.3.1. The self-contained unit has the necessary equipment to generate the active Ce(IV) oxidant, contact the oxidant with the organic materials, remove the rejected chlorine from the vent gas stream and recover the nitric acid from the cathode reduction products (Nelson et al., 1999).

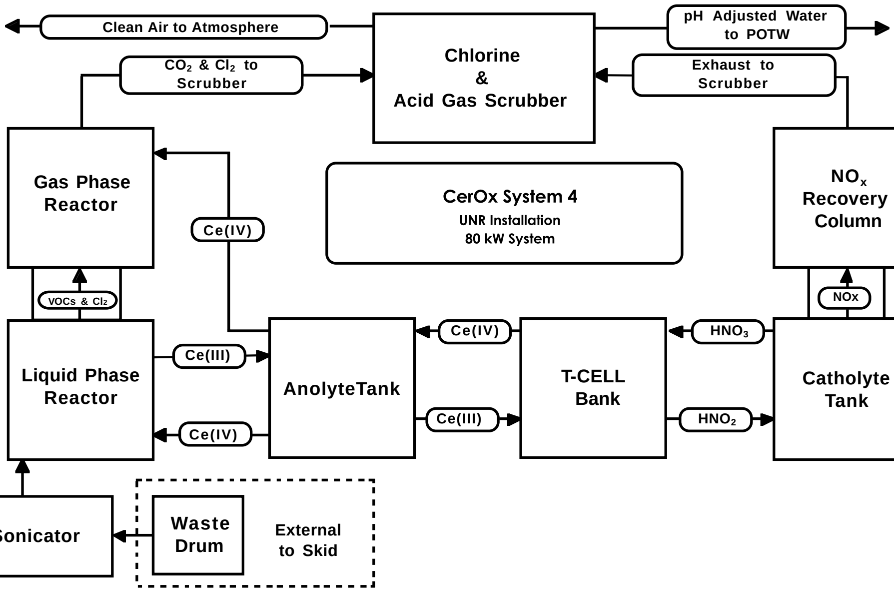

FIGURE 5.2.3.1 Process flow schematic for an 80-kW MEO system. (From Nelson, N.J., Steward, G.A., Pells, W., and Varela, J., The CerOx Process for Hazardous Waste Destruction, Presented at the *1999 Annual Meeting of AIChE,* Dallas, TX, November 1999. With permission.)

As noted, the stability of Ce(IV) allows the system to have two external (to the electrochemical cells) reactors for organic destruction, as indicated in Figure 5.2.3.1. The indicated process flow diagram shows the waste introduction to the Ce(IV) electrolyte through a sonic mixer that emulsifies the aqueous Ce(IV) stream with the (usually) hydrophobic organic waste stream (Surma et al., 1998). The gaseous effluent from this first (liquid-phase) reactor passes into a packed bed reactor against a countercurrent flow of fresh Ce(IV) anolyte before exiting through a scrubber to remove any chlorine product. The second (gas phase) reactor is designed to destroy any organic residuals or adventitious volatiles that may have passed straight through the first reactor (Nelson et al., 1999).

The operation of the system in Figure 5.2.3.1 is completed by the addition of an acid gas scrubber on the exhaust stream to remove the chlorine (Cl_2), formed during the destruction of chlorocarbons, before the CO_2 is vented to the atmosphere. Also incorporated in the system are the absorber columns designed to recapture the NO_x generated by the cathode reaction. The one unit operation critical for mixed waste processing — the recovery and stabilization of the anolyte components — is missing from the operation outlined in Figure 5.2.3.1.

The system in Figure 5.2.3.1 has been operated at the University of Nevada at Reno (UNR) for 2 years. The system has been used to treat UNR's organic wastes and surplus chemicals. It has been operated for most of this time at the 40-kW level with the electrical parameters given above; coulombic efficiency for Ce(III) to Ce(IV) conversion at 500 A is in the 83 to 85% range. The cerium anolyte solution typically contains dissolved cerium nitrate in the 0.9 to 1.4 *M* range in a nitric acid electrolyte of approximately

3 *M*. The catholyte is a nitric acid solution in the 3.0 to 3.5 *M* range. Construction materials for the equipment are restricted to PVDF™ and other fluoropolymers, titanium, and certain Viton™ elastomers.

The system shown in the Figure 5.2.3.1, is not designed for mixed waste operation because the anolyte is required to be sent off-site for mediator and nitric acid recovery and recycle. In commercial operation with the waste stream volume representative of university-level generation, the periodic change-out of the anolyte is the most cost-effective method of operation for these 80-kW and smaller units.

Mixed Waste Processing

MEO technology still resides in the emerging technology category and as such has not found application in processing "real" mixed wastes, although the process is under active study in the National Laboratories, as chronicled above, as these are the custodians of the legacy mixed wastes dating back to the 1940s. In addition, other government studies have included MEO processing as part of an integrated approach to the mixed waste dilemma (Feizollahi and Quapp, 1995).

Most of the laboratory work on MEO conducted in the National Laboratories has involved (at least in part), studies on the destruction of mixed waste surrogate materials. A partial listing of the mixed waste surrogates included in the MEO destruction investigations from several National Laboratories is given in Table 5.2.3.2.

TABLE 5.2.3.2 Partial Listing of MEO Processed Mixed Waste Surrogates

Mixed Waste Surrogate	Laboratory	Mediator	Ref.
Tributyl phosphate and kerosene, and ion exchange resins	AEA	Ag	Steele, 1989
Ion exchange resins	LANL	Ag	Cournoyer and Smith, 1999
Trimsol oil, cellulosic materials, Tyvek, latex materials, polyethylene, and poly (vinylchloride)	LLNL	Ag	Balazs et al., 1997; Chiba et al., 1995
Ion-exchange resins, cellulosic materials, and PCBs	PNNL	Ag & Ce	Ryan et al., 1992
Trimsol cutting oil	PNNL	Ce	Surma et al., 1998
Ion exchange resins	LANL	Ce	Cournoyer and Smith, 1999
Ion exchange resins	LANL	Co	Cournoyer and Smith, 1999
Trimsol oil	LLNL	Co	Gray et al., 1992
Tributyl phosphate	AEA	Ru	Davidson et al., 1999

Given the magnitude of the MEO effort, and the fact that it is ongoing, it is clear that there is definite interest in using this technology for the destruction of mixed waste materials. The promise of this technology for processing this special waste stream is high because no other proposed technology offers the same degree of radionuclide containment during processing. However, the fact that the technology is not being practiced for destruction of real mixed wastes suggests that the technology in not yet sufficiently mature to provide that extra degree of confidence required for disposal of mixed waste materials.

Summary

Mediated electrochemical oxidation (MEO) processes have been investigated primarily at the National Laboratories owing to the early focus of the technology on processing of mixed wastes. The MEO processes use the oxidizing power of high oxidation state metal ions to destroy organic materials in an aqueous electrolyte medium. The use of a condensed-phase medium allows for total containment of the waste materials, their reaction intermediates, and the radioactive components until the organic materials are completely digested. The trace radioactive elements remain behind in, usually, nitric acid solution, a medium compatible with the experience base of the National Laboratories. Further, the use of a condensed-medium process reduces the equipment volume by a factor of 10 compared to a gas-phase process such as incineration.

A preponderance of the effort at the National Laboratories has been directed toward the destruction aspect of the organic portion of the target mixed wastes. While this part of the mixed waste problem must be established, it is only part of the total technology envelope that must be sealed before MEO technology will be adopted for the destruction of mixed waste materials. A considerable amount of effort must also be allocated to the less glamorous, but probably more demanding areas of electrolyte recovery and recycle for recovery of the mediator(s) and the electrolyte acid, as well as isolation and stabilization of the radioactive nuclides.

The cerium MEO process outlined in Figure 5.2.3.1 is directed to commercial applications that, while governed by environmental regulations, do not have the overlay of the much tighter regulations and controls required for the handling and accounting of radioactive materials. It is anticipated that the experience gained in the commercial market will broaden the technology base to include a complete characterization of the destruction process as well as demonstrations of the peripheral processing needed to recover and recycle the mediator(s) and electrolyte acid(s). Acceptance of the technology by the stakeholders in the mixed waste arena will not occur until the total technology package has been demonstrated to the user audience.

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5.2.4 Direct Chemical Oxidation Using Peroxydisulfate

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Introduction

Direct Chemical Oxidation (DCO) is an ambient pressure, nonthermal process that was developed to destroy the organic contaminants in hazardous or mixed wastes by chemical oxidation. DCO uses solutions of the peroxydisulfate ion, the strongest known chemical oxidant (other than fluorine-based chemicals), to convert organic solids and liquids to carbon dioxide, water, and constituent minerals by oxidation at temperatures of 80 to 100°C. The process was developed for applications in bulk waste treatment, chemical demilitarization and decontamination, and environmental remediation by engineers and scientists at Lawrence Livermore National Laboratory, beginning in 1992.[1-8] Peroxydisulfate has also been used alone or with an Ag(II) catalyst in decontamination and etching solutions for removing PuO_2 (as dissolved plutonyl ion) from radioactively contaminated equipment. The process has been demonstrated in transportable pilot-scale operations (15 kg-C/day) on mixed chlorinated solvents. The expended oxidant can be regenerated by electrolysis to minimize secondary wastes. Off-gas volumes are minimal, allowing retention of volatile or radioactive components. For nearly all water-soluble organic liquids, the rate of destruction at 90 to 100°C is about 200 kg (as carbon) per cubic meter of reaction liquid per day.

Chemical Fundamentals

This is an aqueous process that uses solutions of sodium or ammonium peroxydisulfate to oxidize organic material to carbon dioxide and water. The process operates at ambient pressures and at temperatures typically in the range 80 to 100°C. The expended oxidant (sodium- or ammonium hydrogen sulfate) can be regenerated by high-rate electrolysis at platinum anodes to minimize secondary waste or oxidant cost. Commercial equipment is available for supporting this process. The net waste treatment reaction is:

$$S_2O_8^{2-} + (\text{Organics}) \Rightarrow 2HSO_4^- + (CO_2, H_2O, \text{Inorganic residues}) \qquad (5.2.4.1)$$

Acidified ammonium peroxydisulfate has one of the highest redox potentials of any known chemical oxidant. At 2.05 V, it is comparable to ozone, and exceeded only by fluorine and oxyfluorides. The process is being developed for the treatment of organic liquids — neat or in porous solid matrices. It will oxidize the organic fraction of sludge if the matrix is finely divided and slurried with the oxidant solution. Destruction of some organic solids, such as paper, cloth, and styrene resins, is possible, and other plastics and inorganic debris will be partially oxidized and decontaminated. The oxidation potential of peroxydisulfate is high enough to oxidize nearly all organics. Thus, the process has been called "omnivorous." However, perfluorinated polymers (e.g., Teflon) are inert, and reactions with polyethylene and polyvinylchloride (PVC) are slow. With these materials, surface oxidation for decontamination, rather than bulk oxidation, is a practical goal. Carbon tetrachloride and the ammonium ion are not oxidized.

Recalcitrant materials (e.g., PVC polymer) benefit from thermal treatment (140 to 180°C, 24 hr) to partially pyrolyze the material before oxidation by peroxydisulfate. Pyrolysis results in removal of some chloride as HCl, leaving an unsaturated residue that is more readily oxidized.

At room temperature, solid peroxydisulfate salts and moderately concentrated solutions are stable. The ion is thermally activated at moderate temperatures (>80°C) to produce the sulfate radical anion (SRA), which is a strong charge-transfer agent:

$$S_2O_8^{2-} = 2SO_4^{-} \tag{5.2.4.2}$$

This free radical initiates a cascade of oxidation reactions in the organic wastes, producing intermediate organic molecular fragments, organic and hydroxyl free radicals, inorganic ions in high oxidation states (e.g., Ag(II) and Co(III) if these elements are present), and secondary oxidants such as peroxymonosulfate, hydrogen peroxide, ozone, and free oxygen. Reaction (5.2.4.2) can also be catalyzed by UV light, transition metal ions, radiolysis, and noble metals. The chemistry is reviewed by House,[9] Menisci,[10] and Peyton.[11] In general, oxidation by peroxydisulfate in mild acid or base is first order with respect to $[S_2O_8^{2-}]$ and follows the rate equation,

$$d[R]/dt = -\ k_a\ [S_2O_8^{2-}] \tag{5.2.4.3}$$

where ka = 0.01–0.02 min^{-1} when both [R] and $[S_2O_8^{2-}]$ are expressed in units of normality (equivalents per liter). Table 5.2.4.1 shows the rates of destruction of a variety of chemicals with diverse functional groups, for initially low concentrations (<50 ppm, as carbon). Figure 5.2.4.1 shows the temperature dependence of the oxidation rate for dilute and concentrated organics, which extrapolates from data for formation of the SRA at low temperatures. The formation of organic free radicals can accelerate the formation of the sulfate radical, leading to a doubling or tripling in the rate of organic destruction in initially concentrated solutions. (See discussion below of results from bench-scale studies).

TABLE 5.2.4.1 Integral Rate Constants (Equivalence Based) for Compounds with Diverse Functional Groups at Initial Concentrations <50 ppm

Compound	M_w (g/mol)	n (eq/mol)	10^2k_a (min^{-1})	Compound	M_w (g/mol)	n (eq/mol)	10^2k_a (min^{-1})
Urea	60.06	0	0.36	4-Aminopyridine	94.12	20	1.47
Oxalic acid dihydrate	126.00	2	0.38	Acetic acid	60.05	8	1.54
Nitromethane	61.04	8	0.63	Sucrose	342.29	48	1.55
Salicylate-Na salt	160.10	28	0.73	Methylphosphonic acid	96.02	8	1.56
Formic acid	46.03	2	0.73	2,2′-Thiodiethanol	122.18	28	1.71
Triethylamine	101.19	36	0.76	1,4-Dioxane	88.11	20	1.94
DMSO	78.13	18	0.79	Ethylene glycol	62.07	10	1.95
DIMP	180.18	44	1.26	Formamide	45.04	5	2.01
Na-EDTA	372.24	39	1.34	Na-lauryl sulfate	288.38	72	2.32
4-Chloropyridine HCl	150.01	21	1.43				

[a] Conditions: T = 100°C; $[H_3PO_4]$= 0.0574 *M*; $[S_2O_{8-}^{\ 2}]$ = 0.245 N; 0.3 cm^2 Pt wire catalysis. (Adapted from Cooper.[8])

Phosphorus, sulfur, and amino nitrogen groups are converted to their oxyanions. Ammonium ion, perfluorinated polymers (CF_x), and carbon tetrachloride are not oxidized. Organic compounds with functional chlorine are preferentially oxidized to water and free chloride ions. The rate of oxidation (governed by rate of formation of SRA) is independent of pH above pH 1.

Basic solutions are favored for treatment of halide-rich compounds such as chlorinated solvents or PCBs, because chlorine remains in the Cl^- state due to the shift of the chloride-hydroxyl-radical equilibrium[11]:

$$Cl^{o} + OH^{-} = Cl^{-} + OH^{o} \tag{5.2.4.4}$$

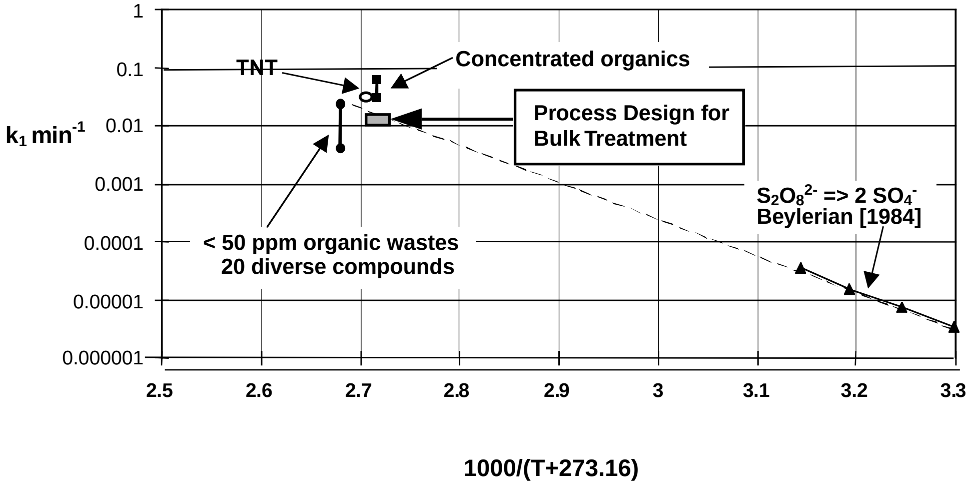

FIGURE 5.2.4.1 The domain of operation of DCO at T = 90–100°C falls on the extrapolated rate of formation of the sulfate radical anion. More concentrated organics are destroyed at higher rates than dilute organics (concentrations <50 ppm) because of the accelerating effect of intermediate free radicals on peroxydisulfate activation.

The steady-state concentration and the half-life of the SRA are very low and the mean-free path of the SRA is short. This accounts for the effectiveness of the peroxydisulfate oxidant when pumped as a concentrated solution into porous media such as soils, filters, or sand — allowing the SRA to be formed at the point of use. Destruction of PCBs and pesticides in soil or sand media has been demonstrated elsewhere.[12] We found no difference in the destruction rates of common surrogates (such as dichloropropanol, ethylene glycol, or phenol) in well-mixed solutions compared with the same materials in slurried sludge, sand, or clay formulations.

Results of Bench-Scale Studies

The oxidation proceeds at a rate of about 200 kg (as carbon) per cubic meter of reaction vessel per day. This rate can be derived from $k_a = 0.03 \pm 0.01$ min^{-1} and an input oxidant concentration of 5 N. This specific rate can be used as a rough estimate for batch and CSTR scaling. Rates of destruction of solids will be lower if the reaction is limited by solution transport or by surface reactions, as in the case of plastics or amorphous carbon. Performance can best be described by a series of examples as follows.

Bulk Rates for Concentrated Wastes

Table 5.2.4.2 summarizes rate data for various surrogate wastes. The percentage destroyed at the given rate is given. Table 5.2.4.3 shows the time-dependent oxidation of kerosene following introduction of the oxidant at 90°C.

TABLE 5.2.4.2 Rates of Oxidative Destruction (Scale Factors) for Compounds at High Concentrations (Bulk)

Compound	Rate (kg/m^3-day)	Percentage Destroyed at Rate
2,4,6-Trinitrotoluene	132	>98.8
Kerosene	186	>99.97
Triethylamine	205	>98.8
Dowex	132	>99
Ethylene glycol	432	>99.93

TABLE 5.2.4.3 Oxidation of Kerosene (Predominately Dodecane) at 90°C

Time (min)	Oxidant Added (Equivalents)	Carbon Determinations (ppm-Wt C)	Residual Carbon (g C)	Destruction Extent (%)
0	0	59060	3.17	0
70	1.4	1.3	0.00073	99.97
140	2.8	0.27	0.00029	99.99

From Cooper, et al. (see Ref. 8 for text).

Oxidation of Chloro-Solvents Without Hydrolysis

Table 5.2.4.4 summarizes data on treatment of chlorinated solvents in sealed vessels, without hydrolysis pretreatment. Pre-hydrolysis avoids the requirements for pressurizing the oxidation step (with CO_2 evolution) to avoid entrainment of the volatile solvents or intermediate oxidation products into the CO_2 off-gas. Hydrolysis prevents such losses, because the products of hydrolysis are water soluble and relatively nonvolatile.

TABLE 5.2.4.4 Oxidation of Chloro-Solvents by Peroxydisulfate in Sealed Vessels

Chloro-Solvent	Extent of Oxidation after 1 hr
Perchloroethylene	0.991
Trichloroethylene	0.996
Methylene chloride	0.991
Chloroform	0.967
Perchloroethylene/chloroform mixtures (50%)	0.991

Destruction of PCBs

Table 5.2.4.5 presents results of treatment of PCBs in very dilute solutions, with and without a hydrolysis pretreatment. PCBs are not highly volatile, and little is gained by the pretreatment. Pentachlorophenol, as surrogate for PCB, is also fully oxidized in basic DCO media.

TABLE 5.2.4.5 Results of DCO Treatment Of Low Concentrations of PCBs (45 ppm Arochlor 1242) by Oxidation in Basic Media, and by Oxidation Following Hydrolysis Pretreatment

Compound	Oxidation #1: Excess Oxidant, 1 *M* NaOH 85–95°C for 1 hr, two samples		4.5 hr Hydrolysis, 100°C Oxidation for 1 hr	48 hr Hydrolysis, 100°C Oxidation for 1 hr
Monochlorobiphenyl	<0.65*	<0.5*	<0.5*	<0.5*
Dichlorobiphenyl	<0.65*	<0.5*	<0.5*	3.47
Trichlorobiphenyl	<0.65*	<0.5*	<0.5*	2.37
Tetrachlorobiphenyl	<1.3*	<1.0*	<1.0*	7.08
Pentachlorobiphenyl	<1.3*	<1.0*	<1.0*	<1.0*
Hexachlorobiphenyl	<1.3*	<1.0*	<1.0*	<1.0*
Heptachlorobiphenyl	<1.9*	<1.5*	<1.5*	<1.5*
Octachlorobiphenyl	<1.9*	<1.5*	<1.5*	<1.5*
Decachlorobiphenyl	<3.2*	<2.5*	<2.5*	<2.5*

Note: Analysis is by EPA Method 608; Analysis by Centre Analytical, Inc.; *corresponds to limit of detection. Values are in microgram/L (ppb).

Engineering Scale and Pilot Studies

Normally, bulk organic destruction is best pursued in a cascaded series of continuously stirred tank reactors (CSTRs). Additional peroxydisulfate can be used in the final stage as a polisher to eliminate the last traces of organic material. The resultant bisulfate or sulfate ion can be recycled to produce new oxidant by electrolysis using industrial electrolysis equipment. This recycle is not hindered by small quantities of common inorganic materials (such as nitrates, chlorides, phosphates, etc.) or by small quantities of organic residuals that might be entrained in the process stream.

An integrated pilot system for the destruction of a wide range of chlorinated organic liquids and organic-contaminated sludge has been demonstrated at LLNL (Figure 5.2.4.2). Many chlorinated solvents benefit (but do not require) hydrolysis to offset difficulties presented by their high volatility at operating temperatures of 100°C. Rapid hydrolysis of mixed waste chloro-solvents to produce water-soluble products was demonstrated here and in similarly scaled laboratory systems (Figure 5.2.4.3). In pilot tests at LLNL, mixed waste solvents based on 1,1,1-trichloroethane (TCA) were hydrolyzed at elevated temperatures (<150°C) (Figure 5.2.4.3). The products of hydrolysis, which are water-soluble and non-volatile, were subsequently oxidized at ambient pressure in a three-stage CSTR system. (Figure 5.2.4.4).

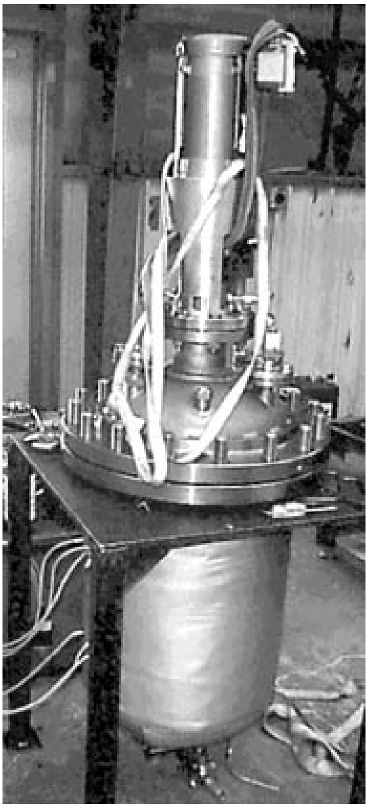

FIGURE 5.2.4.2 One of five, 2-m tall, 75-L hydrolysis (or oxidation) vessels at the LLNL pilot-scale waste treatment facility.

Table 5.2.4.6 presents the results of pilot-scale testing of DCO on the destruction of trichloroethane (methylchloroform) in a two-step process: base hydrolysis in a 60-L vessel, followed by oxidation in a CSTR system (consisting of three 15-L vessels); see Figure 5.2.4.4. The products of hydrolysis are fully destroyed, in good agreement with a process model based on Equation 5.2.4.3. This work establishes that the process scales well from benchtop equipment to pilot scale (i.e., 15 kg C/day).

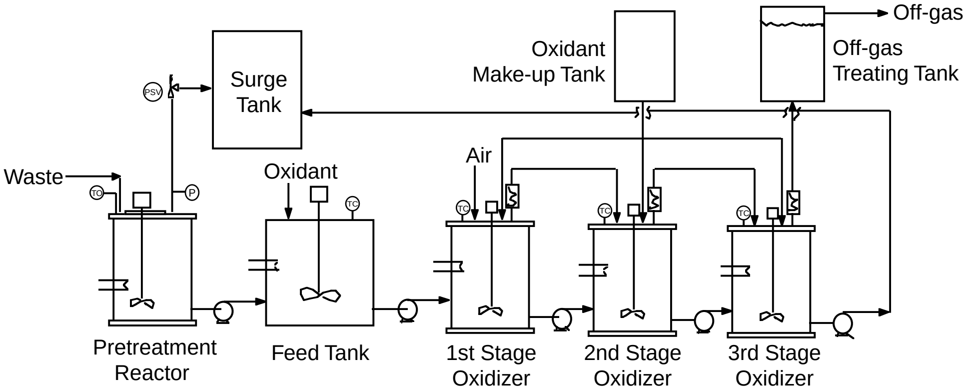

FIGURE 5.2.4.3 Schematic of pilot-scale process tested at LLNL on wastes based on 1,1,1-trichloroethane (methylchloroform). Pre-hydrolysis converts very volatile chlorinated solvents to water-soluble products, which are then oxidized at atmospheric pressure in a series of three CSTRs.

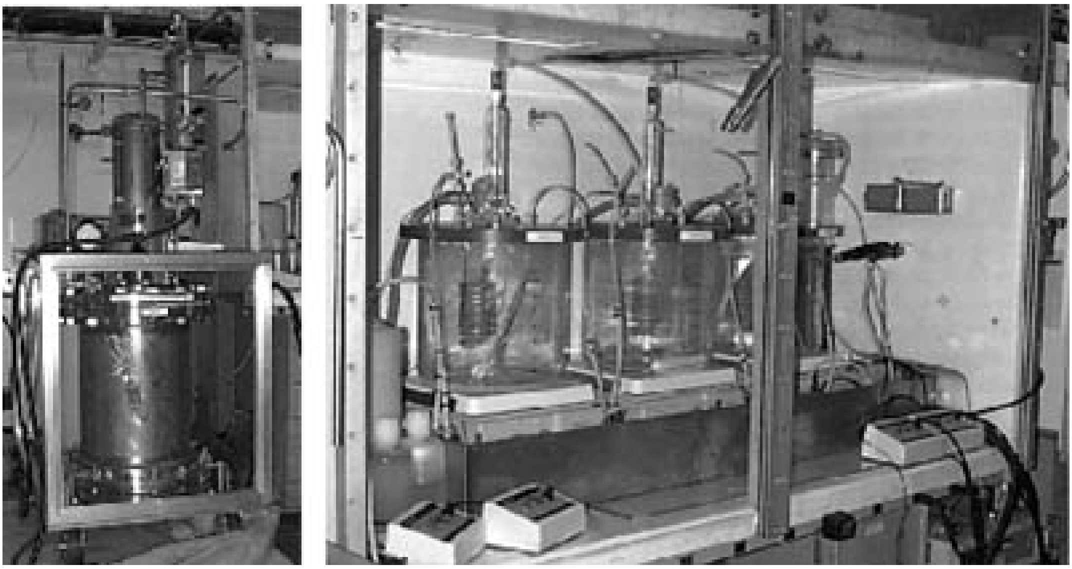

Figure 5.2.4.4 Pilot-scale laboratory unit used in destruction of trichloroethane (TCA) solvents, 15 kg/day. The 60-L hydrolysis vessel (left) converts TCA into water-soluble species, which are oxidized in a three-stage CSTR system (right). Data from this system is presented in Table 5.2.4.6.

Materials of Construction

No unusual or expensive containment materials are required. Oxidation is best pursued in ceramic or glass-lined vessels, or in earthenware. Hydrolysis vessels are stainless steel. Electrolysis vessels are stainless steel, glass, or earthenware; electrodes are graphite and platinum.

The composition of the off-gas stream will depend on the particular waste being processed, but general predictions can be made. Common to all organic waste streams will be carbon dioxide; oxygen will also be produced by a minor, competing side reaction (oxidation of water). In acid solutions, some chlorine will be present in the off-gas resulting from oxidation of chlorine-containing wastes; the chlorine can be neutralized by thiosulfate. The use of DCO in alkaline solutions avoids the formation of chlorine and chlorine released from organic molecule or free inorganic chloride remains as the chloride ion in solution. In cases where the oxidant is recycled by electrolysis, oxygen, ozone, and possibly chlorine (if chloride is present) will be added to the anode off-gas. In industrial electrolysis cells, the hydrogen gas is concurrently

TABLE 5.2.4.6 Experimental and Theoretical Destruction of Waste (Base-Hydrolyzed Trichloroethane) in Three-Stage CSTR T = 90°C; V = 15 L per vessel; flow = 0.10 L/min; process model: rate = $k_a\ [S_2O_8^{2-}]$

Parameter	Experimental	Process Model
Concentration of waste input	0.11 *M*	(0.11 *M*)
CSTR #1 output	0.0061 *M*	0.00701 *M*
Cumulative efficiency	94.45%	93.6%
CSTR #2	0.0006 *M*	0.0005 *M*
Cumulative efficiency	99.46%	99.59%
CSTR #3	0.0003 *M*	0.00003 *M*
Cumulative efficiency	99.76%	99.97%

produced at the cathode; this gas can be oxidized to water (in a catalyzed bed) and the water internally recycled. Commercial catalysts are available for this purpose.

Because of the low volume of off-gas (essentially only the carbon dioxide fraction and water vapor), the off-gas can be captured and retained for test if volatile radionuclides (tritium) or heavy metals (mercury) are present in the waste. At the process operating conditions, formation of dioxins and furans in the off-gas is not believed possible, and analyses to check for these materials have been negative.

Summary of Advantages and Limitations of the DCO Process

Advantages of DCO in rough order of significance are as follows:

1. DCO can treat a wide variety of organic wastes (liquids and solids; water soluble or not) and waste matrices (soils, clays; inorganic substrates; steel machinery; etc.).
2. Process operation and control is simple; scale-up or scale-down follows straightforward conventions.
3. No unusual or expensive containment materials are required; oxidation is best pursued in ceramic, polymer or glass-lined vessels, in earthenware, or in stainless steel equipment.
4. The speed of the oxidation reaction can be selected to provide either full destruction of organic matter; or surface decontamination and etching of metal, ceramic, or plastic debris.
5. Peroxydisulfate reduces to a nontoxic hydrogen sulfate by-product, which can be recycled to reduce material and handling costs and to minimize generation of secondary wastes.
6. Oxidants used in the process are readily available and transportable, and no unusual materials are required for process containment or oxidant storage.
7. The nonthermal process operates below 100°C in liquid media, avoiding formation of dioxins and furans in the off-gas and reducing the offgas treatment requirements and associated costs.

There are disadvantages to the process. Converting the final waste products into a form having minimum volume requires removal of water, unreacted oxidants, and water-soluble materials. Chemical stabilization is required for land burial. Although complete oxidation of organic debris is possible, rates may be too slow and the amount of required oxidant may be too great to justify application. Direct chemical oxidation may be more practical as a surface oxidative decontamination process for solid debris and contaminated equipment. Although peroxydisulfate readily destroys *dilute* organic contamination in aqueous solutions, the water present also dilutes the products of oxidation, making recycle impractical.

Certain limitations and possible hazards need mention. Wastes containing finely divided aluminum, iron, or other metals can be oxidized so rapidly that unsafe conditions can occur. Zinc metal may also form an explosive intermediate in the presence of ammonia. Potential users are urged to consult standard texts on chemical safety.

The process is probably most attractive when a small amount of organic must be removed from a large amount of an inert solid matrix, such as sludge, soil, sand, or filter material. Decontamination is similarly well suited to DCO, using peroxydisulfate alone or with a mediated chemical oxidant couple such as Ag(I)/Ag(II), Ce(III)/Ce(IV), or Co(II)/Co(III). Pre-hydrolysis is not chemically necessary, but is favored because it allows very volatile solvents to be oxidized without the complications of high-pressure containment of evolved gases. Processing of bulk organic materials is also simple, but the cost of oxidant recycle mitigates in favor of incineration whenever the latter is possible.

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5.3

Electrohydraulic Cavitation and Sonolysis

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Introduction

Ultrasonic irradiation has been investigated in the transformation of various environmentally important organic compounds. Sonochemistry results from acoustic cavitation, which is the formation and collapse of cavitation bubbles in response to ultrasonic waves. Extreme temperatures and pressures exist within the collapsing gas bubbles (Mason and Lorimer 1988), leading to thermolytic reactions and the formation of free-radical species. The conditions within the bubble are so extreme that the bubbles emit light, a phenomenon known as sonoluminescence (Young, 1976; Crum, 1994a; b; Putterman, 1995). An important reaction is the thermolysis of water vapor to form hydroxyl radical and hydrogen atoms. Thermolysis and radical reactions dominate inside the bubble and at the liquid/bubble interface. Any radicals that have not been scavenged in these regions, as well as hydrogen peroxide formed from the free-radical combination, will be available for reactions in the bulk liquid phase. Hydrolysis reactions can also be enhanced, particularly for compounds that partition to the bubble interface (Hua et al., 1995a; b; Tuulmets and Raik, 1999).

Although the precise pressures and temperatures generated within the bubbles during acoustic cavitation are difficult to measure experimentally or to determine theoretically, knowledge of these parameters is necessary for elucidating the mechanisms behind sonochemical effects (Suslick, 1989). Numerous theoretical models indirectly approximate the dynamics of acoustic cavitation with varying degrees of accuracy (Kamath et al., 1993; Roberts and Wu, 1998). However, the difficulty, even with models, is accurately describing the cavity dynamics during the latter stages of bubble implosion. The most robust and rigorous models predict final temperatures in the thousands of Kelvins (Flint and Suslick, 1991), pressures varying from the hundreds to thousands of atmospheres (Suslick et al., 1993a), and collapse times on the order of picoseconds (Barber et al., 1992).

Sonoluminescence (SL) induced in solution during ultrasonic irradiation has been used to probe directly into these characteristics of rapid cavity expansion and implosion. Flint and Suslick (1991) compared the observed spectra of SL from silicone oil with synthetic spectra modeled after known rotational and vibrational temperatures of similarly excited diatomic emissions and found the effective cavitation temperature to be approximately 5000K. Further experiments by Suslick and co-workers (Suslick et al., 1986) using comparative rate thermometry with metal carbonyls have corroborated these results. Suslick et al. (1993a) have also investigated the SL spectra of metal carbonyls and have used this information to determine collisional lifetimes of the corresponding emitting atoms to estimate the effective local pressures upon cavitation. Using this procedure, pressures of approximately 1700 atm have been calculated during metal atom excitation and emission occurring upon cavity collapse (Suslick et al., 1993).

Other researchers (Barber et al., 1992; Gaitan et al., 1992; Hiller et al., 1992) have investigated the SL of a single, stable cavitating bubble in water and found that the SL spectra can only be fitted by a blackbody spectrum. With this method, temperatures during single-bubble sonoluminescence have been estimated to approach 40,000K upon bubble implosion. The difference in temperatures between single- and multiple-bubble SL is attributed to fundamentally different mechanisms (Crum, 1994a; b; Matula et al., 1995). The physical conditions within the bubbles during cavitation are thus sufficient for rapid destruction of aqueous contaminants.

Product Studies

The use of power ultrasound to degrade environmentally important compounds has been studied extensively for the past 20 years. Most of the studies have focused on optimizing the conditions of sonochemistry by varying such parameters as ultrasonic frequency, ultrasonic power, saturating gas, and initial compound concentration. A number of these studies have also involved identifying intermediates and products of sonolysis. The most extensively studied compound has been carbon tetrachloride (CCl_4) (Cheung et al., 1991; Wu et al., 1992; Inazu et al., 1993; Francony and Petrier, 1996; Hua and Hoffmann, 1996; Petrier and Francony, 1997a; b; Hung and Hoffman, 1998; 1999). Other compounds that have been studied include phenol (Serpone et al., 1992; Petrier et al., 1994; Trabelsi et al., 1996; Petrier and Francony, 1997a; b; Kruus et al., 1998), chlorophenols (Petrier et al., 1992; Serpone et al., 1994; Catallo and Junk, 1995; Petrier et al., 1996; Ku et al., 1997; Kruus et al., 1998; Weavers et al., 1998), chlorobenzene (Kruus et al., 1997; Drijvers et al., 1998; Petrier et al., 1998; Drijvers et al., 1999), hydrogen sulfide (H_2S) (Kotronarou et al., 1992), trichloroethylene (TCE) (Cheung et al., 1991; Inazu et al., 1993; Drijvers et al., 1996; Drijvers et al., 1999), and methyl *tert*-butyl ether (MTBE) (Kang and Hoffman, 1998; Kang et al., 1999). Most of these compounds have been studied at a frequency of 20 kHz.

Carbon tetrachloride exhibits the fastest degradation rate, with a first-order rate constant of 0.234 min^{-1} at a power of 135 W, an initial concentration of 19.5 m*M*, a pH of 11.8, and an argon sparge (Hua and Hoffmann, 1996). The slowest first-order decomposition rate observed at 20 kHz for the listed compounds was that of 2-chlorophenol. 2-Chlorophenol had a first-order rate constant of 0.00033 min^{-1} at a power intensity of 38.1 W/cm^2, an initial concentration of 12.6 mM, a pH of 11, a temperature of 60°C, and an oxygen sparge (Ku et al., 1997). Chlorobenzene and TCE were studied at 520 kHz. Chlorobenzene exhibited degradation rate constants between 0.0057 and 0.0243 min^{-1} when the concentration was decreased from 3.44 to 0.86 m*M* at a power of 14 W, a pH of 7, a temperature of 29.5°C, and an air sparge (Drijvers et al., 1999). The TCE rate constant increased from 0.0194 to 0.0617 min^{-1} when the concentration was decreased from 6.68 to 1.67 m*M* at the same conditions as above (Drijvers et al., 1999). It should be noted that these kinetic constants are dependent on reactor configurations, and thus are not directly comparable.

The ideal outcome of sonolysis (or any other treatment technology) is to completely mineralize the parent compound to carbon dioxide (CO_2), water, and inorganic, nontoxic ions. For the purposes of this chapter section, all other compounds are referred to as "intermediates" or "by-products," as they are intermediate between the parent compound and desired final products. The identification of reaction intermediates is necessary to confirm that toxic or persistent intermediates do not form during sonolysis. The chemical structures of intermediates can also yield information about predominant reaction pathways for a given compound. The studies that have been performed to date have dealt with compounds that represented a class of compounds with environmental significance so that sonochemical decomposition products and intermediates can be predicted for entire classes of similar compounds.

Many methods are possible for analysis of sonolytic reaction intermediates and products. The most important method has been gas chromatography coupled with a mass spectrometer (GC/MS). The utilization of GC/MS allows for detection of very low levels of compounds that can be unambiguously identified based on the "fingerprint" obtained from the MS. Some compounds are not amenable to GC, however. These compounds can often be analyzed by high-performance liquid chromatography (HPLC), sometimes coupled with MS (LC/MS). However, most researchers have confirmed compound identification with HPLC by comparing the retention times on the column. This method is also employed in ion chromatography (IC) for the identification of smal-chain organic acids and other anions such as chloride ion (Cl^-) for chlorinated compounds and nitrate (NO_3^-) and nitrite (NO_2^-) for nitrogenated compounds.

The purpose of this section is to consider compounds for which extensive product studies have been performed by various investigators. Kinetics and reaction pathways for each compound and its products and intermediates are discussed. The effects of frequency, power, initial concentration of parent compound, and saturating gas, if any, are summarized. The analyses employed for identification of key intermediates and mineralization products are also discussed.

Carbon Tetrachloride

The sonochemical decomposition of CCl_4 has been well-characterized. The mineralization reaction of CCl_4 proceeds as follows:

$$CCl_4 + 2\ H_2O \rightarrow CO_2 + 4\ Cl^- + 4\ H^+ \tag{5.3.1}$$

The proposed decomposition mechanism is thermolysis of the carbon-chlorine bond and subsequent reactions of the radicals formed during thermolysis which occurs inside the cavitation bubble (Francony and Petrier, 1996; Hua and Hoffmann, 1996). Many researchers have analyzed formation of the main product, chloride ion (Cl^-) (Francony and Petrier, 1996; Hua and Hoffmann, 1996; Petrier and Francony 1997a; b; Hung and Hoffman, 1998; 1999), primarily by IC or ion selective electrode. Formation of both Cl^- and CO_2 was found to be faster at 500 kHz than at 20 kHz, following the trend of the parent compound (Francony and Petrier, 1996). Hung and Hoffmann (1999) found that the Cl^- formation rate was quite similar to the CCl_4 degradation rate for frequencies ranging from 20 to 1078 kHz, and the maximum rate of Cl^- formation was obtained at 500 kHz.

The main intermediate, dichlorocarbene, was identified and quantified by Hua and Hoffmann (1996) by trapping the carbene with 2,3-dimethyl-2-butene to form 1,1-dichloro-2,2,3,3-tetramethylcyclopropane, which was then identified by GC/MS. Formation of dichlorocarbene was determined to occur through three possible mechanisms: removal of one chlorine atom from CCl_4 and subsequent removal of another chlorine atom; simultaneous removal of two chlorine atoms; and reaction of two trichloromethyl radicals to form CCl_4 and dichlorocarbene (Hua and Hoffmann, 1996). Thermolysis as the main decomposition pathway is suggested by formation of dichlorocarbene. Furthermore, when a hydroxyl radical scavenger, 1-butanol, was added during sonolysis of CCl_4, (Francony and Petrier, 1996), no inhibition of the destruction rates was observed, which is also consistent with a thermolysis mechanism. Minor products such as tetrachloroethylene and hexachloroethane have been identified as well (Francony and Petrier, 1996; Hua and Hoffmann, 1996; Hung and Hoffman, 1998; 1999). The formation of these products has also been modeled (Hung and Hoffmann, 1999) and minimized when ozone is added to an argon atmosphere in the sparge gas (Hua and Hoffmann, 1996). Both of these products are found in small concentrations when compared to Cl^-. Thus, sonolysis has been demonstrated to almost completely mineralize CCl_4.

Phenols

The sonolysis of phenol, chlorophenols, and 4-nitrophenol has been studied by many researchers. Phenol does not exert a high vapor pressure or gas-liquid partitioning coefficient, so its destruction will occur primarily in the interfacial region surrounding the bubble or in the bulk liquid phase. Phenol is also deprotonated above pH 10. In this case, the phenolate ion would be even less likely to partition into the bubble than the phenol. The mineralization products of phenol are CO_2 and water. The main reaction intermediates found in the sonolysis of phenol are catechol, hydroquinone, and *p*-benzoquinone (Serpone et al., 1992; Petrier et al., 1994; Trabelsi et al., 1996). HPLC has been the main analysis method employed to detect both parent compound and intermediates. The addition of 1-butanol as a radical scavenger has completely inhibited the sonolysis of phenol; thus, it was proposed that decomposition of phenol is accomplished through reaction with hydroxyl radicals formed from the thermolytic decomposition of water (Petrier and Francony, 1997a; b). The identified intermediates of phenol sonolysis varied with pH: catechol, hydroquinone, and benzoquinone were found at pH 3, only catechol and hydroquinone were found at pH 5.7, and no intermediates were found at pH 12, although all three intermediates were determined to be extremely unstable at this pH (Serpone et al., 1992). When frequency was varied at 20 and 487 kHz, phenol degradation and intermediate formation and subsequent degradation were much faster at 487 kHz (Petrier et al., 1994). When the total organic carbon (TOC) of the phenolic solution was analyzed, very little reduction in TOC was observed after 12 hr of ultrasonic irradiation, indicating that mineralization of phenol is slow (Serpone et al., 1992).

Chlorophenols and 4-nitrophenol (*p*-NP) behave similarly to phenol when sonicated. The main reaction has been found to be reaction with hydroxyl radicals. Release of Cl^-, a mineralization product, from 4-chlorophenol exhibited a lag relative to decay of the parent compound (Serpone et al., 1994; Petrier et al., 1998). The primary organic intermediates of 4-chlorophenol sonolysis are 4-chlorocatechol and hydroquinone (Serpone et al., 1994; Petrier et al., 1998), while the intermediates of 3-chlorophenol are 3- and 4-chlorocatechol and chlorohydroquinone, and those of 2-chlorophenol are chlorohydroquinone and catechol (Serpone et al., 1994). The nitrogenous mineralization products of *p*-NP, NO_2^- and NO_3^-, were quantified by IC and observed to form exponentially as a total ($NO_2^- + NO_3^-$) (Kotronarou et al., 1991). The main organic intermediates identified were 4-nitrocatechol (4-NC) and p-benzoquinone by UV spectrophotometer and formate and oxalate by IC (Kotronarou et al., 1991). The formation rate of 4-NC increased with initial *p*-NP concentration (Kotronarou et al., 1991). The fraction of *p*-NP converted to 4-NC was the largest when argon alone was the saturating gas, and much less 4-NC was formed when argon mixed with oxygen or oxygen alone were the saturating gases (Hua et al., 1995). Higher concentrations of 4-NC were observed at 500 kHz when compared to that at 20 kHz and degradation of the intermediate was observed at 500 kHz, indicating that *p*-NP would more quickly mineralize at this frequency (Weavers et al., 1998).

Mixtures of Compounds

Following demonstration that ultrasound is effective for destroying single compounds, a logical extension of previous studies is to determine the viability of the technique for treating mixtures of compounds. The motivation for this work is to model a wastewater that would contain multiple compounds. The two studies discussed in this section involve TCE mixed with chlorobenzene (Drijvers et al., 1999) and chlorobenzene mixed with 4-chlorophenol (Petrier et al., 1998). When TCE and chlorobenzene, both volatile solutes, were mixed, it appeared that the degradation rate of TCE was affected (because of a lower temperature, and thus fewer thermolysis reactions, with added substrate), but that of chlorobenzene was not (Drijvers et al., 1999). However, upon analysis of the behavior of styrene, an intermediate of sonolysis of both compounds, it was found that less styrene was formed when TCE was added to a chlorobenzene solution. Thus, TCE inhibits the thermal degradation of chlorobenzene (Drijvers et al., 1999). The addition of TCE to a chlorobenzene solution increased the concentration of dichlorobenzene (created from reaction of chlorine atoms and chlorophenyl radical formed only from chlorobenzene), indicating that secondary radical reactions of chlorobenzene are enhanced by addition of TCE. Thus, the inhibition of thermal degradation and enhancement of secondary radical reactions negated each other when only chlorobenzene disappearance was analyzed (Drijvers et al., 1999). There were also some new intermediates discovered by GC/MS when the mixture was sonicated, all from reaction of chlorobenzene, chlorophenyl radicals, or phenyl radicals with TCE, chloroacetylene, dichloroacetylene, or dichloroethenyl radical. These intermediates were $C_8H_4Cl_2$, $C_8H_6Cl_2$, $C_8H_5Cl_3$, and $C_8H_4Cl_4$ (Drijvers et al., 1999). Thus, it was found that mixing these two volatile organic compounds (VOCs) affected sonolysis of each. Mixing chlorobenzene, a volatile solute, and 4-chlorophenol, a nonvolatile solute, resulted in the inhibition of degradation of the less volatile solute by addition of the volatile solute (Petrier et al., 1998). The decomposition of 4-chlorophenol was inhibited by addition of chlorobenzene because chlorobenzene thermolysis in the bubble reduces the amount of water that can thermolyze to form hydroxyl radicals which then degrade 4-chlorophenol (Petrier et al., 1998).

Another study of interest involved chloroform degradation and the effect of adding phenol or benzene to the chloroform solution (Kruus et al., 1998). Tetrachloroethene and hexachloroethane were found (by GC/MS) to be the principal intermediates when chloroform alone was sonicated. During sonolysis of a mixture of 500 mg/L each of phenol and chloroform, intermediates detected at significant concentrations included tetrachloroethene, 2-chlorophenol, and hexachloroethane, with the 2-chlorophenol forming when chloride atoms from chloroform decomposition combined with phenol (Kruus et al., 1998). Sonolysis of 500 mg/L each of benzene and chloroform resulted in chlorobenzene and phenol formation in addition to the formation of tetrachloroethene (Kruus et al., 1998). Addition of benzene to the chloroform solution inhibited both parent compound degradation and intermediate formation by quite a bit more than phenol addition because the benzene is much more volatile than phenol and will result in higher concentrations in the bubble, and thus a much lower temperature in the bubble (Kruusl et al., 1998).

The products and intermediates of sonolytic decomposition reactions can indicate the types of reactions that are occurring inside a sonochemical reactor. Frequency affects the decomposition of the parent compound, as well as the formation of key intermediates. Saturating gas can also impact formation rates of intermediates. Volatile solutes form by-products that indicate thermolysis as the initial step of sonolytic degradation. The intermediates of sonolysis of nonvolatile solutes indicate that radical reactions, primarily reaction with hydroxyl radical, dominate.

Combination with Other Advanced Oxidation Technologies

Sonolytic destruction rates fall within a wide range. In an effort to increase decomposition rates and enhance mineralization by minimizing organic intermediates, ultrasound has been studied in conjunction with other oxidation technologies. For example, the concurrent use of ultrasound and ozone has been shown to improve decomposition rates for a variety of compounds compared to rates achieved by either method separately (Dahi, 1976; Sierka, 1985; Olson and Barbier, 1994; Kang and Hoffman, 1998; Weavers et al., 1998). Ozone itself decomposes in water by a complex set of reactions that occur both in series and in parallel (Staehelin and Hoigne, 1982). As ozone decomposition proceeds, free radical products such as $O_2^{-\bullet}$, $O_3^{-\bullet}$, and •OH are produced and will react with ozone until it is completely depleted. During sonolysis, ozone thermolytically decomposes within the gas phase of the cavitation bubble as shown (Hart and Henglein, 1985; 1986):

$$O_3 \rightarrow O_2 + O(^3P) \tag{5.3.2}$$

$$O(^3P) + H_2O \rightarrow 2\ {\bullet}OH \tag{5.3.3}$$

The products formed can then migrate to the interfacial region of the bubble where they can interact with target contaminants. In the absence of sufficient radical scavengers in the gas phase, they can also react by the following pathways:

$$O(^3P) + O_3 \rightarrow 2\ O_2 \tag{5.3.4}$$

$$2\ {\bullet}OH \rightarrow H_2O_2 \tag{5.3.5}$$

or recombine to form water molecules. Additional hydroxyl radicals are now formed from the decomposition of ozone in the vapor phase and, along with •OH radicals created during the homolytic cleavage of water, play significant roles in degrading environmental contaminants.

Olson and Barbier (1994) examined the oxidation of natural organic matter under the influence of ultrasound and ozone together. In these experiments, they applied constant ultrasonic irradiation (intensity 55 W, frequency 20 kHz) to a 450-mL batch reactor system that contained a 10 mg/L fulvic acid solution and was being supplied ozone at 3.2 mg/min. After continuous ozonation and irradiation with ultrasound for 60 min, the total organic carbon (TOC) removed was 91% while 87% of the original carbon had been mineralized. In similar experiments using only ozonation, the TOC removal was 40% and only 28% of the original carbon had mineralized. These results showed that while a significant fraction of the TOC removed using ozone alone was removed as volatile organic carbon, most of the original carbon in the sonozone process was removed as CO_2. They noted that this was due to the additional effect of the pyrolytic decomposition of volatile organics in the cavitation bubble, along with the oxidation of the organics by free radicals during ultrasonic irradiation and ozonation. The disinfection of microbial contaminants with ozone has also been shown to improve with the addition of ultrasound as well. Dahi (1976) studied *E. coli* activity during ozone and ultrasound applications and found that ultrasonic treatment intensified the action of ozone with respect to inactivation of the microorganism. These effects were attributed to the enhanced decomposition of ozone in aqueous solution to form free radicals and the increased transfer of ozone into solution.

The enhancement of ultrasonic processes with concomitant ozone addition has also been demonstrated during treatment of other environmental contaminants. Weavers et al., (1998) examined the degradation of nitrobenzene (NB), 4-nitrophenol (4-NP), and 4-chlorophenol (4-CP) in aqueous solutions at two different ultrasonic frequencies (20 and 500 kHz), in the presence of ozone. While examining the decomposition of all three compounds, they observed a synergism from using both ultrasound and ozone together at 20 kHz; that is, the kinetic rate constant during simultaneous application was greater than the sum of the individual kinetic rates. However, at 500 kHz, an antagonistic effect was observed, and the sonozone kinetic rate was less than the sum of the individual rates. They concluded that the main enhancement mechanism due to the combination of ultrasound and ozone came from an increase in •OH formed during the thermal decomposition of O_3 and not enhanced mass transfer effects of ozone into aqueous solution. In separate studies, Weavers and Hoffmann (1998) also showed that the primary mechanism behind the mass transfer of gaseous O_3 into solution during sonolysis resulted from the thermal decomposition of ozone in cavitation bubbles, subsequently creating a large driving force for O_3 to dissolve. Mass transfer effects due to turbulence from acoustic streaming and cavitation were considered inconsequential.

Kang and Hoffman (1998) examined the removal of the gasoline oxygenate methyl *tert*-butyl ether (MTBE) in aqueous solution using sonolysis and ozone, and found considerable increases in the decomposition rate. Using an ultrasonic frequency of 205 kHz and a power of 200 W, the rate of MTBE degradation increased by a factor of nearly 4 with the addition of 0.3 m*M* ozone. They proposed that the mechanism behind MTBE degradation involved three pathways: direct pyrolytic decomposition of MTBE, oxidation of MTBE by hydroxyl radical, and direct reaction between MTBE and ozone. In similar studies, Kang et al., (1999) applied ozone during the ultrasonic destruction of MTBE over a large range of frequencies (205, 358, 618, and 1078 kHz) and found that ozone increased the rate of degradation at each frequency, with substantial enhancements at 358 and 618 kHz.

In a number of studies, ultrasound technology has also been combined with ultraviolet light (UV). Sierka (1985) examined the catalytic effects of UV and sonolysis during the ozone oxidation of humic acid and trihalomethane precursors, and found that the most effective condition for the destruction of the organic carbon compounds utilized both UV photolysis and ultrasound in combination with ozone. The aqueous decomposition of 1,1,1–trichloroethane was found to be much more extensive with sonolysis and concomitant photolysis when compared to the use of either process alone (Toy et al., 1990). Ultrasound has also been shown to play a key role in various bimolecular photochemical reactions by providing ideal assimilation of the reaction mixtures and quenching triplet excited states formed along the reaction pathways leading to more effective photochemical reactions or a beneficial change of product ratios (Toy and Stringham, 1984; 1985; Gaplovsky et al., 1997).

Shirgaonkar and Pandit (1998) used a combination of ultrasound and photocatalysis to effectively destroy 2,4,6-trichlorophenol in aqueous solution. Using an ultrasonic probe with a frequency of 22 kHz and a UV tube of 15 W, they examined the effect of different operating conditions such as insonation intensity, solution temperature, and UV transmission. Experiments using 1000 mL of a 100 ppm concentration of 2,4,6-trichlorophenol were performed using ultrasound and UV irradiation separately and together under similar conditions. Anatase TiO_2 (0.1 g/L) was used as the semiconductor catalyst in the experiments. From the experiments, they ascertained that the degradation rates from the combined methods increased as the temperature of the solution increased. The cumulative effects of sonolysis and photocatalysis were more pronounced at lower intensities, while increasing the ultrasonic intensity did not provide any significant benefits in kinetic rates over the results of the methods performed individually. The degradation rates in the combined experiments were completely independent of the mode of UV transmission. Separate studies have shown that the photocatalytic dechlorination of PCBs using TiO_2 as the catalyst is dramatically more efficient in the presence of ultrasound (Mason, 1992). This improvement in process efficiency is the result of the mechanical effects on the TiO_2 particles, including continual surface cleaning, faster mass transfer rates, and particle size reduction which increases the effective surface area.

The oxidation of phenol in wastewater has been examined using the novel process of combining ultrasound and electrolysis (Trabelsi et al., 1996). Without the addition of ultrasound, phenol radicals are known to polymerize on the surface of the electrodes, ultimately stopping the electrolysis after a very short period of time. In these experiments, ultrasound was shown to significantly improve the rate of phenol oxidation through mechanical effects of bubble implosion, such as the cleaning of the electrode surfaces by dissolving or pitting the inhibiting layers, resulting in more effective transfer of the contaminant to the electrode surface. In fact, using insonation frequencies of 20 and 540 kHz led to 75 and 95% conversions of phenol after 10 min, respectively. Furthermore, at 540 kHz, complete degradation of phenol took place after 20 min with no production of toxic aromatic intermediates. In addition to improving mass transport to the electrode surfaces by keeping them clean, ultrasound can also be used in electrochemistry to degas the electrode and inhibit ion depletion around the electrode surface by disturbing the surrounding diffusion layer (Mason, 1992).

Not only has ultrasound been proven to be very beneficial when used concurrently with other advanced oxidation processes, it has also been used successfully as a pretreatment step in series with other environmental treatment technologies. In studies performed by Ma and Lin (1998), an ultrasound probe with a frequency of 20 kHz was used to irradiate a solution containing 50 mg/L of humic acids prior to chlorination. The results indicated an increase in TOC removal and a decrease in chlorine demand. This effectively decreased the production of chlorinated disinfection by-products that would have formed without the ultrasonic application. Ultrasound has also been shown to enhance the biodegradability of wastewater by breaking down larger organic compounds into short-chain organic acids. Gonze et al., (1999) examined the ultrasonic irradiation of a model compound sodium pentachlorophenate (NaPCP) and found that biodegradability increased with insonation and the toxicity of the NaPCP solution decreased dramatically. In addition, sonication followed by wet oxidation with a catalyst has been shown to effectively remove pollutants from a contaminated waste stream (Ingale and Mahajani, 1995).

Ultrasonic Reactors: Design and Modeling

Most sonoreactors are included in one of several categories. A horn (or probe) system employs a vibrating probe that is immersed in solution (Figure 5.3.1). A reactor incorporating the ultrasound transmitting surface at the base or side of the reactor referred to as a "disk" type reactor (Figure 5.3.2). There are also a few reports of a larger parallel plate flow-through reactor. There also exist some novel sonoreactors with different transducer or unique reactor shapes. Horn, disk, and plate reactors were observed to give very different results when compared at similar power levels (Faid et al., 1998). Horn systems yield standing waves only at low power input and the standing wave becomes distorted when input power exceeds a certain limit. The pressure fields are more concentrated around the horn. On the other hand, wave type and pressure field distributions were more even for disk-type systems. The plate system yielded a threefold higher mass transfer coefficient than the disk system at the same power intensity level.

Ultrasonic reactors designed for large-scale applications typically employ multiple transducers. Reactor geometry is also an important factor for larger sonoreactors (Berlan, 1992). Bolleman and Dunwoody

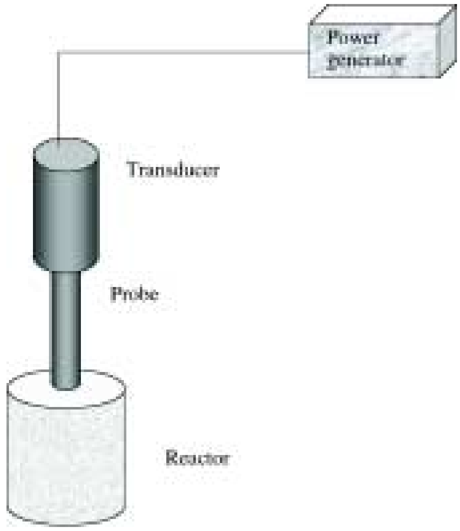

FIGURE 5.3.1 Schematic of a conventional ultrasonic probe reactor. Typical operating frequency = 20 kHz.

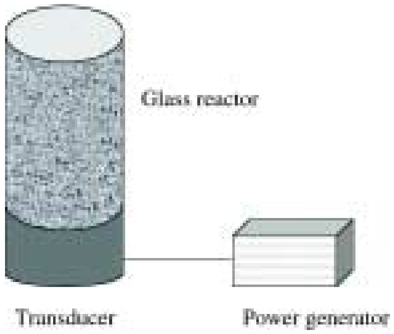

FIGURE 5.3.2 Higher frequency ultrasonic reactor and transducer system. Note that the glass reactor fits over the transducer, and the ultrasonic waves travel vertically through the solution.

(1995) designed a novel sonoreactor in the form of a horizontal vessel with an interior wall that holds a process liquid. The electrostatic film transducer is attached to the interior wall to substantially envelop a selected volume of process liquid. The transducer's acoustic impedance is approximately equal to that of the liquid. This reactor operates in flow-through mode and is employed in industrial plants for waste treatment (Bolleman and Dunwoody, 1995). It is designed for degassing liquids, mixing chemicals, and selected sonochemical reactions. A batch reactor originally designed for chemical synthesis employs multiple (nine or more) transducers mounted at the bottom and on the wall of the stirred vessel. The shape of the vessel is typically cylindrical (Berger et al., 1996).

Few efforts have been made to construct mathematical models for sonoreactors, due in part to a lack of "standard" reactor configurations. Batch sonoreactors are usually modeled from the viewpoint of the bubble dynamics to predict the cavitation field or ultrasonic yield. These models involve assumptions that are very specific to the investigated system, so the results may be difficult to extrapolate to other reactor types. Flow-through sonoreactors, however, are modeled as a unit chemical processor in terms of hydraulic behavior to predict reaction rates. The models are much simpler and more applicable to various systems.

Naidu et al. (1994) used the classic Rayleigh-Plesset bubble dynamic equation to predict reaction rates of KI at various reactant concentrations and with different dissolved gases. The model follows the life of a gas bubble and then extends the result to the entire reactor (100 mL working volume) by assuming the number of bubbles and the initial bubble size (at 25 kHz). The prediction agreed with experimental measurements of concentrations, but the validity for other systems is unclear. However, the result supports the assumption of complete mixing within the sonoreactor.

Laborde (1998) employed classic linear acoustic equations and non-linear fluid dynamic equation to predict the pressure field in a cylindrical disk sonoreactor. It was found that at low frequency (20 kHz), neither calculation represented the experimental results very well. The pressure field predictions were more accurate at higher frequency (500 kHz). The investigators suggested that was because nonlinear terms are more likely negligible at high frequency.

Based on theoretical investigation concerning the sound field, Horst et al. (1996) studied energy conversion paths from electrical power, mechanical energy to energy consumption in the liquid, and finally usable energy in the cavitation bubble. Based on these calculations, the investigators proposed that the best shape for horn system reactors was a conical funnel. They further demonstrated the applicability of the conical shape by employing the sonoreactor as an external module in a flow-through loop (flow rates up to 0.6 L/hr). Maltby (1998) also designed a sonic transducer shroud in the shape of conical funnel, but it was the inverse configuration compared to Horst's design.

Gondrexon et al. (1998) measured the residence time distribution (RTD) for a flow-through disk sonoreactor and found that the system behaved as an ideal continuously stirred tank reactor (CSTR). The investigators further connected three ultrasonic units (volume 0.1 L) in series and predicted the ultrasonic yield using an identical CSTR in series model. The flow rate used was 0.4 to 3.6 L/hr. Both steady state and unsteady state were considered and the model prediction agreed with experimental measurement (Gondrexon et al., 1999).

Hua demonstrated that the incorporation of RTD within the near-field acoustical processor (NAP) did not impact the interpretation of results during decomposition of *p*-nitrophenol, thus both CSTR and plug flow reactor (PFR) models were applicable to NAP (Hua et al., 1995). The flow rate used was 192 L/hr with working volume varying from 0.2 to 1.8 L. Thoma accounted for the sorption and volatilization in the NAP (Thoma et al., 1997). The investigators chose to use mass balance to describe the chemical concentration profile in two sub-systems: the mixing reservoir and the sonication reservoir. Least square parameter fitting was employed to determine coefficients for sorption, desorption, and volatilization.

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5.4

Gas-Phase Destruction

5.4.1 Electron Beam Processing of Volatile Organic Compounds

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Introduction

Volatile organic compounds (VOCs) are emitted from manufacturing the multitude of consumer products used every day. In most manufacturing processes, either for the raw materials, intermediates, or the finished product, VOC-containing materials are present as chemicals, solvents, release agents, coatings, and decomposition products that eventually must be disposed. In such manufacturing, there is usually a large volume of gaseous effluent that contains dilute concentrations of VOCs that is vented into the atmosphere. Cost-effective technologies for disposal of VOCs are being sought by government and industry.

The control of VOC emissions from dilute, large volume sources is a challenging problem. Conventional technologies, such as carbon adsorption/solvent recovery or catalytic/thermal oxidation, have high annual costs per ton of VOC emissions controlled. With a large gas flow rate (85,000 to 400,000 m^3/hr) and low solvent concentrations (100 ppm or less) of no possible reuse value, operating costs for conventional systems over several years can greatly exceed the installed capital cost. To reduce the operating cost, novel low-temperature (ambient to 125°C) treatment technologies are being sought. The emerging technologies include low-temperature catalysts, biofiltration, and non-thermal plasmas. Catalysts easily suffer from plugging, fouling, or poisoning by particulates and non-VOC materials in the exhaust stream; this results in high maintenance costs (Bertelsen, 1992). The major disadvantage of biofilters is their large specific footprint, typically 5 to 25 m^2 per 1000 m^3/hr of treated gas (Leson and Dharmavaram, 1995). Biofilter systems and filter materials may also require costly maintenance and replacement.

Non-thermal plasma techniques represent a new generation of air emission control technology that potentially could treat large-volume emissions containing dilute concentrations of VOCs (Penetrante and Schultheis, 1993a; b). Non-thermal plasma processing operates by producing a plasma in which the majority of the electrical energy goes into the production of energetic electrons. These plasmas are characterized by electrons with kinetic energies much higher than those of the ions or molecules. Although the electrons are short-lived under atmospheric conditions and rarely collide with the pollutant molecules, they undergo collisions with the dominant bulk-gas molecules. Electron-impact dissociation and ionization of the background gas molecules create a mix of reactive species, in the form of radicals, ions, and secondary electrons, that permits unique and diverse chemical reactions to be possible even at relatively low temperatures. The potential of the approach to gas clean-up arises from the fact that these species react selectively with the pollutant molecules, which are often present in very small concentrations.

Non-thermal plasmas can be produced using either electron beams or electrical discharges. In the electron beam method, electrons are accelerated by high-voltage in a vacuum region before being injected through a thin foil window that serves as a vacuum seal. The high-energy electrons going through the thin window can then be used to produce a large volume of plasma as they collide with the gas molecules in an atmospheric-pressure processing chamber. In the electrical discharge method, the high-voltage electrodes are immersed in the atmospheric-pressure gas, instead of a vacuum. The electrons collide with and transfer energy immediately to the gas molecules as they drift along the high-voltage region. The electrical discharge method therefore results in an electron energy distribution that is much lower compared to that from the electron beam method. The numbers of secondary electrons, ions, and reactive free radicals are strongly influenced by this energy distribution.

Electrical discharge and electron beam methods can both be implemented in many ways. There are many types of electrical discharge reactors, the variants depending on the electrode configuration and electrical power supply (pulsed, ac, or dc). Some of the types of electrical discharge reactors that have been investigated for the treatment of contaminated air include the pulsed corona, ferroelectric pellet bed, dielectric-barrier discharge, and surface discharge. The pulsed corona and dielectric-barrier discharge are two of the more extensively investigated types of discharge reactors. In the pulsed corona method, the reactor is driven by very short pulses of high-voltage, thus creating short-lived discharge plasmas that consist of energetic electrons, which in turn produce the free radicals responsible for the decomposition of the undesirable molecules. In a dielectric-barrier discharge reactor, one or both of the electrodes are covered with a dielectric. Whereas in the pulsed corona method the transient behavior of the plasma is controlled by the applied voltage pulse, the plasma that takes place in a dielectric-barrier discharge self-extinguishes when charge buildup on the dielectric layer reduces the local electric field.

There are also many types of electron beam reactors, the variants depending on the type of cathode (e.g., thermionic or cold), electrode configuration, and voltage. In the past, the high capital cost and X-ray hazard associated with conventional MeV-type electron beam accelerators have discouraged the use of electron beam processing in many pollution control applications. Recently, however, compact low-energy (<200 keV) electron accelerators have been developed to meet the requirements of industrial applications such as crosslinking of polymer materials, curing of solvent-free coatings, and drying of printing inks. Special materials have also been developed to make the window thin and rugged. Some of these compact electron beam sources could be utilized for air pollution control applications (Matthews et al., 1993; Paur et al., 1995; Slater and Douglas-Hamilton, 1981). The compact electron beam method has been applied to the removal of various VOCs (Bromberg et al., 1993; Hirota et al., 1995; Koch et al., 1995; Penetrante et al, 1995; Vitale et al., 1997).

The most significant difference between electrical discharge and electron beam reactors is the efficiency by which they produce various reactive species. In electrical discharge methods, the electrons collide with and transfer energy immediately to the gas molecules as they drift along the high-voltage region, thus resulting in an electron energy distribution that is much lower compared to that from the electron beam method. Electrical discharge methods are typically very efficient in producing O radicals through electron-impact dissociation of O_2. On the other hand, electron beam methods are much more efficient in producing N atoms through electron-impact dissociation of N_2. Electron beam methods are also much more efficient in producing ions and secondary electrons through electron-impact ionization of the major gas molecules.

In this section, the efficiencies of electron beam and electrical discharge methods for processing of VOCs are compared. It will be shown that electron beam processing is the most cost-effective non-thermal plasma technique. The physics and chemistry behind the high efficiency of electron beams for decomposing VOCs are explained. Finally, it is shown that electron beam processing is cost-competitive with advanced thermal and catalytic methods that employ heat recovery or hybrid techniques.

Fundamentals

The intent in using a non-thermal plasma is to selectively transfer the input electrical energy to the electrons. In the kinetic analysis of non-thermal plasma methods, the first step is to understand the deposition of energy into the contaminated air. This is controlled primarily by the major components, N_2 and O_2. Because of the resonance in electron scattering by N_2 near 2 eV, low-energy electrons lose considerable energy through vibrational excitation, which does little to enhance the desired reactions. Thus, raising the average electron energy above 2 eV is necessary for efficient treatment.

The most useful energy deposition into N_2 and O_2 is usually associated with the production of N and O atoms through electron-impact dissociation, and ionization, producing either atomic or molecular ions. One must also account for the creation of metastables, especially in the dissociated atoms O and N. For example, the reaction rates for the metastable $O(^1D)$ are almost always larger than those for the corresponding reactions with ground-state $O(^3P)$. These metastables can enhance both desired and undesired reactions.

The electron energy distribution in a plasma reactor is important because it determines the types of radicals produced in the plasma and the input electrical energy required to produce those radicals. In electrical discharge processing, the rate coefficients for electron-impact dissociation reactions strongly depend on the electron mean energy in the discharge plasma. In electrical discharges, the non-thermal plasma is produced through the formation of statistically distributed microdischarges known as streamers. The electrons dissociate and ionize the background gas molecules within nanoseconds in the narrow channel formed by each microdischarge. The electron energy distribution in the plasma is complicated because the electric field is strongly nonuniform (e.g., because of strong space-charge field effects) and time dependent. During the microdischarge formation phase, the electron number rises drastically. Due to field strength enhancement in the ionization wave, the highest electron energies occur during this phase. The mean electron energy reaches values of more than 10 eV — suitable for large dissociation and ionization of the gas. However, because this is a highly transient phase, and because the ionization wave covers only small parts of the gap at the same time, this phase appears to be less important in producing most of the active radicals. Most of the species responsible for the chemical processing are generated during the main current flow in established microdischarge channels. In each microdischarge column, the electrons acquire a drift velocity, v_d, and an average energy corresponding to an effective E/n (i.e., the value of the electric field E divided by the total gas density n).

The efficiency for a particular electron-impact process can be expressed in terms of the G-value (number of reactions per 100 eV input energy) defined as:

$$\frac{100k}{V_d(E/n)} \tag{5.4.1.1}$$

where k is the rate coefficient (cm^3/molec-s). The quantity knn_e represents the number of reactions in a unit volume per unit time, where n_e is the electron density. The quantity v_dEn_e represents the amount of energy expended by the electrons in a unit volume per unit time. The G-value is the ratio of the number of reactions to the amount of energy expended by the electrons.

Figure 5.4.1.1 shows the breakdown values for the reduced field strength, E/n, as a function of the electrode gap spacing for an atmospheric pressure discharge. For commercial reactors, the need for high flow rates can be met economically only with electrode gap spacings greater than 1 mm. For typical electrode gap spacings and voltage waveforms used in the implementation of pulsed corona or dielectric-barrier discharge reactors, the breakdown E/n is limited to values between 100 and 300×10^{-17} V-cm^2. For N_2 and air-like mixtures, the effective E/n is around 150×10^{-17} V-cm^2. Figure 5.4.1.1 also shows the calculated average electron energy in an atmospheric pressure discharge as a function of E/n. Note that for E/n around 150×10^{-17} V-cm^2, the corresponding electron mean energy is between 3 and 4 eV.

The dissipation of input electrical power as a function of the average kinetic energy of the electrons in a dry air discharge is shown in Figure 5.4.1.2. The electron mean energy in most electrical discharge reactors operating at atmospheric pressure is typically between 3 to 6 eV, as shown in Figure 5.4.1.1. In this range, Figure 5.4.1.2 shows that a large fraction of the input power is wasted in vibrational excitation of N_2 and a significant fraction goes into dissociation of O_2. The electron mean energy in electrical discharge reactors is optimum for the electron-impact dissociation of O_2, which is important for the production of O radicals. These oxidizing radicals play a key role in the generation of ozone. In a later chapter subsection it will be shown that the condition for efficient generation of ozone is not necessarily the same condition that is optimum for the decomposition of many pollutant molecules. The attainable electron mean energy in electrical discharge reactors operating at atmospheric pressure is rather limited.

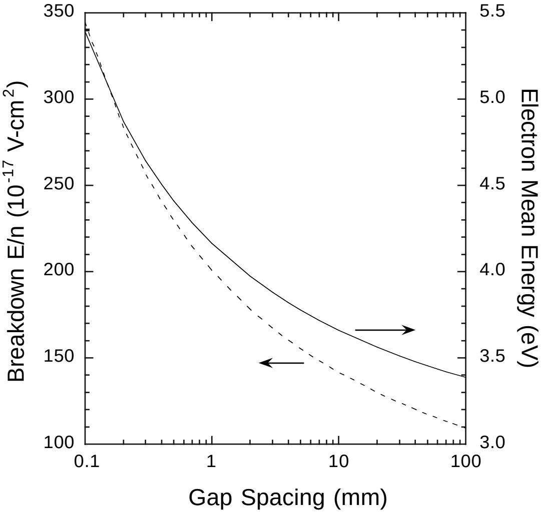

FIGURE 5.4.1.1 Breakdown values for the reduced field strength, E/n, and average kinetic energy of the electrons, as a function of the electrode gap spacing for an atmospheric-pressure air discharge. E is the electric field and n is the total gas density. The E/n experienced by the plasma in electrical discharge reactors is typically less than 300 × 10^{-17} V-cm^2. The average electron kinetic energy is thus limited to values less than 10 eV.

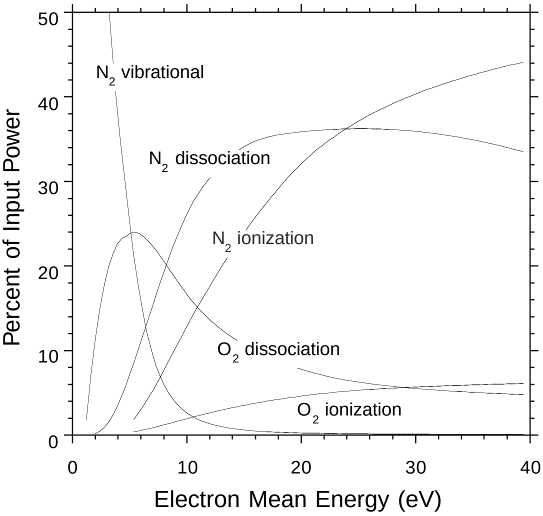

FIGURE 5.4.1.2 Power dissipation in an atmospheric-pressure dry air discharge, showing the percent of input power consumed in the electron-impact processes leading to vibrational excitation, dissociation, and ionization of N_2 and O_2.

There are two ways of increasing the electron mean energy: (1) use very narrow gap spacings (100 μm or less) to increase the breakdown E/n for the same applied voltage, or (2) use very fast-rising voltage pulses (10 ns or less risetime) to increase the breakdown E/n for typical gap spacings. In the case of very fast-rising voltage pulses, the breakdown E/n could increase to about twice the normal breakdown E/n (i.e., around 300 × 10^{-17} V-cm^2). A reasonable upper limit for the effective E/n is 400 × 10^{-17} V-cm^2 for an extremely fast-rising voltage pulse; this condition corresponds to an electron mean energy that is still well below 10 eV.

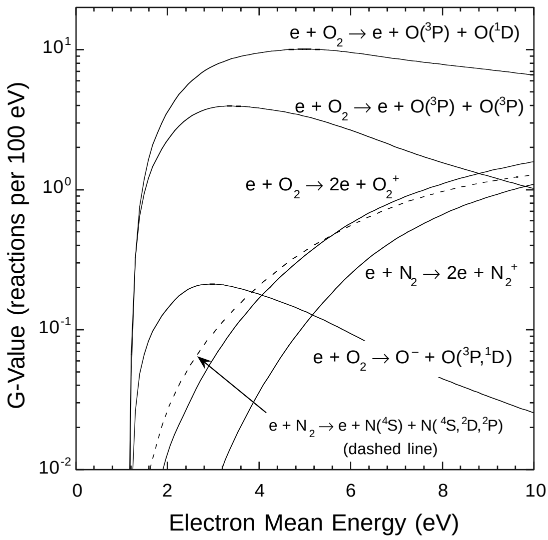

FIGURE 5.4.1.3 Calculated G-values (number of reactions per 100 eV of input energy) for dissociation and ionization processes in dry air, shown as functions of the electron mean energy in an atmospheric-pressure discharge plasma.

Figure 5.4.1.3 shows calculated G-values for dissociation and ionization processes in dry air, shown as functions of the electron mean energy in an atmospheric-pressure air discharge plasma.

In electron beam processing, the efficiency for a particular electron-impact process can be expressed in terms of the G-value, which is defined as:

$$\frac{100N_j}{\varepsilon_p} \tag{5.4.1.2}$$

where N_j is the number of dissociation or ionization events, and ε_p is the primary electron energy in eV. Table 5.4.1.1 shows a comparison of the calculated G-values for ionization processes in dry air using an electron beam and a discharge reactor.

TABLE 5.4.1.1 Calculated G-values (number of reactions per 100 eV of input energy) for Ionization Processes in Dry Air Using an Electron Beam and an Electrical Discharge Reactor

Reaction	Electron Beam	Discharge
$e + N_2 \rightarrow 2e + N(^4S, ^2D) + N^+$	0.69	$<10^{-6}$
$e + N_2 \rightarrow 2e + N_2^+$	2.27	0.044
$e + O_2 \rightarrow 2e + O_2^+$	2.07	0.170
$e + O_2 \rightarrow 2e + O(^1D) + O^+$	1.23	0.0016

The efficiency for production of electron-ion pairs is much higher in an electron beam reactor compared to that in a discharge reactor. For electron beam processing of dry air, the ionization G-value corresponds to a specific energy consumption of 33 eV per electron-ion pair produced. For corona discharge processing, the specific energy consumption is around 1400 eV per electron-ion pair, assuming an effective electron mean energy of 4 eV in the discharge plasma. Table 5.4.1.2 shows a comparison of the calculated G-values for dissociation processes in dry air using an electron beam and a discharge

TABLE 5.4.1.2 Calculated G-values (number of reactions per 100 eV of input energy) for Ionization Processes in Dry Air Using an Electron Beam and an Electrical Discharge Reactor

Reaction	Electron Beam	Discharge
$e + N_2 \rightarrow e + N(^4S) + N(^4S, ^2D, ^2P)$	1.2	0.17
$e + O_2 \rightarrow e + O(^3P) + O(^3P)$	1.3	4.0
$e + O_2 \rightarrow e + O(^3P) + O(^1D)$	2.65	10.0
$e + O_2 \rightarrow O^- + O(^3P, ^1D)$	0.11	0.19

reactor. Discharge plasma conditions are optimum for the dissociation of O_2, whereas electron beam conditions are optimum for the dissociation of N_2.

In humid air mixtures, OH radicals can be produced in a variety of ways. In electrical discharge reactors for which the electron mean energy is low, the OH radicals are produced via three types of reactions:

Electron attachment:

$$e + H_2O \rightarrow H^- + OH \tag{5.4.1.3}$$

Direct dissociation by electron impact:

$$e + H_2O \rightarrow e + H + OH \tag{5.4.1.4}$$

Dissociation by $O(^1D)$:

$$O(^1D) + H_2O \rightarrow 2\ OH \tag{5.4.1.5}$$

In electron beam reactors, the OH radicals come mainly from the positive ions reacting with H_2O. The sequence of fast steps is as follows:

Electron-impact ionization:

$$e + O_2 \rightarrow 2e + O_2^+ \tag{5.4.1.6}$$

and similar ionization processes to produce molecular ions N_2^+, H_2O^+, CO_2^+.

Electron-impact dissociative ionization:

$$e + O_2 \rightarrow 2e + O + O^+ \tag{5.4.1.7}$$

and similar dissociative ionization processes to produce N^+, H^+.

Charge-transfer reactions to form additional O_2^+ ions, such as:

$$N_2^+ + O_2 \rightarrow N_2 + O_2^+ \tag{5.4.1.8}$$

Formation of water cluster ions:

$$O_2^+ + H_2O + M \rightarrow O_2^+\ (H_2O) + M \tag{5.4.1.9}$$

Dissociative reactions of water cluster ions to form OH:

$$O_2^+\ (H_2O) + H_2O \rightarrow H_3O^+ + O_2 + OH \tag{5.4.1.10}$$

$$O_2^+ (H_2O) + H_2O \rightarrow H_3O^+ (OH) + O_2 \qquad (5.4.1.11)$$

followed by:

$$H_3O^+ (OH) + H_2 \rightarrow H_3O^+ + H_2O + OH \qquad (5.4.1.12)$$

Figure 5.4.1.4 shows the contributions of various processes to the production of OH as a function of the electron mean energy in an atmospheric-pressure plasma for a gas mixture containing 5% O_2 and 10% H_2O. In electron beam processing, the OH radicals come mainly from the positive ions reacting with H_2O. Electron beams are more effective in producing larger numbers of OH radicals. These calculations show theoretical limits on the number of OH radicals that can be produced in atmospheric-pressure air plasmas based on the contribution from various atomic and molecular reactions.

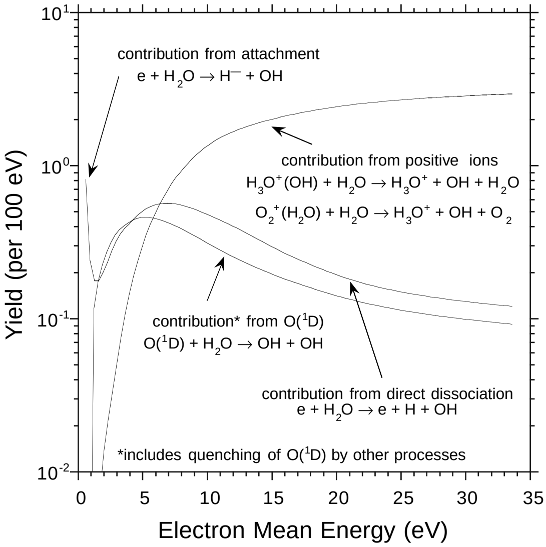

FIGURE 5.4.1.4 Contributions of various processes to the production of OH as a function of the electron mean energy in an atmospheric-pressure plasma for a gas mixture containing 5% O_2 and 10% H_2O. In electron beam processing, the OH radicals come mainly from the positive ions reacting with H_2O.

Test Facility

All of the tests reported were performed in a flow-through configuration. To characterize the energy consumption of the process for each VOC, the composition of the effluent gas was recorded as a function of the input energy density. The input energy density, Joules per standard liter, is the ratio of the power (deposited into the gas) to gas flow rate at standard conditions (25°C and 1 atm). The amount of VOC was quantified using an FTIR analyzer and a gas chromatograph.

The electron beam reactor, shown schematically in Figure 5.4.1.5, uses a cylindrical electron gun designed to deliver a cylindrically symmetric electron beam that is projected radially inward through a 5-cm-wide annular window into a 17-cm-diameter flow duct. An electron beam of 125 keV energy is introduced into the reaction chamber through a 0.7-mil-thick titanium window. The electron beam current is produced from a low-pressure helium plasma in an annular vacuum chamber surrounding the flow duct. This novel design facilitates highly uniform irradiation of the flowing gas.

The pulsed corona reactor was a 1.5-mm-diameter wire in a 60-mm-diameter metal tube 300 mm long. The power supply was a magnetic pulse compression system capable of delivering up to 15 to 35 kV output into 100-ns FWHM pulses at repetition rates from 15 Hz to 1.5 kHz. The power input to the processor is varied by changing either the pulse energy or pulse repetition frequency. For the same energy

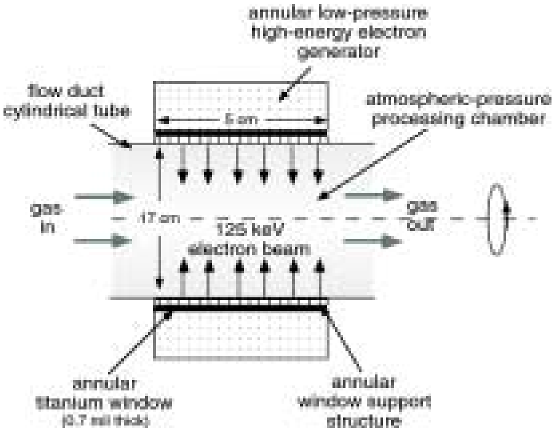

FIGURE 5.4.1.5 Schematic of the compact electron beam reactor developed by First Point Scientific, Inc. The cylindrical electron gun is designed to deliver a cylindrically symmetric, highly uniform electron beam that is projected radially inward into the gas flow duct.

density input, either method produces almost identical results. The gas mixtures are set with mass flow controllers.

The dielectric-barrier discharge electrode structure has a similar electrode structure except that it has a dielectric material on the inside surface of the outer tube electrode. It consists of a 1.5-mm-diameter wire in a 290-mm-long alumina tube with inner and outer diameters of 53 and 58 mm, respectively. The middle 170 mm of the dielectric tube has aluminum foil coating the outside to form the other electrode.

Applications

Carbon Tetrachloride

Figure 5.4.1.6 shows the results of experiments on electron beam and electrical discharge processing of 100 ppm carbon tetrachloride (CCl_4) in dry air (20% O_2, 80% N_2) at 25°C. Under identical gas conditions (gas composition and gas temperature), there is no significant difference in the basic energy efficiency of various types of electrical discharge reactors. The solid lines are fits to the experimental data points. For all cases studied here, the pollutant removal can be described with relatively good accuracy by the form:

$$[X] = [X]_0 \exp[-(E/\beta)^\gamma] \tag{5.4.1.13}$$

where $[X]_0$ is the initial pollutant concentration, and E is the input energy density. The cases in which the fit can be described with $\gamma = 1$ correspond to those where the energy consumption for pollutant decomposition depends only on the energy required to produce electrons, ions, or radicals. Whenever there is a scavenging reaction that competes with the pollutant decomposition, the fit is best described with $\gamma < 1$. For $\gamma = 1$, the β parameter is simply the energy density necessary to bring down the concentration to 1/e of its initial value (i.e., the energy density necessary for 63% decomposition). The initial concentration should be noted when referring to the β parameter. The energy density necessary to obtain 90% decomposition is equal to 2.3β. Based on Figure 5.4.1.6, electrical discharge processing requires 1277 Joules/L for 90% decomposition of CCl_4, whereas electron beam processing requires only 20 Joules/L to achieve the same level of decomposition.

Figure 5.4.1.7 compares the results of experiments on electron beam processing of 100 ppm CCl_4 in dry air and humid air. Note that humidity is deleterious to the decomposition of CCl_4.

The results shown in Figures 5.4.1.6 and 5.4.1.7 bring about two questions regarding the decomposition of CCl_4. First, why is electron beam processing much more energy efficient than electrical discharge processing? Second, what is the reason for the deleterious effect of humidity on the decomposition

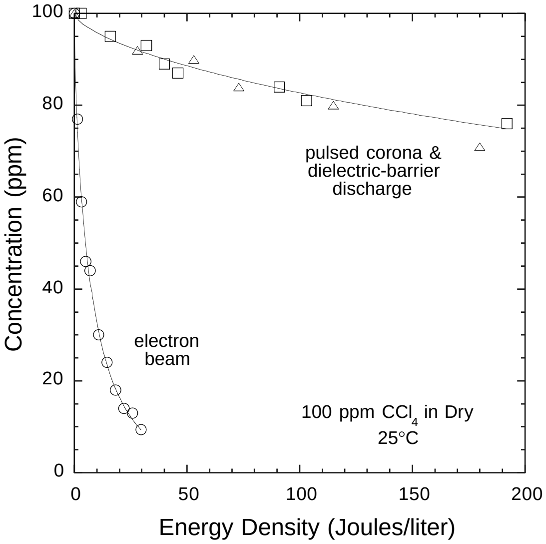

FIGURE 5.4.1.6 Comparison between electron beam, pulsed corona, and dielectric-barrier discharge processing of 100 ppm carbon tetrachloride in dry air at 25°C.

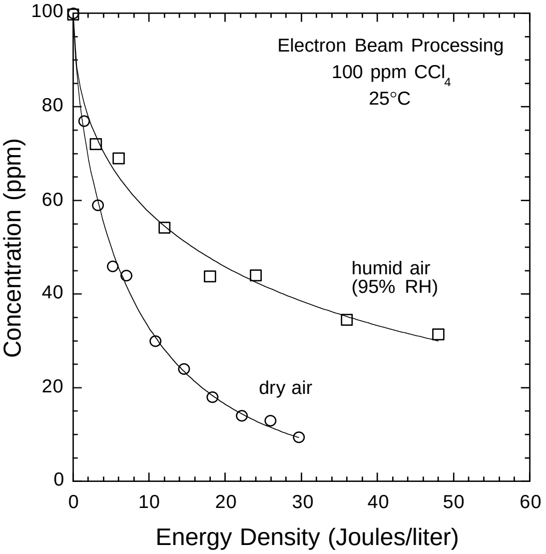

FIGURE 5.4.1.7 Electron beam processing of 100 ppm carbon tetrachloride in dry air and humid air at 25°C.

efficiency? To answer these questions, one needs to determine the main mechanism responsible for the decomposition of CCl_4.

In non-thermal plasma processing of a mixture containing very dilute concentrations of VOC molecules, the input electrical energy is dissipated by the primary electrons, mostly in interactions with the background gas molecules. The energetic primary electrons produce free radicals and electron-ion pairs through electron-impact dissociation and ionization. Among the products of the primary electron-molecule reactions are atomic oxygen, $O(^3P)$ and $O(^1D)$, and atomic nitrogen, N. These radicals, as well as the secondary electrons, can subsequently react with CCl_4 and lead to its decomposition.

TABLE 5.4.1.3 Rate Coefficient for Carbon Tetrachloride Decomposition Reactions

Eq.	Reaction	Rate Coefficient (cm^3/s)	Comment
(5.4.1.14)	$O(^3P) + CCl_4 \rightarrow ClO + CCl_3$	3.2×10^{-16}	Not probable
(5.4.1.15)	$O(^1D) + CCl_4 \rightarrow ClO + CCl_3$	3.3×10^{-10}	$O(^1D)$ lost preferentially to O_2; see Reaction (5.4.1.19)
(5.4.1.16)	$N + CCl_4 \rightarrow NCl + CCl_3$	2.5×10^{-17}	Not probable
(5.4.1.17)	$OH + CCl_4 \rightarrow HOCl + CCl_3$	1.0×10^{-12}	Irrelevant for dry air
(5.4.1.18)	$e + CCl_4 \rightarrow Cl- + CCl_3$	4.0×10^{-7}	Most likely; competes with electron attachment to O_2; see Reactions (5.4.1.20)–(5.4.1.22)

Table 5.4.1.3 shows the rate coefficients of several possible decomposition reactions. Note that the three largest rate coefficients correspond to reactions of CCl_4 with secondary electrons, $O(^1D)$, and hydroxyl radicals, OH. Because of the large concentration of O_2 in air-like mixtures, the $O(^1D)$ species are lost preferentially to quenching by O_2 (see Table 5.4.1.4). Any decomposition of CCl_4 via oxidation by oxygen radicals is therefore unlikely because of the very small rate coefficient for the $O(^3P) + CCl_4$ reaction. For dry mixtures, the reaction with OH radicals is irrelevant. For humid mixtures, the OH oxidation will be significant only if the secondary electrons produced in the plasma are depleted substantially because of attachment to O_2 (see Table 5.4.1.4); otherwise, the CCl_4 molecules will be preferentially decomposed by dissociative electron attachment.

TABLE 5.4.1.4 Rate Coefficients of Reactions Competing for Electrons and $O(^1D)$

Eq.	Reaction	Rate Coefficient[a]	Comment
(5.4.1.19)	$O(^1D) + O \rightarrow O(^3P) + O_2$	4.0×10^{-11}	Dominates over Reaction (5.4.1.15)
(5.4.1.20)	$e + O_2 + O_2 \rightarrow O_2^- + O_2$	2.5×10^{-30}	$k_{eff} = 1.2 \times 10^{-11}$ for 20% O_2
(5.4.1.21)	$e + O_2 + N_2 \rightarrow O_2^- + N_2$	1.6×10^{-31}	$k_{eff} = 2.9 \times 10^{-12}$ for 75% N_2
(5.4.1.22)	$e + O_2 + H_2O \rightarrow O_2^- + H_2O$	1.4×10^{-29}	$k_{eff} = 1.7 \times 10^{-11}$ for 5% H_2O

[a] Rate coefficients in units of cm^3/s for Reaction (5.4.1.19) and cm^6/s for Reactions (5.4.1.20) through (5.4.1.22).

An analysis of the rate coefficients shown in Table 5.4.1.3 suggests that the rate-limiting step in the decomposition of CCl_4 is determined by the dissociative attachment of CCl_4 to the thermalized electrons in the created plasma. The specific energy consumption for CCl_4 removal is therefore determined by the specific energy consumption (or G-value) for creating electron-ion pairs.

To first order, the calculated specific energy consumption for electron-ion pair production agrees very well with the experimentally observed specific energy consumption for CCl_4 decomposition. The results shown in Figure 5.4.1.6 demonstrate that for pollutant compounds requiring copious amounts of electrons for decomposition, electron beam processing is much more energy efficient than electrical discharge processing.

What is the probability that the electrons will attach to CCl_4 instead of oxygen? First consider the case of a dry mixture. After the concentration of CCl_4 has decreased to a few tens of ppm, the three-body attachment of thermal electrons to oxygen molecules [Reactions (5.4.1.20) to (5.4.1.22) in Table 5.4.1.4] becomes a significant electron loss pathway compared to Reaction (5.4.1.18). The attachment frequency of secondary electrons to O_2 in dry air at atmospheric pressure is:

$$\nu_{O2} = k_{(5.4.1.20)}\,[O_2]^2 + k_{(5.4.1.21)}\,[N_2]\,[O_2] \text{ Ý } 0.8 \times 10^8\ s^{-1} \qquad (5.4.1.23)$$

For 100 ppm CCl_4, the attachment frequency to CCl_4 is:

$$\nu_{\mathrm{CCl4}} = k_{(5.4.1.18)}\ [\mathrm{CCl_4}]\ \text{Ý}\ 10^9\ \mathrm{s}^{-1} \qquad (5.4.1.24)$$

When the concentration of CCl_4 is down to around 10 ppm, the electrons will attach to oxygen molecules as frequently as to CCl_4 molecules.

In humid air, the attachment frequency of secondary electrons to O_2 is:

$$\nu_{\mathrm{O2}} = k_{(5.4.1.20)}\ [\mathrm{O_2}]^2 + k_{(5.4.1.21)}\ [\mathrm{N_2}]\ [\mathrm{O_2}] + k_{(5.4.1.22)}\ [\mathrm{H_2O}]\ [\mathrm{O_2}]\ \text{Ý}\ 1.5 \times 10^8\ \mathrm{s}^{-1} \qquad (5.4.1.25)$$

Humidity enhances the attachment of electrons to O_2, thus effectively decreasing the efficiency for decomposition of CCl_4.

The main products in the plasma processing of CCl_4 in humid air are Cl_2, $COCl_2$, and HCl. These products can be easily removed from the gas stream; for example, they dissolve and/or dissociate in aqueous solutions and combine with $NaHCO_3$ in a scrubber solution to form NaCl. The chemical kinetics of plasma decomposition of CCl_4 in air is discussed in detail by [Penetrante et al. (1995)].

Methylene Chloride

Table 5.4.1.5 shows the rate coefficients of several possible decomposition reactions for methylene chloride (CH_2Cl_2). Note that the three largest rate coefficients correspond to reactions of CH_2Cl_2 with nitrogen atoms, hydroxyl radicals and secondary electrons. Any decomposition of CH_2Cl_2 via oxidation by oxygen radicals is unlikely because of the very small rate coefficient.

TABLE 5.4.1.5 Rate Coefficients for Methylene Chloride Decomposition Reactions

Eq.	Reaction	Rate Coefficient (cm^3/s)	Comment
(5.4.1.26)	$O(^3P) + CH_2Cl_2 \rightarrow OH + CHCl_2$	6.3×10^{-16}	Not probable
(5.4.1.27)	$N + CH_2Cl_2 \rightarrow$ Products	1.5×10^{-12}	Most likely
(5.4.1.28)	$OH + CH_2Cl_2 \rightarrow H_2O + CHCl_2$	1.6×10^{-13}	Irrelevant for dry air
(5.4.1.29)	$e + CH_2Cl_2 \rightarrow$ Products	6.5×10^{-13}	Competes with electron attachment to O_2; see Reactions (5.4.1.20)-(5.4.1.22)

The rate constant for dissociative electron attachment to CH_2Cl_2 is five orders of magnitude lower compared to CCl_4. A comparison of the rate coefficient for Reaction (5.4.1.29) with that for Reactions (5.4.1.20) to (5.4.1.22) shows that the electrons will be scavenged by electron attachment to O_2. For 100 ppm CH_2Cl_2, the attachment frequency to CH_2Cl_2 is:

$$\nu_{\mathrm{CH2Cl2}} = k_{(5.4.1.29)}\ [\mathrm{CH_2Cl_2}]\ \text{Ý}\ 1.6 \times 10^3\ \mathrm{s}^{-2} \qquad (5.4.1.30)$$

The frequency of electron attachment to CH_2Cl_2 is much smaller compared to the frequency of electron attachment to O_2 [see Equations (5.4.1.23) and (5.4.1.25)]. For air-like mixtures, the decomposition of CH_2Cl_2 by dissociative electron attachment is unlikely. The efficiency for producing electron-ion pairs is therefore not likely to be the key to the efficient decomposition of methylene chloride.

The most likely mechanism for decomposition of CH_2Cl_2 in dry mixtures is the reaction with nitrogen atoms. For mixtures containing little or no O_2, the number of secondary electrons produced in the plasma has to be more than a factor of two greater than the number of N atoms for dissociative electron attachment to be the dominant decomposition mechanism for methylene chloride. For humid air mixtures, the number of OH radicals produced in the plasma has to be an order of magnitude greater than the number of N atoms for OH oxidation to be the dominant decomposition mechanism for methylene chloride.

The processing of dilute concentrations of CH_2Cl_2 in N_2 provides a good starting point for determining the primary decomposition mechanism because there are only a couple of decomposition reactions that are possible. For electron beam processing in N_2, it costs 33 eV to produce an electron via electron-impact ionization, and around 40 eV to produce an N atom via electron-impact dissociation. The decomposition of CH_2Cl_2 in this case will therefore likely be dominated by Reaction (5.4.1.27). For electrical discharge processing in N_2, it costs around 1400 eV to produce an electron via electron-impact ionization, and about 240 eV to produce an N atom via electron-impact dissociation. The number of N atoms produced in an electrical discharge plasma greatly exceeds the number of secondary electrons. The decomposition of CH_2Cl_2 in this case will therefore also be dominated by Reaction (5.4.1.27). In both electron-beam generated plasmas and electrical discharge plasmas, we therefore expect the energy consumption for decomposition of CH_2Cl_2 to be determined by the energy consumption for production of N atoms.

Figure 5.4.1.8 shows results from electron beam and pulsed corona processing of 100 ppm CH_2Cl_2 in N_2. To first order, the calculated specific energy consumption for nitrogen atom production agrees very well with the experimentally observed specific energy consumption for CH_2Cl_2 decomposition.

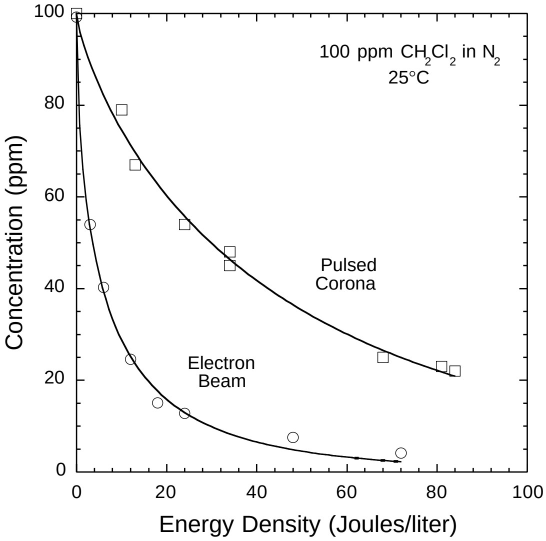

FIGURE 5.4.1.8 Electron beam and pulsed corona processing of 100 ppm methylene chloride in N_2 at 25°C.

The energy consumption for production of N atoms by electron-impact dissociation of N_2 can also be measured using dilute concentrations of NO in N_2. In this mixture, the N atoms are consumed in the reduction of NO via the reaction.

$$N + NO \rightarrow N_2 + O \tag{5.4.1.31}$$

The energy consumption for reduction of NO is thus equal to the energy consumption for production of N atoms.

Figure 5.4.1.9 shows results from electron beam (empty squares) and pulsed corona (empty circles) processing of 100 ppm methylene chloride in N_2 at 25°C. Shown for comparison are the results from electron beam (filled squares) and pulsed corona (filled circles) processing of 100 ppm NO in N_2 at 25°C. If the decomposition of methylene chloride is dominated by Reaction (5.4.1.27), we would expect that, for the same initial concentrations, the energy consumption for processing of methylene chloride in N_2 should be the same as that for processing of NO in N_2. The rate-controlling step is the production of N atoms. This has been verified in the experiments, as evident from Figure 5.4.1.9.

In dry air, other possible reactions for decomposition of methylene chloride include:

$$O(^3P) + CH_2Cl_2 \rightarrow OH + CHCl_2 \tag{5.4.1.26}$$

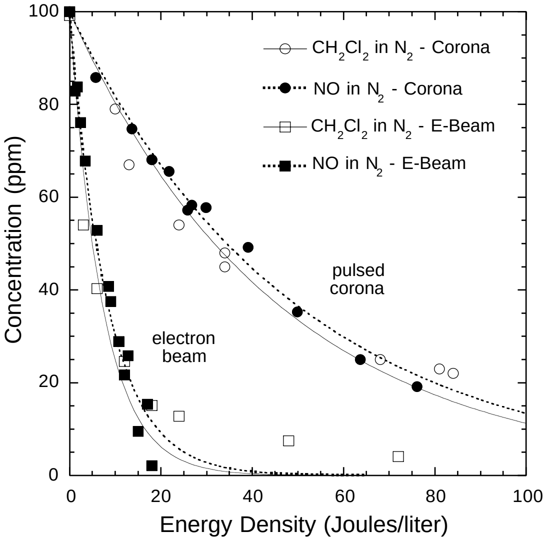

FIGURE 5.4.1.9 Electron beam and pulsed corona processing of 100 ppm methylene chloride in N_2. Shown for comparison are the results from electron beam and pulsed corona processing of 100 ppm NO in N_2.

and

$$O(^1D) + CH_2Cl_2 \rightarrow OH + CHCl_2 \qquad (5.4.1.32)$$

where the ground-state oxygen atom, $O(^3P)$, and the excited-state oxygen atom, $O(^1D)$, are produced by electron-impact dissociation of O_2:

$$e + O_2 \rightarrow e + O(^3P) + O(^3P) \qquad (5.4.1.33)$$

$$e + O_2 \rightarrow e + O(^3P) + O(^1D) \qquad (5.4.1.34)$$

In electron beam reactors, dissociative ionization also contributes to the production of $O(^1D)$:

$$e + O_2 \rightarrow 2e + O(^1D) + O^+ \qquad (5.4.1.35)$$

The rate for Reaction (5.4.1.26) at 25°C is very low, (6.3×10^{-16} cm^3/molecule-s). This reaction is therefore not probable. In air-like mixtures, the $O(^1D)$ species are lost preferentially to quenching by O_2:

$$O(^1D) + O_2 \rightarrow O(^3P) + O_2 \qquad (5.4.1.19)$$

because Reaction (5.4.1.19) has a high rate (4.0×10^{-11} cm^3/molecule-s), and the concentration of O_2 is much higher compared to that of methylene chloride. The most likely mechanism for decomposition of methylene chloride in dry air mixtures is therefore also the reaction with N atoms.

Figure 5.4.1.10 shows results from electron beam (circles) and pulsed corona (square) processing of 100 ppm methylene chloride in dry air at 25°C. It is evident from Figure 5.4.1.10 that plasma processing of methylene chloride in dry air is much less efficient compared to that in N_2. It appears that a large fraction of N atoms is not being consumed in the decomposition of methylene chloride.

The dissociative excitation of N_2 contributes a large fraction to the total N_2 dissociation. A significant species produced by dissociative excitation of N_2 is the excited N atom, $N(^2D)$:

$$e + N_2 \rightarrow e + N(^4S) + N(^2D) \qquad (5.4.1.36)$$

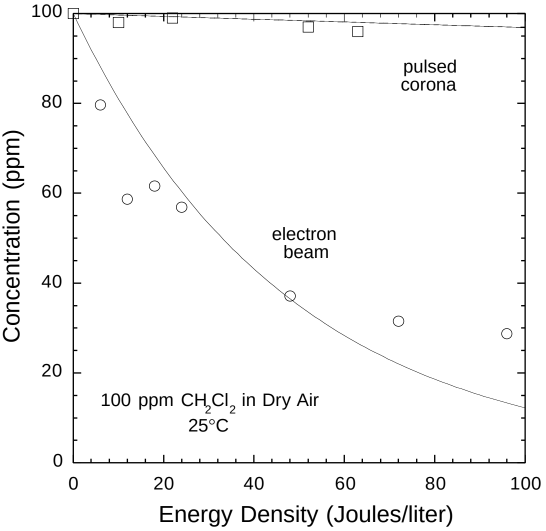

FIGURE 5.4.1.10 Electron beam and pulsed corona processing of 100 ppm methylene chloride in dry air at 25°C.

where N(^{2}S) is the ground-state nitrogen atom and N(^{2}D) is the excited-state nitrogen atom. The N(^{2}D) species is a long-lived metastable species. In electron beam processing, almost half of the total N atoms produced are in the excited metastable state. The rate constant characterizing the interaction of the metastable species N(^{2}D) with O_2 is significant (6×10^{-12} cm^3/molecule-s). Because the oxygen concentration is also much higher compared to that of methylene chloride, the N(^{2}D) species is therefore consumed in reactions with O_2:

$$N(^2D) + O_2 \rightarrow NO + O \tag{5.4.1.37}$$

This means that N(^{2}D) is consumed in the production of NO rather than in the decomposition of methylene chloride. Only N(^{4}S) is then available for the decomposition of methylene chloride. Some of the NO is oxidized by the O radicals to NO_2:

$$NO + O(^3P) + M \rightarrow NO_2 + M \tag{5.4.1.38}$$

where M is either N_2 or O_2. Any remaining NO consumes N(^{4}S) in the reduction reaction:

$$N(^4S) + NO \rightarrow N_2 + O \tag{5.4.1.39}$$

Whereas the reaction of N(^{2}D) with O_2 can proceed even at room temperature, the reaction of N(4S) with O_2 can proceed only at very high temperatures. Because the electron mean energy in a pulsed corona reactor is relatively low (around 4 eV), one would suspect that the N_2 dissociation in this case would lead mostly to the production of N(^{4}S) only; that is:

$$e + N_2 \rightarrow e + N(^4S) + N(^4S) \tag{5.4.1.40}$$

and that NO production would therefore be insignificant. The pulsed corona experiments in dry air, however, show significant NO production at high input energy densities, presumably because of localized gas heating in the filamentary streamer channels. In pulsed corona reactors, the non-thermal plasma is produced through the formation of statistically distributed microdischarges known as streamers. Significant gas heating within the streamer channels can occur when the electrode gap distance is much higher compared to the channel diameter (typically around 100 microns). Localized gas heating is suspected to be occurring in the pulsed corona reactor, leading to the consumption of $N(^4S)$ by O_2:

$$N(^4S) + O_2 \rightarrow NO + O \tag{5.4.1.41}$$

In both the electron beam and pulsed corona, the decomposition of methylene chloride in air is degraded substantially because the N atoms are consumed by O_2 in the production of NO.

Trichloroethylene

Table 5.4.1.6 shows the rate coefficients of several possible decomposition reactions for trichloroethylene (C_2HCl_3).

TABLE 5.4.1.6 Rate Coefficients for Trichloroethylene Decomposition Reactions

Eq.	Reaction	Rate Coefficient (cm^3/s)	Comment
(5.4.1.42)	$O(^3P) + C_2HCl_3 \rightarrow$ Products	1.0×10^{-13}	Likely
(5.4.1.43)	$N + C_2HCl_3 \rightarrow$ Products	2.7×10^{-14}	Not likely
(5.4.1.44)	$OH + C_2HCl_3 \rightarrow$ Products	2.2×10^{-12}	May be significant in humid air
(5.4.1.45)	$e + C_2HCl_3 \rightarrow$ Products	2.0×10^{-9}	Competes with electron attachment to O_2; see Reactions (5.4.1.20)-(5.4.1.22)

The rate constant for dissociative electron attachment looks significant. However, a comparison of the rate coefficient for Reaction (5.4.1.45) with that for Reactions (5.4.1.20) to (5.4.1.22) shows that the electrons will be scavenged by electron attachment to O_2. For 100 ppm C_2HCl_3, the attachment frequency to C_2HCl_3 is:

$$\nu_{C2HCl3} = k_{(5.4.1.45)}\,[C_2HCl_3]\ \text{Ý}\ 5 \times 10^6\ s^{-1} \tag{5.4.1.46}$$

The frequency of electron attachment to C_2HCl_3 is about an order of magnitude smaller compared to the frequency of electron attachment to O_2 [see Equations (5.4.1.23) and (5.4.1.25)]. In the case of 100 ppm C_2HCl_3, the electrons would attach preferentially to O_2. Nevertheless, when the initial concentration of C_2HCl_3 is large (e.g., 1000 ppm), dissociative electron attachment could play a significant role in decomposing C_2HCl_3. For small initial concentrations of C_2HCl_3, the reaction with O radicals seems to be the likely primary decomposition mechanism.

Figure 5.4.1.11 compares electron beam and pulsed corona processing of 100 ppm C_2HCl_3 in dry air at 25°C. The energy consumption for C_2HCl_3 removal is relatively small using either electron beam or electrical discharge methods. This is because of a chain reaction mechanism involving chlorine (Cl) radicals. The reaction of C_2HCl_3 with electrons or O radicals initiates the detachment of Cl radicals. Other C_2HCl_3 molecules then decompose by Cl radical addition to the carbon-carbon double bond:

$$Cl + C_2HCl_3 \rightarrow \text{Products} \tag{5.4.1.47}$$

This decomposition pathway regenerates more Cl radicals, which react with other C_2HCl_3 molecules, causing a chain reaction. The chemical kinetics of electron beam decomposition of C_2HCl_3 is discussed in detail by Vitale et al., (1997).

Methanol

Table 5.4.1.7 shows the rate coefficients of several possible decomposition reactions for methanol (CH_3OH). Note that the three largest rate coefficients correspond to reactions of CH_3OH with positive ions and hydroxyl radicals.

Figure 5.4.1.12 shows a comparison between electron beam and pulsed corona processing of 100 ppm CH_3OH in dry air at 25°C. For methanol, the electron beam method is more efficient because the

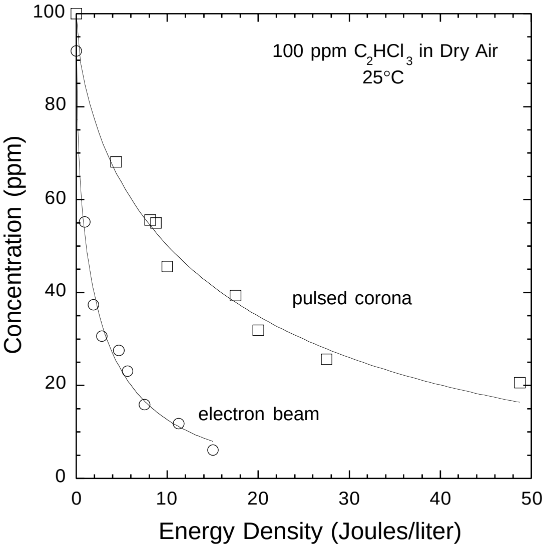

FIGURE 5.4.1.11 Electron beam and pulsed corona processing of 100 ppm trichloroethylene in dry air at 25°C.

TABLE 5.4.1.7 Rate Coefficients for Methanol Decomposition Reactions

Eq.	Reaction	Rate Coefficient (cm^3/s)	Comment
(5.4.1.48)	$O(^3P) + CH_3OH \rightarrow CH_3O + OH$	6.4×10^{-15}	Not probable
(5.4.1.49)	$N + CH_3OH \rightarrow HNO + CH_3$	2×10^{-15}	Not probable
(5.4.1.50)	$OH + CH_3OH \rightarrow CH_3O + H_2O$	10^{-12}	Significant
(5.4.1.51)	$N_2^+ + CH_3OH \rightarrow CH_3^+ + OH + N_2$	10^{-7}	Most likely

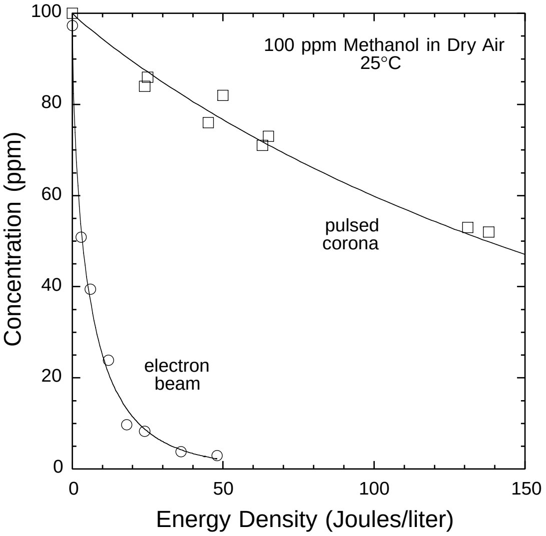

FIGURE 5.4.1.12 Electron beam and pulsed corona processing of 100 ppm methanol in dry air at 25°C.

decomposition proceeds mainly via a dissociative charge exchange Reaction (5.4.1.51). The OH radicals resulting from the initial decomposition Reaction (5.4.1.51) in turn may lead to additional decomposition of methanol via Reaction (5.4.1.50). To verify that the primary decomposition during electron beam processing does not proceed through an oxidation pathway using O radicals, the experiment were performed using N_2 as the background gas. As shown in Figure 5.4.1.13, the specific energy consumption for electron beam processing of methanol in dry air is almost identical to that in N_2.

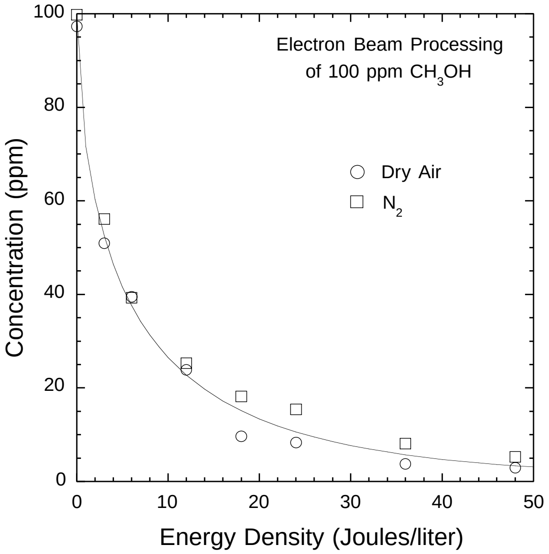

FIGURE 5.4.1.13 Electron beam processing of 100 ppm methanol in N_2 and dry air at 25°C.

Because an electron-ion pair is produced during an ionization event, the energy consumption for producing electrons should be the same as that for producing ions. In the case of CCl_4, the electrons do the decomposition. In the case of CH_3OH, the positive ions do the decomposition. The energy consumption for decomposing CCl_4 should therefore be the same as that for decomposing CH_3OH. Figure 5.4.1.14 shows a comparison between electron beam processing of 100 ppm CH_3OH in dry air and electron beam processing of 100 ppm CCl_4 in dry air at 25°C. Note that the energy consumption for electron beam decomposition of CH_3OH is identical to that of CCl_4.

Economics

Table 5.4.1.8 shows the nominal air pollution control costs for various technologies according to the U.S. EPA handbook of *Control Technologies for Hazardous Air Pollutants* (Sink, 1991). This information is not specific to any particular application and therefore indicates approximate costs only.

Table 5.4.1.9 shows the comparison between pulsed corona and electron beam processing of various VOCs in dry air at room temperature. As mentioned, there is no significant difference in the performance of pulsed corona and dielectric-barrier discharge reactors. For all the compounds tested, electron beam processing is more energy efficient than either pulsed corona or dielectric-barrier discharge processing.

Assuming a nominal energy cost of 10 Joules/L to decompose a mixture of volatile organic compounds from 100 to 10 ppm, the electron beam power required for an 80,000 cfm total gas flow rate application is 380 kW. Some commercial electron beam generators now cost as low as $2 per beam watt. A 380 kW electron beam system would therefore have a capital cost of $760,000. This corresponds to a capital cost of less than $10 per cfm. This is cheaper than thermal oxidation methods that use advanced heat recovery. Similarly, the 5-year operating cost (based on $0.05/kWh electricity cost with 4000 hr operation/year) is less than $5 per cfm. Again, the operating cost of the electron beam method is much lower than that of advanced thermal oxidation and carbon adsorption.

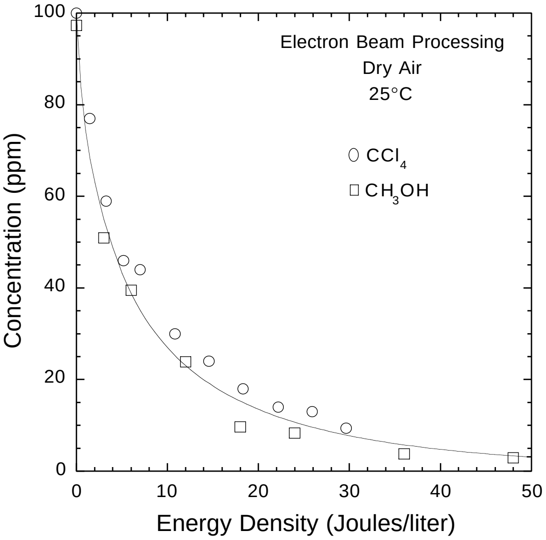

FIGURE 5.4.1.14 Electron beam processing of 100 ppm methanol in dry air and 100 ppm carbon tetrachloride in dry air at 25°C.

TABLE 5.4.1.8 Nominal Air Pollution Control Costs According to the US EPA Handbook on *Control Technologies for Hazardous Air Pollutants*

Technology	Capital Cost Range	Operating Cost Range
Thermal oxidation with regenerative heat recovery[a]	\$30–450/cfm	\$20–150/cfm
Thermal oxidation with recuperative heat recovery[b]	\$10–200/cfm	\$15–90/cfm
Carbon adsorption with steam regeneration	\$15–120/cfm	\$10–350/cfm
UV/ozone oxidation	\$10–140/cfm	Not available

[a] Regenerative heat recovery utilizes large, heavy beds of ceramic materials for heat recovery and storage. Up to 95% heat recovery is possible.

[b] Recuperative heat recovery utilizes metallic shell and tube heat exchangers for direct heat recovery. Up to 70% heat recovery is possible.

TABLE 5.4.1.9 Comparison Between Pulsed Corona and Electron Beam Processing of 100 ppm VOC/HAP in Dry Air at Room Temperature

VOC	Electron Beam	Pulsed Corona
Trichloroethylene	6	38
o-Xylene	10	370
Ethylene	15	83
Methanol	15	450
Carbon tetrachloride	20	1277
Toluene	34	1586

Note: Energy density (Joules per standard liter) required for 90% decomposition of the VOC/HAP.

Straightforward engineering is the major advantage of electrical discharge methods. However, the electrical energy consumption of electrical discharge reactors is excessive, as can be deduced from Table 5.4.1.9. If one assumes that a pulsed corona or dielectric-barrier discharge reactor consumes only 5 times more energy per VOC molecule (i.e., 50 Joules/L to decompose the VOC from 100 to 10 ppm), then the power required is 1.9 MW. Although the capital cost for discharge reactors may be low, the operating costs over several years can greatly exceed the capital cost because of the large electrical energy consumption.

Table 5.4.1.10 shows nominal air pollution control costs using electron beam, pulsed corona, and dielectric-barrier discharge processing. An energy cost in the range of 10 to 30 Joules/L was assumed to decompose 100 ppm VOC using electron beam processing. A pulsed corona or dielectric-barrier discharge reactor consumes at least 5 times more energy per VOC molecule. For the capital costs, it was assumed that \$2/W for electron beam, \$1/W for pulsed corona, and \$0.20/W for dielectric-barrier discharge are required. The 5-year operating cost is based on \$0.05/kWh electricity cost with 4000 hr operation/year. For control of emissions from dilute, large volume sources of VOCs, these preliminary cost estimates show that:

1. The operating cost of electrical discharge methods such as pulsed corona or dielectric-barrier discharge is excessive.
2. The electron beam method is the preferable non-thermal plasma technique.
3. The electron beam method may be cost-competitive with thermal and catalytic methods that employ heat recovery or hybrid techniques.

TABLE 5.4.1.10 Nominal Air Pollution Control Costs Using Non-Thermal Plasma Process

Technology[a]	Capital Cost Range[b]	Operating Cost Range[c]
Electron beam	\$9–27/cfm	\$4–12/cfm
Pulsed corona	\$4–12/cfm	\$20–360/cfm
Dielectric-barrier discharge	\$1–3/cfm	\$20–360/cfm

[a] Assuming a nominal energy cost of 10–30 Joules/L to decompose 100 ppm VOC/HAP using electron beam processing. A pulsed corona or dielectric-barrier discharge reactor consumes at least 5 times more energy per VOC/HAP molecule.

[b] Assuming \$2/W for electron beam, \$1/W for pulsed corona, and \$0.20/W for dielectric-barrier discharge.

[c] Based on \$0.05/kWh electricity cost with 4000 hr operation/year.

To provide a more rigorous cost analysis for comparison with other VOC and air toxics control technologies, it is imperative that we establish how the electrical energy consumption of these plasma methods depends on exhaust stream parameters such as moisture level and VOC mixture. The experiments presented here were performed for single VOCs. For applications in which the exhaust gas consists of a mixture of VOCs, it is not yet clear how the decomposition of one VOC will affect the decomposition of the other. These studies will require proper characterization of the emission source and need to be done on a case-by-case basis for each application.

Conclusions

Non-thermal plasma processing methods have been shown to be effective in treating dilute concentrations of VOCs in large-volume, atmospheric-pressure air streams. Determinations of the energy efficiency and by-products of the treatment process are critical to the commercial success of this technology. By understanding what plasma species is responsible for the decomposition of a pollutant molecule, it is possible to establish the electrical power requirements of the plasma reactor and help identify the initial reactions that lead to the subsequent process chemistry. This section presented results from basic experimental and theoretical studies aimed at identifying the reaction mechanisms responsible for the primary decomposition of four representative VOCs, namely carbon tetrachloride, methylene chloride, trichloroethylene, and methanol. Each of these compounds was shown to be decomposed by a different plasma species: electrons, nitrogen atoms, oxygen radicals, and positive ions, respectively. The decomposition mechanisms for these compounds provide good examples of how the electron-molecule interaction physics could strongly affect the economics of the non-thermal plasma process. For VOCs requiring copious amounts of electrons, ions, N atoms, or OH radicals, the use of electron beam reactors is generally the best way of minimizing the electrical power consumption. The studies presented here explain why electron beam processing is much more energy efficient compared to electrical discharge processing. These studies are essential for predicting the scaling of the process to commercial size units. Preliminary cost analyses based on these data also show that the electron beam method is cost-competitive with advanced thermal and catalytic methods.

Acknowledgment

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5.4.2 Applications of Electric-Discharge Driven Non-Thermal Plasmas to Hazardous Chemical Decomposition in Mixed Waste Treatment

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Introduction

Several commercial methods are currently employed to treat hazardous chemical compounds at industrial scale. The traditional method is incineration, which is limited both fundamentally and politically. The treatment of difficult-to-combust compounds (e.g., halocarbons) requires very high temperatures that are usually achieved by employing a two-stage process and the addition of fuel such as natural gas. High-temperature processes do not necessarily destroy all the hazardous material and also generate undesirable by-products such as dioxins, furans, NO_x, and increased greenhouse gas emissions. In the present regulatory climate, the permitting of a hazardous waste incinerator is very slow, laborious, and expensive. Other commercial processes are available (catalytic oxidation/reduction, UV/ozone/hydrogen peroxide, and supercritical water), but do not have broad-range applicability, are both treatment- and cost-sensitive to the targeted species, operate at very high temperatures and/or pressures, and sometimes employ precious or poisonous metals.

Non-thermal plasmas (NTPs) are an attractive treatment alternative because they can direct electrical power into favorable hazardous-chemical decomposition/destruction processes at reasonable temperatures and pressures.

A plasma in electrical terminology is a state of matter that is composed of electrons, electrically charged atoms or molecules (ions), and neutral (uncharged) species. Plasmas are useful for waste processing because they are composed of, or can generate, free radicals and other highly reactive species that can decompose waste compounds. In thermal plasmas (e.g., electric arcs, plasma torches, etc.), the plasma electrons, ions, and neutral species are all at the same temperature (equilibrium plasma). In non-thermal plasmas (NTPs), the plasma electrons are energetic or *hot* (temperatures of a few to several electron volts [eV]), while the neutrals are at near-ambient temperature or *cold* (non-equilibrium plasma).

NTPs can be created by the application of a high voltage to a gas (electrical discharge) or the injection of energetic electrons (~ several keV to MeV) into a gas. The key idea in either case is to direct electrical energy, using the vehicle of the plasma to create reactive chemical reagents *in situ*, into favorable chemistry for pollutant decomposition. This section deals with electrical-discharge driven NTPs for gas-phase waste processing (off-gases, hazardous air pollutants, etc.) in connection with mixed radiochemical waste treatment. However, the real efficacy of NTP waste processing is that the waste need not be in the gas phase initially; one can combine the NTP processing with another stage that turns the waste into a gas suitable for NTP processing. The desired end result is to convert waste materials into simpler, more easily managed compounds or materials. For mixed radiochemical wastes, one can separate the radioactive compounds from the hazardous compounds by thermal processing (over a broad temperature range), collect the radioactive component(s), and treat the hazardous components such that the waste is no longer classified as mixed waste but is simply radioactive waste alone (an easier category to handle).

Fundamentals of Non-thermal Plasma Waste Processing

Introduction

Non-thermal plasma techniques are an emerging technology, generally directed at the treatment of gas-phase hazardous air pollutants (e.g., hydrocarbons and halocarbons), criteria air pollutants (e.g., NO_x), or other chemical compounds contained in off-gases or flue gases. Some example chemical compounds of interest are toluene ($C_6H_5CH_3$), acetone (CH_3COCH_3), xylene ($C_6H_4 [CH_3]_2$), benzene (C_6H_6), trichloroethylene (TCE, $CHCl{:}CCl_2$), trichloroethane (TCA, $C_2H_3Cl_3$), perchloroethylene (PCE, CCl_2CCl_2), carbon tetrachloride (CCl_4), nitric oxide (NO), sulfur dioxide (SO_2), polychlorinated dibenzo dioxins (PCDDs), and polychlorinated dibenzo furans (PCDFs).

Several overviews of exhaust-gas treatment fundamentals and applications are available in the literature (Penetrante and Schultheis, 1993; Chang et al., 1991; Rosocha, 1997; Rosocha and Korzekwa, 1999). In such applications, the NTP generates energetic electrons in a pollutant-laden process gas stream. The energetic plasma electrons are the agents responsible for the decomposition of entrained hazardous chemicals, either through direct electron collisions with pollutants or indirectly through the creation of free radicals that subsequently attack entrained pollutants. Because a variety of active species with large radical-attack (or electron-decomposition) reaction rate constants are usually produced, even multiple pollutants can be decomposed at the same time. A particular advantage of NTPs is their ability to generate both oxidative and reductive radicals, therefore allowing one to simultaneously perform oxidative and reductive chemistry on many hazardous chemical species.

The primary mode of operation is generally end-of-pipe emissions treatment (right before discharge to the atmosphere). The simplest end-of-pipe architecture is to employ an NTP reactor (or array of reactors) as a stand-alone gaseous emissions control device for exhaust gases. For mixed waste treatment, the plasma is also used for gas-phase treatment as a secondary stage in a form adaptable to treating gases arising from a primary-stage treatment unit.

Because mixed wastes generally do not exist in the gas phase, the primary treatment unit must be capable of handling the more prevalent forms of mixed wastes: liquids, sludges, and solids. Figure 5.4.2.1 shows the NTP mixed waste treatment concept in schematic form. Here, a primary-stage unit is used to destroy and/or gasify the hazardous components of the waste, collecting or filtering out the radioactive components, and passing the off-gas through the secondary-stage NTP unit. There are two main operating modes for such a system: (1) the primary stage unit destroys most of the hazardous components, while the NTP second stage unit is used as a polisher (i.e., further treating the gasified hazardous components to a very high DRE [destruction and removal efficiency]); or (2) the primary stage unit is mainly used to gasify the hazardous components, leaving the NTP second stage unit to handle most of the job of destroying them. The choice of operating mode will depend on factors such as the form of the waste, the particular hazardous species in the waste, and the concentrations of those species.

The primary stage devices are generally thermal treatment units, of which several types exist. Some examples are discussed below. The collectors or filters must be specially designed to trap the radioactive components. These components are normally trapped as solids because most radioactive wastes are not volatile until very high temperatures are reached (well beyond the usual operating regime of typical first-stage thermal treatment units).

Example NTP Reactors

Figure 5.4.2.2 shows example NTP reactors for gas-phase pollutant processing (Penetrante and Schultheis, 1993; Chang et al., 1991; Rosocha, 1997; Mizuno et al.,1986; Penetrante et al., 1995; Virden et al., 1992). For the electrical discharge case, a high voltage sufficient to cause electrical breakdown (electron-avalanche streamers) is applied across electrodes in the gas or along a surface adjacent to the gas. The electron

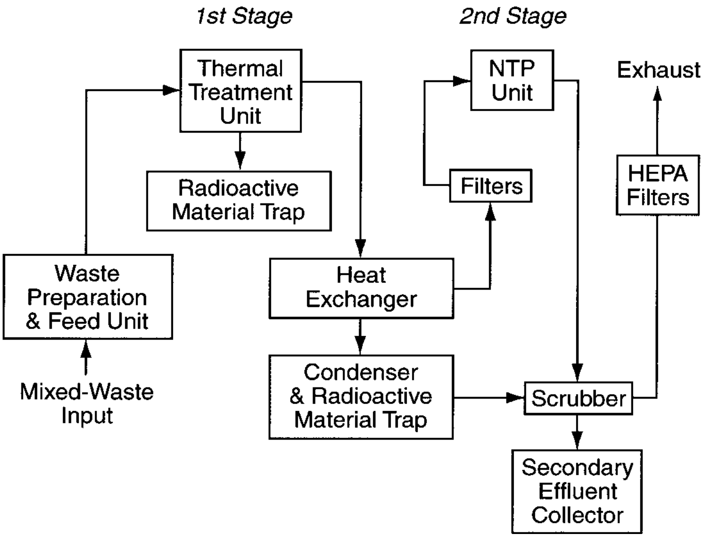


FIGURE 5.4.2.1 Schematic diagram of a generalized, staged mixed waste treatment unit.

beam reactor case requires an electron accelerator to produce the energetic electron beam (~100 keV to 1 MeV) that is injected into the process gas.

Generation of Active Species (Free Radicals, Excited States, and Others)

In the NTP unit, highly reactive species (free radicals and energetic electrons) are generated by electrical discharges in a gas or as ionization products of the electron bombardment of the gas by highly energetic electrons from an electron accelerator. Post-dissociation secondary reactions can also play key roles in active species formation. In addition, the decomposition of pollutants itself can lead to the formation of free-radical species, which are usually constituted from fragments of the destroyed pollutant molecules. Some reactive species of interest are electrons, $O(^3P)$, OH, N, H, NH, CH, O_3, H_2O_2, and the excited states O_2 $(^1\Delta)$, and N_2 (A). Example formation mechanisms are shown in Table 5.4.2.1.

The radical yields (i.e., the number of particular radicals produced per unit energy deposited in the plasma) depends on factors such as the gas composition, the gas pressure, and the average electron temperature. For the example of humid, atmospheric pressure air, the yields of $O(^3P)$, OH, and N radicals in typical electric-discharge reactors (operating at a reduced electric field $E/N \sim 100$ Td) are of order 10, 1, and 1 per 100 eV of deposited energy, respectively (Penetrante and Schultheis, 1993; Rosocha, 1997).

Decomposition of Pollutants Entrained in Exhaust Gas

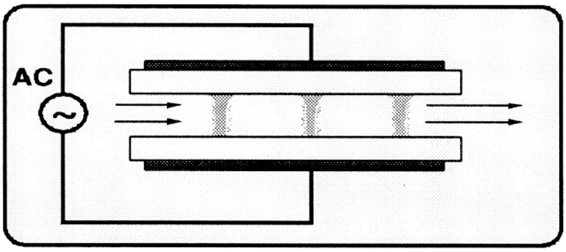
In simple terms, the active species (radicals and secondary electrons) generated in the plasma initiate pollutant decomposition reactions. Two major channels for decomposing a gas-phase chemical pollutant X are direct electron impact and chemical (radical-promoted) attack:

$$e + X \rightarrow \text{Products} \tag{5.4.2.1}$$

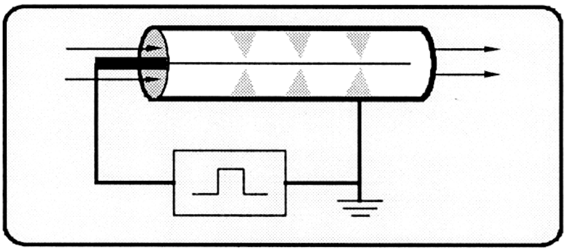
$$\text{O or OH} + X \rightarrow \text{Products.} \tag{5.4.2.2}$$

In addition, ion-molecule reactions sometimes come into play, causing decomposition through the mechanism of dissociative charge exchange.

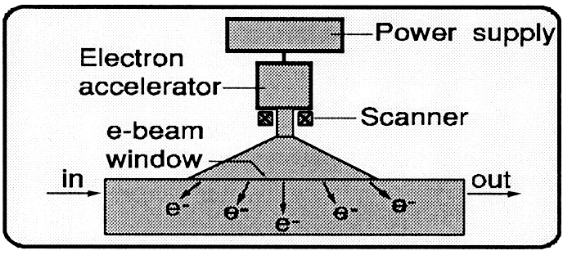
Volatile organic compounds (VOCs) typically go through a series of more complicated reactions before the final products result. The decomposition of a common chlorocarbon solvent such as trichloroethylene is dominated by free-radical reactions at the relatively high E/N (roughly several tens of Td or greater) of electric discharges (Evans et al., 1993; Falkenstein, 1997):



Silent discharge
(dielectric-barrier discharge)



Pulsed or DC corona



Electron beam

FIGURE 5.4.2.2 Schematic diagrams of representative NTP reactors. Top: silent discharge plasma (SDP) or dielectric-barrier discharge reactor. Center: pulsed corona reactor (wire-tube example). Bottom: electron beam reactor.

$$O(^3P) \text{ or } OH + C_2HCl_3 \rightarrow CO_2 + CO + HCl + Cl_2 + COCl_2 + \ldots, \qquad (5.4.2.3)$$

while strong electron attachers (e.g., CCl_4) are preferentially decomposed by direct electron attack (dissociative electron attachment) at low E/N (Penetrante et al., 1995)

$$e + CCl_4 \rightarrow CCl_3 + Cl^- \qquad (5.4.2.4)$$

$$CCl_3 + O_2 \rightarrow COCl_2 + Cl + ClO. \qquad (5.4.2.5)$$

The molecular structure of a compound can also affect the energy required for decomposition. For example, chlorinated ethenes are very susceptible to radical substitution to their carbon-carbon double bond. This process, followed by chain reactions involving radicals formed as a result of the substitution reaction, enhances the net decomposition. However, chlorinated ethanes, which do not have such a double bond, are much more difficult to decompose (Vitale et al., 1997).

TABLE 5.4.2.1 Active-Species Formation Mechanisms

Electron-Impact Ionization and Dissociation	Decomposition Induction
$e + O_2 \rightarrow O_2^+ + e$	$e + CCl_4 \rightarrow CCl_3 + Cl^-$
$e + O_2 \rightarrow O + O^* + e$	$CCl_3 + O_2 \rightarrow Cl + ClO$
$e + N_2 \rightarrow N + N + e$	$O + C_2HCl_3 \rightarrow CHOCl + CCl_2$
$e + O_2 \rightarrow O + O + e$	$O + CHOCl \rightarrow COCl + OH$
$e + H_2O \rightarrow OH + H + e$	$O + COCl \rightarrow CO + ClO$
$e + N_2 \rightarrow N_2^* + e$	$CCl_2 + O_2 \rightarrow ClO + COCl$
$e + NH_3 \rightarrow NH + H_2 + e$	$COCl + O_2 \rightarrow CO_2 + ClO$
Quenching of Excited Dissociation Products	Transformation
$O^* + H_2O \rightarrow 2OH$	$HO_2 + NO \rightarrow OH + NO_2$
$N_2^* + O_2 \rightarrow N_2 + O + O$	$NH + NO \rightarrow N_2 + OH$
Ion Clustering	Recombination
$O_2^+ + H_2O \rightarrow O_2^+ (H_2O)$	$O + O_2 + M \rightarrow O_3 + M$
$O_2^+ (H_2O) + H_2O \rightarrow HO_3^+ + O_2 + OH$	$H + O_2 + M \rightarrow HO_2 + M$
$O_2^+ (H_2O) + H_2O \rightarrow HO_3^+ (OH) + O_2$	$H + O_3 \rightarrow OH + O_2$
$HO_3+ (OH) + H_2O \rightarrow HO_3^+ + H_2O + OH$	$OH + OH + M \rightarrow H_2O_2 + M$

The detailed decomposition chemistry for many compounds, including the formation of terminal products and by-products, is very complicated and is not discussed in this section. The reader is referred to the literature for more information on this subject (Penetrante and Schultheis, 1993; Rosocha, 1997; Penetrante et al., 1995; Evans et al., 1993;, Falkenstein et al., 1997; Vitale et al., 1997). It should be noted that decomposition is not necessarily complete treatment — the goal is to produce less-toxic or more easily-managed final products.

Example Applications of NTPs to Mixed Waste Treatment

Five examples of combining an NTP stage with another treatment stage for the overall goal of mixed waste treatment are presented here.

Single-Stage Off-gas Treatment

The simplest application of an NTP process to mixed waste management is to use it to treat the off-gas from a separate mixed waste treatment unit (e.g., an incinerator, electric-arc furnace, or plasma torch) to remove any remaining hazardous chemical pollutants in the exhaust gas. Gas-phase pollutant removal is discussed as part of the subsection below.

Two-Stage, NTP-Packed Bed Reactor Treatment of Liquid and Solid Mixed Waste

Los Alamos National Laboratory has developed a two-stage process aimed at treating low-radiation-level mixed-waste liquids and solids (in the form of a pumpable slurry) (Rosocha et al., 1993; Gill et al., 1994). Figure 5.4.2.3 illustrates the concept. Typical liquids used in laboratory tests are listed in Table 5.4.2.2. Los Alamos has also tested several waste solids, ground up and slurried in water. Examples include cellulose (paper, wood), polyethylene, and vinyl (gloves).

In the first stage, a liquid or slurried solid in a carrier-gas stream (Ar/O_2 mixtures) is atomized and injected into a packed-bed reactor (PBR), a metal cylinder filled with aluminum oxide (alumina) beads heated by an external furnace, that converts the waste into simpler chemical compounds by thermal combustion. Laboratory experiments employed two different size PBRs, the first having a diameter of 6.4 cm (2.5 in.) and a length of 102 to 114 cm (40 to 45 in.) and a larger one with a nominal diameter of 15 cm (6 in.) and an active length similar to the smaller reactor. This stage can treat many difficult-to-combust organic liquids over a wide temperature range (300 to 1200°C), with almost complete combustion taking place at temperatures between 800 and 1,000°C. In most cases, chlorocarbons can be removed to levels of less than 1 ppm at these temperatures.

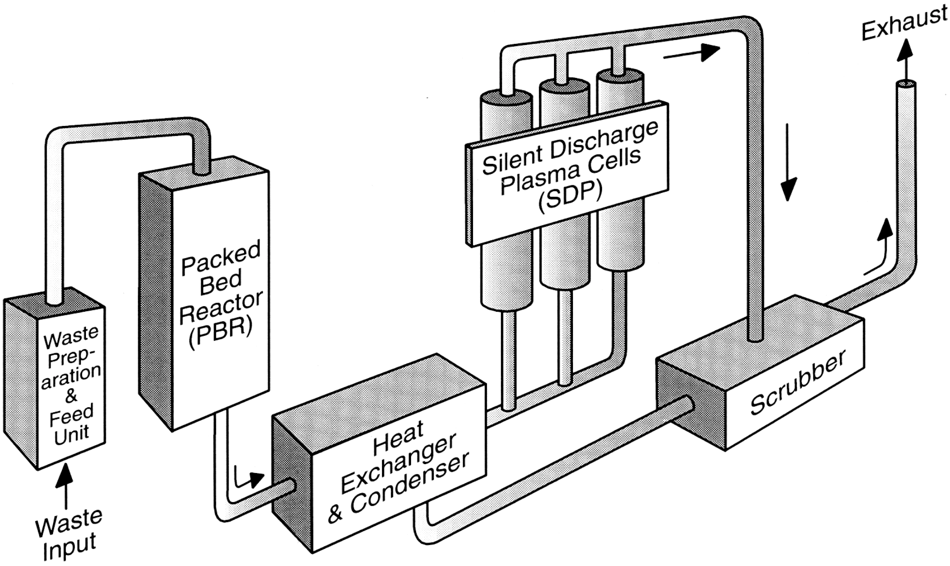


FIGURE 5.4.2.3 Artist's conceptual drawing of two-stage PBR-NTP unit.

TABLE 5.4.2.2 Representative Liquids Tested with Packed-Bed Reactor

Liquid	Concentration (by volume)
TCE (trichloroethylene), C_2HCl_3	Up to 10%
Carbon tetrachloride, CCl_4	3%
TCA (trichloroethane), $C_2H_3Cl_3$	Up to 10%
Freon TF	Up to 20%
Hydrocarbon machining oils	Up to 100%
Halocarbon oil	Up to 100%
TrimSol™ machining oil	Up to 100%
Scintillation fluids	Up to 100%

Any remaining contaminants in the PBR off-gas are then removed by the second-stage non-thermal plasma reactor (in this case, a silent discharge plasma [SDP] unit), with its share of waste loading determined by the desired PBR operating temperature. The second-stage NTP chemical reactor is able to reduce off-gas emissions from the first stage to very low levels (approaching tens of ppm to several ppb) by the free-radical-initiated process (sometimes called *cold combustion*) described in earlier subsections.

The two-stage unit must be equipped with some type of filter mechanism, either in the PBR stage (sometimes the alumina beads themselves) or between stages, to collect the low-level radioactive components.

Under thermal equilibrium, chemical decomposition in a PBR can be described by the integral equation (Folger, 1992):

$$V = Q_m \int_0^{R_{out}} \frac{dR}{k[X]} \tag{5.4.2.6}$$

where V is the reactor volume, Q_m is the molar flow rate of the processed compound, R_{out} is the fractional degree of removal at the PBR exit, dR is the incremental degree of removal, *k* is the reaction rate constant, and [X] is the concentration of the subject compound. The reaction rate constant can be described by a typical Arrhenius expression, $k = A \exp(-E/RT)$, in terms of a reaction constant A, the activation energy E, the gas constant R, and the absolute temperature T, where the values of A and E are specific to the compound being processed. Within this framework, the degree of removal of the processed compound increases exponentially with the reaction temperature. The residence time in the PBR is quite short (<1 s); thus, combustion/pyrolysis reactions within it do not necessarily proceed to equilibrium, and a kinetic treatment would give more accurate results for such cases.

Removal of gas-phase pollutants by the NTP stage can, in general, be described by:

$$[X] = [X]_0 \exp(-\bar{E}/\beta) \tag{5.4.2.7}$$

where $[X]_0$ is the initial pollutant concentration, [X] is the pollutant concentration after depositing a plasma specific energy of $\bar{E}$ (plasma power divided by gas flow rate) into the treated gas, and β is a specific energy characteristic of a given compound, which reduces the concentration by 1/e (one e-fold reduction). The specific energy $\bar{E}$ in general depends on the plasma physics of the reactor excitation, while the characteristic β-value generally depends on the radical production efficiency, the decomposition chemical reaction kinetics, and the initial pollutant concentration (Penetrante and Schultheis, 1993; Rosocha, 1997].

Low-Temperature Thermal Desorption Combined with NTP

Low-level mixed wastes and acutely hazardous/toxic materials are subject to regulation under the Resource Conservation and Recovery Act (RCRA), the Toxic Substances Control Act (TSCA), and the Atomic Energy Act (AEA). Under the RCRA, such wastes are subject to land disposal restriction (LDR). If the RCRA and TSCA components are removed from mixed-waste debris (e.g., clothing, rags, paper products, broken glass, soils, and metal turnings) without actual treatment of the mixed waste matrix itself, the land disposal of such debris is much simplified. The key to successful implementation of this method is a reliable off-gas treatment system.

A variety of desorption techniques have been identified under federal regulations and programs to remove organics from LDR wastes. These technologies have been given priority because they can handle a wide variety of waste streams, and operate at low temperatures and under the constraints of the debris rule. However, these technologies can only be considered a first stage because no hazardous compounds are actually destroyed — the regulated VOCs are only separated from the heterogeneous matrix. Usually, off-gases are contained by the addition of GAC (granular activated carbon) and/or condensation stages, but again no waste is actually destroyed. Air-like or oxidizing gas streams cannot be used under the debris rule because the volatilized organics cannot be treated or modified during the separation process. Therefore, because the off-gas consists of an inert gas (usually nitrogen, although argon offers chemical and economic advantages) containing the volatilized organics, conventional oxidation techniques cannot be applied without the addition of significant oxygen and fuel. This increases secondary waste volumes and complicates any attempts at closed-loop operation (an architecture that provides better process control, higher DREs, and increased safety through off-gas recycling). However, the silent discharge plasma (a plasma formed by a dielectric-barrier-ballasted electrode configuration in which charge accumulation on the barrier terminates the discharge before thermal arc formation occurs) and other NTPs use energetic electrons to form free radicals that rapidly oxidize hazardous organics — in both air-like and inert gas streams, while the stream remains at near-ambient temperatures. The use of NTPs provides a complete low-temperature system that does more than simplify the waste stream: NTPs actually destroy the hazardous/toxic wastes.

A prototype system that exploited the debris rule for combustible mixed wastes was operated at the Rocky Flats Environmental Technology Site (RFETS), using dry nitrogen mixtures. A schematic diagram of this system, which treated a mixed waste containing soils, plutonium, and a range of solvents, is shown in Figure 5.4.2.4. Further testing has confirmed the ability of NTPs to destroy both benzene-toluene-xylene (B-T-X) and chlorinated VOCs (TCE, TCA, and carbon tetrachloride) in both dry and humid nitrogen feeds.

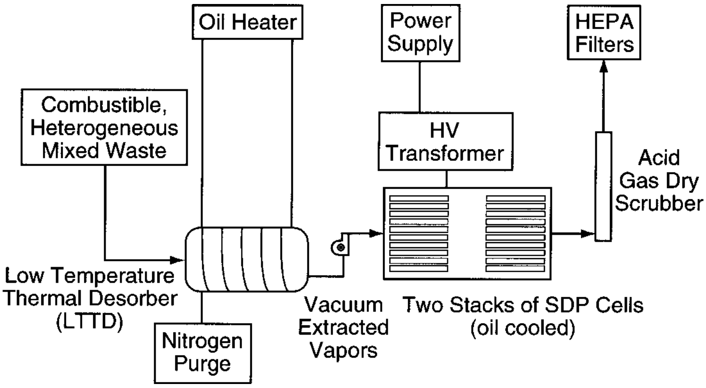


FIGURE 5.4.2.4 Low temperature thermal desorber/NTP unit schematic.

Typical oxygen levels (1 to 5%) from the prototype low-temperature thermal desorption (LTTD) system are close to optimal for the efficient destruction of both halogenated and non-halogenated VOCs. It has been shown that replacing the normally used nitrogen purge with an argon purge would dramatically affect the scale of the NTP unit. For TCE streams, the energy density required for 90% removal is reduced by over an order of magnitude (from 80 to 100 J/L to 3 to 6 J/L). This is a result of both chemical and physical processes. Chemically, the use of reduced oxygen allows for longer propagation chain reactions using chlorine-mediated oxidation. On the other hand, excess O_2 increases the rates for critical chain terminating reactions. Physically, the use of argon increases the average electron temperature in the plasma, better accessing other energetic-electron reactions. The prototype NTP unit used at RFETS in 1995 could treat off-gases from 10 LTTD units, if the nitrogen purge was replaced with an argon purge.

Removal of RCRA Waste from Spent Granular Activated Carbon

Existing steam reforming techniques, while able to volatilize entrained organics from granular activated carbon (GAC), do not destroy them and therefore produce large quantities of secondary wastewater. Under a Los Alamos-RFETS collaboration, a design for a two-stage, commercially available, thermal carbon regeneration unit combined with a silent discharge NTP unit was completed to treat toxic off-gases evolved from the GAC regeneration process, simplifying disposal and removing storage and transportation expenses. For mixed-waste GAC, the technology must also handle the trace amounts of radioactive materials present. The proposed system is similar to the LTTD system described above (but operates over a slightly higher temperature range). In the proposed system, spent GAC is fed from a storage bin into a rotary kiln operating at 125 to 250°C (depending on the target compound with highest boiling point). The kiln volatilizes both the water and the organics contained in the GAC. Off-gases composed primarily of steam are sent immediately into an NTP system operating at the exit temperature of the kiln. The reactive oxygen atoms and hydroxyl radicals, generated in the plasma from the water vapor already present, oxidize the organics. After treatment in the plasma chamber, water vapor is condensed and the by-products of the cold plasma combustion are “scrubbed out.” This water is passed through an initial cleaning process and then sent through a conventional wastewater treatment plant. Any remaining gases are sent back into the GAC storage bin. To simplify this, an inert carrier gas (such as argon) can be added. The cleaned, dry GAC is then ready for reuse or disposal. When high-temperature reactivation is required, the dry GAC is again sent into the kiln. This time, it is treated at a higher temperature to reactivate the carbon pores that trap organics. As a precaution, off-gases from this process could again be treated within the plasma chamber.

By controlling added flush gases, the NTP system can function over a wide range of off-gas conditions from an oxygen-rich (air-like) to an “inert” gas matrix, increasing system flexibility and simplifying the possible implementation of a closed-loop design. As with the LTTD process described previously, oxygen levels can be adjusted to optimize system efficiency.

Pyrolysis Combined with NTP

One additional example of applying NTP technology to mixed waste solids treatment is that of a combined pyrolytic-NTP system. At Los Alamos, a prototype, glovebox-compatible system was constructed and tested for the treatment of polystyrene cubes (polycubes) containing plutonium oxide (Anderson et al., 1999). In this system (see Figure 5.4.2.5), the main principle is to use an electrically heated pyrolyzer to vaporize polycubes into styrene gas, which is sent to a bank of NTP reactors (SDP cells) for destruction in the gas phase, while plutonium oxide residue is safely collected in the pyrolyzer chamber. In the Los Alamos system, only polycube surrogates were used (i.e., they did not actually contain Pu).

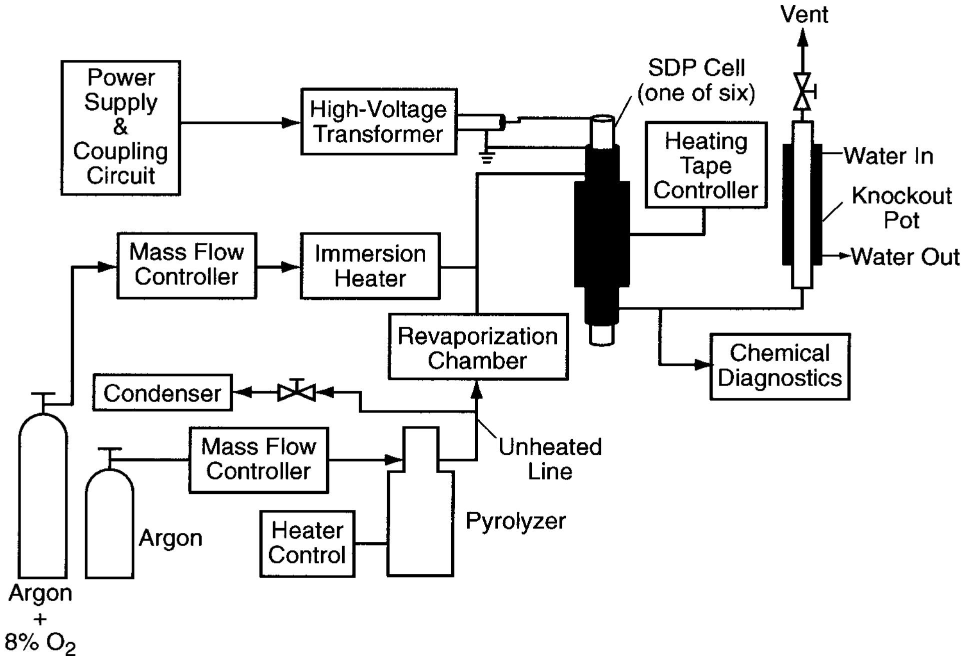


FIGURE 5.4.2.5 Schematic of combined pyrolyzer-NTP system. (From: Korzekwa, R., Anderson, G., Snyder, H., and Rosocha, L. 1998. Treatment of Pyrolyzer Off-Gas Using Non-Thermal Plasmas, Los Alamos National Laboratory Unpublished Report LA-UR-98-5317. With permission.)

The pyrolyzer, described in greater detail elsewhere (Anderson et al., 1999), operates with a controlled temperature profile (using temperatures ranging from about 500 to 700°C) so that the hydrocarbon-gas production rate is carefully controlled to provide a fairly uniform feed to the NTP reactor bank. Argon gas is used to flush the hydrocarbon vapor from the pyrolyzer and the argon-hydrocarbon gas mixture is transported to the six-element SDP cell bank via tubing heated to 350°C. Before entering the SDP cells, the argon-hydrocarbon gas flow is mixed with a 92% argon/8% oxygen main gas flow. The oxygen content is a key design point, important in keeping the mixture free of the danger of explosion (the maximum safe oxygen level for styrene in argon is ~10% oxygen).

The individual SDP cells are constructed in a single-barrier coaxial arrangement. Stainless steel is used for the electrodes, while ceramic tubes are used for the dielectric barrier. High-purity alumina (ceramic) is used for the dielectric-barrier material so that the cells can operate at a high enough temperature to avoid polymerization of styrene (>300°C), but at a low enough temperature to prevent thermally initiated dielectric failure. Each cell can operate at plasma powers up to 1 kW.

The exhaust gas from the cells was characterized with commercial gas analyzers to monitor the hydrocarbon and CO/CO_2 concentrations and to identify individual species in the exhaust gas. With a controlled pyrolyzer temperature profile, good thermal management in the SDP cells, and the use of high-purity alumina ceramic dielectric materials, a robust, reliable, and reasonably sized prototype SDP off-gas treatment system was developed and proven in the laboratory. It was able to treat the pyrolyzer off-gas with 99.9% destruction of total hydrocarbons (conversion to CO, CO_2, and H_2O) at peak hydrocarbon outputs from the pyrolyzer of up to 1 g/min using 4.5 kW of plasma power (or a specific plasma energy of $\bar{E} = 2.25$ kJ/L) for six cells. The technology is now ready for application to actual mixed waste polycubes.

Summary

Various non-thermal plasma systems have been successfully developed, using surrogate wastes in the laboratory or controlled test environments, for mixed radiochemical waste treatment applications. By operating with a low oxygen fraction, gas mixtures can be kept well below the lower explosive limit (LEL), which is very desirable from an engineering standpoint. At present, these systems show promise for treating a variety of waste streams: gases, liquids, slurried solids, and vaporized solids. However, to date, none have actually been commercialized for the actual treatment of mixed wastes.

An even wider range of wastes may be appropriate for closed-loop systems, including chemical weapons. NTP technology may enable the implementation of closed-loop treatment methods that will offer significant advantages for mixed waste treatment.

Defining Terms

Non-thermal plasmas (NTPs): A plasma (neutral ionized gas) in which the electrons are not in thermal equilibrium with ions and the background gas; the electrons are energetic, while the ions and neutral species have a much lower temperature.

Free radical: An atom or molecule with an unpaired electron, which is extremely reactive with other chemical species.

Decomposition: Breaking a molecule into smaller parts or fragments.

Destruction and removal efficiency (DRE): The fraction of a chemical compound that is destroyed (decomposed) or removed from a waste stream.

NTP reactor: A device that generates a non-thermal plasma and associated active species used to react with (decompose) pollutants in a gas stream.

Volatile organic compounds (VOCs): Organic chemical compounds having a tendency to vaporize at near-ambient temperature and pressure.

Packed-bed reactor (PBR): A thermal device that uses combustion to decompose chemical compounds.

Plasma specific energy: The electrical energy per unit volume deposited in a plasma.

Desorption: The process of liberating chemical compounds from a waste matrix (usually by heat).

Closed loop: A waste treatment architecture characterized by the capturing of all effluents before their eventual release.

Pyrolyzer: A device using thermal energy (heat) rather than combustion to decompose or transform chemical compounds.

Acknowledgments

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For Further Information

More information on non-thermal plasmas for hazardous chemical processing can be found in the following:

1. *The Journal of Advanced Oxidation Technologies* (published by Science & Technology Integration, Inc., London, Ontario, Canada).
2. *IEEE Transactions on Plasma Science* (published by the Institute of Electrical and Electronics Engineers, Piscataway, NJ).
3. *The Journal of Plasma Chemistry and Plasma Processing* (published by the Plenum Publishing Corp., New York).
4. *The Journal of Applied Physics* (published by the American Institute of Physics, New York).
5. *The International Conference on Plasma Science.*
6. *The International Conference on Advanced Oxidation Technologies for Water and Air Remediation.*

5.5

Radiation-Induced Oxidation

5.5.1 The Electron Beam Process for Waste Treatment

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Introduction

The understanding of ionizing radiation, high-energy electron beam, γ- or x-radiation provides the underlying chemistry for the innovative electron beam waste treatment process. In this section and the one that follows, the fundamental chemistry of the electron beam process and γ- or X-radiation processing will be presented, respectively. Selected applications are discussed. Throughout the discussion the differences and similarities between these processes and others are discerned. All of the studies reported were either conducted at the large-scale Electron Beam Research Facility (EBRF) in Miami, Florida (a detailed description of the facility has been published elsewhere by Kurucz et al., 1995) or with a mobile 20-kW system (Nickelsen et al., 1998).

Radiolysis involves the chemical effects produced when materials (in this case water) are exposed to ionizing radiation. The types of radiation most commonly used are those produced by the decay of radioactive nuclei (γ-radiation), beams of accelerated charged particles (electrons), and short-wavelength radiation (x or Brehmsstralung) produced when a beam of electrons hits a target (e.g., tantalum or other heavy metallic material).

In the radiolysis of aqueous solutions, organic contaminants are destroyed either by a "direct" or "indirect" interaction with the incident radiation. In aqueous solution, the direct interaction of radiation with organic compounds only becomes significant when the contaminant concentration is Š0.1 *M*. At these high concentrations, direct radiolysis may account for as much as 10% of the observed effect. The major chemical pathway leading to the destruction of chemicals is the result of indirect radiolysis or reaction of the chemical with the radiolysis products of water.

Chemical changes to contaminants, are usually the result of reactions between the reactive intermediate products of water, e^-_{aq}, HX, XOH, and in some cases the molecular product hydrogen peroxide (H_2O_2). In aqueous solution, these reactive intermediates are formed according to the following equation

$$H_2O \xrightarrow{e^-} [2.6]\ e^-_{aq} + [0.6]\ HX + [2.7]\ XOH + [0.7]\ H_2O_2 + [2.6]\ H_3O+ + [0.45]\ H_2 \qquad (5.5.1.1)$$

$$H_2O \xrightarrow{e^-} [0.26]\ e^-_{aq} + [0.06]\ HX + [0.27]\ XOH + [0.07]\ H_2O_2 + [0.26]\ H_30+ + [0.045]\ H_2 \quad (5.5.1.2)$$

Unlike photochemical reactions in which one photon of light initiates one (molecular) reaction, a high-energy electron (or photon of γ- or x-radiation) is capable of initiating several thousand reactive species as it dissipates its energy. The efficiency of conversion of a high-energy electron, ionizing radiation, to a chemical process is defined as G (shown in brackets). G is the number of radicals, excited states, ions, or other products, formed or lost in a system absorbing 100 eV of energy [Equation (5.5.1.1)], or in SI units, μmol J^{-1} [Equation (5.5.1.2)]. G values in Equation (5.5.1.1), molecules per 100 eV^{-1} are converted into SI radiation chemical yields of μmol/J^{-1} by multiplying by 0.1036.

Of the radiolysis products formed in aqueous solution, the most reactive are the oxidizing hydroxyl radical (XOH) and the reducing aqueous electron (e^-_{aq}) and hydrogen atom (HX). Thus, the chemistry of primary interest in the high-energy electron beam process is of the three reactive species and their interaction with pollutants and other constituents in the water to be treated. The fact that ionizing radiation produces both oxidizing and reducing species simultaneously differentiates it from most other advanced oxidation technologies, with the exception of sonication and electrohydraulic cavitation, in which both oxidizing (XOH) and reducing (HX) species are formed. As seen later in this section the HX is not as reactive (in most cases) as the e^-_{aq}, however, reductive processes can and do occur when it is present.

One of the little-recognized aspects of the electron beam process is that the underlying chemistry of the process is relatively well understood. The G values, radiolytic yields, shown in Equations (5.5.1.1) or (5.5.1.2) have been determined very precisely and are shown for the time 10^{-7} seconds after electron injection (Buxton et al., 1988). Estimates for the concentration of the three species and the molecular H_2O_2 at several doses are summarized in Table 5.5.1.1. As dose increases, the simple assumptions that were used to calculate the concentrations in Table 5.5.1.1 probably no longer hold, and the concentrations are probably overestimated. However, in a contaminated system where the reactive species are being rapidly scavenged, Table 5.5.1.1 does provide order-of-magnitude estimates of the reactive species available for reaction with the organic or inorganic chemicals.

TABLE 5.5.1.1 Estimated Concentrations of Transient Reactive Species in Pure Water at Several Doses Using High-Energy Electron Irradiation

Dose		Concentration (m*M*)			
(krads)	(kGy)	e^-_{aq}	HX	XOH	H_2O_2
100	1	0.27	0.06	0.28	0.07
500	5	1.4	0.3	1.4	0.4
1000	10	2.7	0.6	2.8	0.7

There are 40 equations (see subsection entitled "Kinetic Modeling") with known bimolecular rate constants that describe the fate of these species in pure aqueous solution. These reactions form the basis of the kinetic model that is being developed to describe solute (pollutant) destruction in aqueous solutions (Mak et al., 1997; Tobien et al., 2000a; b; Zele et al., 1998).

Dose (Energy) Required For Treatment

The design parameter needed for an electron-beam treatment system is the dose or the energy required per unit volume of water to be treated to meet the specified treatment objectives. Dose is a measure of the amount of energy absorbed by an irradiated material per unit mass. In other words, dose is a measure of the energy transferred to the irradiated material, in this case water, which is capable of producing chemical or physical changes in that material. A common unit of dose is the rad, defined as the energy

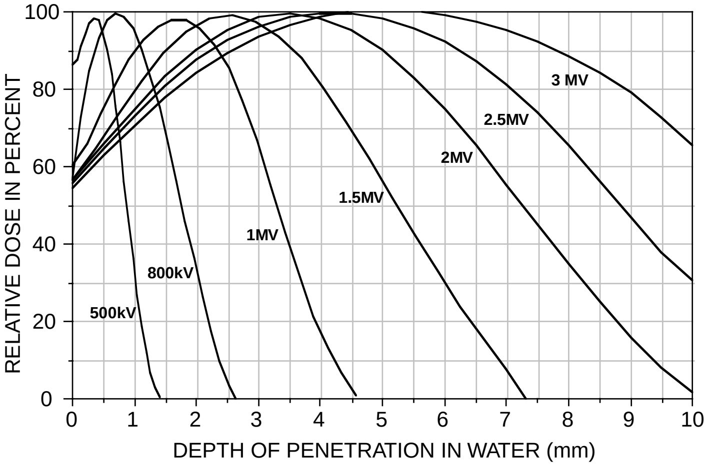

FIGURE 5.5.1.1 High-energy electron penetration in water (unit density material) at several energies.

absorption of 100 ergs per gram of material. The SI unit for dose is Gray, Gy, 1 rad = 0.01 Gy, where 1 Gray is defined in J/kg.

The amount of energy transferred to the water from a high-energy electron is not constant along the path of the electron as it returns to ground potential. The maximum depth of penetration is directly proportional to the energy of the incident electrons and inversely proportional to the density of the material being irradiated (Figure 5.5.1.1). Thus, the absorbed dose depends on the type and thickness of the material, the beam power, and the length of time the material is exposed to the electron beam. The penetration of an electron is critical when relatively high removal is required in one pass. For example, in the case of biological activity (inactivation of viruses, bacteria, or protozoa) or chemical removal, if 0.01% of the material is not irradiated, then, because the thickness of the water exceeds the penetration depth of the incident electrons, the maximum removal possible is 99.99%. This assumes that the process is one pass and is then independent of the dose received.

One of the advantages of the electron beam (E-beam) process is that electrons can penetrate solid material. It has been shown that the presence of clay, up to 3 to 5%, does not adversely affect the removal of the pollutant chemicals (Cooper et al., 1993a; Lin et al., 1995; Mak et al., 1996; Nickelsen et al., 1992). Another advantage of this penetrability is that closed systems can be engineered wherein the solution to be irradiated at no time comes in contact with the electron accelerator. As discussed in Section 5.5.2, γ- and x-radiation have even better penetration and may be ideally suited for treating organic and some inorganic contaminants in mixed wastes.

In a typical treatment system that is flowing, the absorbed dose can be determined by measuring the temperature difference of the water stream before and after irradiation. The relationship is derived for pure water by the following relationships:

$$1 \text{ rad} = 100 \text{ erg/g} \tag{5.5.1.3}$$

or

$$1 \text{ Mrad} = 1.0 \times 10^8 \text{ erg/g} \tag{5.5.1.4}$$

Substituting

$$1 \text{ erg} = 2.39 \times 10^{-8} \text{ cal} \tag{5.5.1.5}$$

then,

$$1 \text{ Mrad} = 2.39 \text{ cal/g} \tag{5.5.1.6}$$

Converting to °C,

$$1 \text{ Mrad} = 2.39 \text{ °C} = 10 \text{ kGy} \tag{5.5.1.7}$$

or

$$\Delta T = 0.418 \text{ Mrad or } 4.18 \text{ kGy/°C} \tag{5.5.1.8}$$

The relationship between dose and temperature is one way to estimate relative energy consumed for the treatment of a compound(s). It provides an estimate of the temperature increase in the treated solution and this can then be related to energy (and cost) for the treatment.

To obtain better estimates of the dose required for a particular treatment, pilot studies (demonstrations) are performed to determine the E-beam dose required to achieve the desired effluent concentration. These are best conducted at the site with the actual water. The E-beam dose required for a specific water is based on examining the effect of the treatment in the presence of selected process variables such as pH, alkalinity, and suspended solids.

Figure 5.5.1.2 is an example of the typical E-beam treatment curve resulting from a single test run where removal is plotted at several doses. Although the reactions between the contaminant and the reactive species are second order, these species are continuously being produced, thereby making the contaminant concentration the limiting reagent. These conditions give rise to pseudo-first-order reaction systems, and a linear relationship can be derived by plotting the ln of the contaminant concentration as a function of E-beam dose, as shown in Figure 5.5.1.3. A linear regression of the resulting line, the slope of which is the dose constant, can be utilized to calculate the E-beam dose necessary to achieve any effluent concentration.

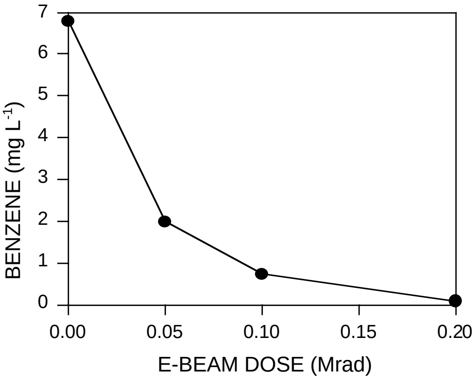

FIGURE 5.5.1.2 Typical example of pollutant destruction with increasing electron beam dose.

There are many variables that affect the slope of curve in Figure 5.5.1.3. For example, in solutions where the pollutant concentration is very high, the initial radical attack results in the formation of reaction by-products. These by-products also react with the reactive species and act as scavengers competing with the pollutant of interest. Therefore, as the treatment proceeds, or as the dose is increased, the slope of the line may decrease. This results in an increase in the efficiency of destruction, at the higher doses and lower concentrations, because of net decrease in radical scavengers (i.e., the process has destroyed the reaction by-products as well as the initial solute) in the solution. This is not unique to the E-beam system, and any advanced oxidation process (or destruction technology with the possible exception of thermal plasma) will show the same effect.

One aspect that does differentiate the E-beam process from other advanced oxidation technologies is that with the constant production of both oxidizing and reducing species, when by-products are formed that do not react efficiently with the oxidizing XOH and do with the e^-_{aq}, increased efficiency can result.

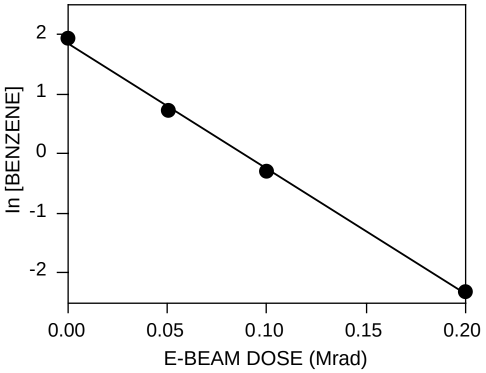

FIGURE 5.5.1.3 A natural log (ln) transformation of the concentration data in Figure 5.5.1.2, the slope of the line being the dose constant.

An example of this would be if acetone were formed as a reaction by-product. The XOH reaction rate is relatively slow (1.3×10^8 M^{-1} s^{-1}) and, in a predominantly oxidizing system, acetone might accumulate. However, the reaction rate constant of acetone with the e^-_{aq} is rapid (6.5×10^9 M^{-1} s^{-1}) and destruction is initiated via a reducing pathway.

Acetone is also a good molecule to demonstrate the difference between the reducing capability of the e^-_{aq} and the HX. The reaction between the HX and acetone is relatively slow (2.6×10^6 M^{-1} s^{-1}) and would not contribute significantly to the overall destruction. There are other chemicals for which the rate constants between the e^-_{aq} and the HX are reversed and the presence of the HX would facilitate destruction. A good example is toluene, for which the reaction rate of HX is 2.6×10^9 M^{-1} s^{-1} and that for the e^-_{aq} is 1.5×10^7 M^{-1} s^{-1}. A cautionary note is worthwhile here because, as stated, the overall electron beam process efficiency destruction of any chemical can be very complicated and the rate constants are but one of several variables that must be considered.

Process Efficiency

Another common misconception about the E-beam process is equating the idea of high-energy electrons with high-energy costs. In fact, it was recently shown that the E-beam process (using insulated core transformers in the electron accelerator) is the most energy efficient means of creating XOH, when compared to UV/H_2O_2 or UV/TiO_2 (Bolton et al., 1998). In that study, the EE/O (electrical energy per order), kilowatt-hours of electricity required to reduce the concentration of a contaminant in 1000 gallons by one order of magnitude (or 90%), was utilized for comparison purposes and is a measure of the treatment achieved in a fixed volume of water as a function of E-beam dose. The unit for EE/O is kWh/1000 U.S. gallons/order. For example, if it takes 10 kWh of electricity to reduce the concentration of a contaminant from 100 mg/L to 10 mg/L in 1000 gal wastewater, then the EE/O is 10 kWh/1000 gallons/order. It would then take an additional 10 kWh to reduce the compound one additional order, from 10 to 1 mg/L; that is, to an overall destruction removal efficiency of 99%.

The linear relationship between E-beam dose and the ln of contaminant concentration (as shown in Figure 5.5.1.3) has important treatment implications. First, the linear relationship observed in Figure 5.5.1.3, for any contaminant, can be described by a single number, the EE/O. This allows for the comparison of competing technologies by comparing their EE/O values. The lower the EE/O value, the more effective and efficient the treatment method. However, care should be exercised when comparing various processes using a figure of merit such as the EE/O. In some processes, it is necessary either to take into account all of the energy costs associated with each treatment or examine both EE/O and operational costs. For example, if H_2O_2 is added during the treatment, there is an electrical cost associated with the production of the peroxide and it needs to be taken into consideration in the comparison, either as an addition to the EE/O calculation or in the operational costs.

The EE/O value determined from a feasibility study is specific to the water being tested and to the contaminant of interest and the starting concentration. That is, benzene may have an EE/O value of 1.2 for one application and a value of 2.7 for another. Typical EE/O ranges for several compounds of interest in environmental restoration are summarized in Table 5.5.1.2. These were determined at the large scale Electron Beam Research Facility in Miami at a flow rate of approximately 100 gal per minute in potable water to which the contaminant was added (Cooper et al., 1992a; b; 1993a; b; Lin et al., 1995; Mak et al., 1996; 1997; Nickelsen et al., 1992; 1994). The range in EE/O values for any one compound results from treatment at various influent concentrations and changes in pH that affect the concentration of the carbonate ion (see below).

TABLE 5.5.1.2 Typical EE/O Values (and Range) for Contaminant Destruction by the E-beam Process

Contaminant	EE/O (kWh/1000 U.S. gal/order)
Benzene	0.5–3
Toluene	0.4–3
Xylene(s)	1–3
Phenol	0.4–7
Methylene blue (dye)	0.2–2
Trichloroethylene	0.5–2
Tetrachloroethylene	2–6
Chloroform	2–12
Carbon tetrachloride	0.5–5
Vinyl chloride	0.5–2

Once an EE/O value has been determined, either through feasibility studies or estimated from a table of values, the E-beam dose required for a specific application is calculated using the following equation:

$$\text{E-beam dose} = \text{EE/O} \times \log C_i/C_f \tag{5.5.1.9}$$

where C_i is the initial contaminant concentration, and C_f is the desired treatment objective. For waste streams with complex mixtures of contaminants, the energy required for treatment is not additive but is determined for the contaminant with the highest EE/O in the actual water to be treated.

Another way to determine the dose required was proposed by Kurucz et al. (1995), for which empirical models were developed for a number of organic contaminants. These models developed destruction curves using several different variables obtained from empirical studies. These empirical models are extremely useful when comparing various technologies during the preliminary evaluation stage.

Natural Water Scavengers

An important consideration in extending laboratory data to natural waters, for all AOPs, is the effect of radical scavengers on the removal of the solute of interest. In hazardous waste site remediation, the natural constituents of the water must be considered; while for industrial and mixed waste treatment, there may be other organic and inorganic chemicals, not targeted for removal that can compete with the target compound for the reactive species.

Table 5.5.1.3 summarizes factors or parameters that can reduce treatment efficiency by acting as radical scavengers.

Oxygen

Both e^-_{aq} and HX rapidly reduce O_2 to form O_2^- ($pK_a = 4.8$). At a dose of 100 krads (1 kGy) and a dissolved oxygen concentration of 3.7 mg/L (0.12 m*M*), 35% of the e^-_{aq} and HX would be removed. However, in the same solution and at a dose of 800 krads (8 kGy), only 5% of the e^-_{aq} and HX would

TABLE 5.5.13 Rate Constants (M^{-1} s^{-1}) of Chemical Species Commonly Found in Natural Waters with Transient Reactive Species Formed in Irradiated Aqueous Solution

Compound	e^-_{aq}	HX	XOH
Bicarbonate ion	1.0×10^6	4.0×10^4	8.5×10^6
Carbonate ion	3.5×10^5	NF[a]	3.9×10^8
Bromide ion	NF[a]	2.8×10^7	1.1×10^{10}
Nitrate ion	9.7×10^9	1.4×10^6	NF[a]
Nitrite ion	3.5×10^9	7.1×10^8	1.0×10^{10}
Oxygen	1.9×10^{10}	2.1×10^{10}	NF[a]

NF = Not found.

be removed from solution via reaction with oxygen, leaving the remainder available for reaction with the solute of interest.

Bicarbonate/Carbonate Ion

A common XOH scavenger in natural waters is carbonate ion. Alkalinity, estimated in a natural system as the total bicarbonate/carbonate ion concentration, exists in a relatively complicated equilibrium in natural waters:

$$H_2CO_3 + H_2O \leftrightarrow HCO_3^- + H_3O^+ \quad pK_a = 6.35 \tag{5.5.1.10}$$

$$HCO_3^- + H_2O \leftrightarrow CO_3^{2-} + H_30^+ \quad pK_a = 10.25 \tag{5.5.1.11}$$

The effect of alkalinity on the scavenging of the XOH depends on the pH of the solution (see Table 5.5.1.3 for the relative scavenging rates). For example, although a secondary wastewater (pH 7) had an alkalinity five-fold higher than a potable water, the XOH scavenging was approximately 2.5 times higher in a potable water (at pH 9) based on bicarbonate/carbonate equilibrium.

Nitrate Ion

Nitrate ion (NO_3^-) in solution acts as an e^-_{aq} scavenger and is reduced to nitrite ion. The NO_2^- ion is known to react with the XOH and the resulting radical leads to the addition of NO_2 to aromatic solutes. For example, we have shown that in a solution of benzene with extremely high nitrate ion concentrations, nitrobenzene was formed as an intermediate in experiments conducted on a simulated mixed waste containing high concentrations of benzene (Cooper et al., 1996; Dougal et al., 1998).

Dissolved Organic Carbon

Another common component in natural waters is the poorly characterized fraction referred to as dissolved organic carbon (DOC) which acts as a very efficient scavenger of radicals.

Engineering the Chemistry of the Process for Pollutant Destruction

Equation 5.5.1.1 showed that both reactive oxidizing and reducing species are formed when aqueous solutions are irradiated using high-energy electrons. Table 5.5.1.4 summarizes these reactive transients and their primary mode(s) of reaction. There is a vast literature of bimolecular reaction rate constants for the three reactive species, and the reader is referred to the Notre Dame Radiation Laboratory Web site for an online searchable (current) listing of these rates (http://www.rcdc.nd.edu).

In designing a system to destroy chemicals, it is important to know what the reaction rates are or at least be able to predict order-of-magnitude reaction rates. Because of the wealth of data available for the reactions of the species and both organic and inorganic compounds, it is possible to gain insight into where or for which system the process will work and where it may not work, and, how to optimize the process efficiency using chemistry.

TABLE 5.5.1.4 Properties of Transient Reactive Species Formed by the Electron Beam Process

Reactive Species	XOH	e^-_{aq}	HX
Redox Properties	Strongly oxidizing	Strongly reducing	Reducing
Mode of Action	Electron transfer XH abstraction XOH Addition	Electron addition	XH abstraction XH Addition
G Values	2.7	2.6	0.6

For example, if the removal of CCl_4 is the objective, CCl_4 does not react with XOH, one way to increase the effective concentration of e^-_{aq}, and therefore the removal efficiency, is to "scavenge out" the XOH. By scavenging the XOH, the recombination reaction of the two species [Equation 5.5.1.12], which would lead to a loss of both species, is minimized and CCl_4 removal optimized.

$$e^-_{aq} + XOH \rightarrow OH^- \qquad 3.00 \times 10^{10}\ M^{-1}\ s^{-1} \tag{5.5.1.12}$$

The most effective natural water XOH scavenger is the carbonate ion. Therefore, carbonate ion could be added to the water or, in the case of a water with high carbonate alkalinity, the pH adjusted to 10 by the addition of lime (CaO). This would leave the e^-_{aq} to react with the CCl_4 and the destruction efficiency is increased.

Another option available is to add ozone immediately prior to the injection of electrons. The effect this has is to convert all of the e^-_{aq} and HX to XOH (Sehested et al., 1983)

$$e^-_{aq} + O_3 \rightarrow O_2 + XO^- \qquad 3.6 \times 10^{10}\ M^{-1}\ s^{-1} \tag{5.5.1.13}$$

$$HX + O_3 \rightarrow O_2 + XOH \qquad 2.2 \times 10^{10}\ M^{-1}\ s^{-1} \tag{5.5.1.14}$$

Gehringer et al. (1988) have demonstrated empirically that this concept results in a substantial reduction in the dose required (or increase in flow rate for a give power) to remove tetrachloroethylene from groundwater. The cost savings on power enabled the authors to design a system with a smaller accelerator, reducing the capital cost of the system. Another side benefit of the addition of ozone in waters that are high in nitrate ion is that it minimizes (if not eliminates) the formation of nitrite ion.

It is also possible to use hydrogen peroxide (H_2O_2) to increase the concentration of XOH. The reactions of both the e^-_{aq} and HX with H_2O_2 result in the formation of XOH according to the following equations:

$$e^-_{aq} + H_2O_2 \rightarrow XOH + OH^- \qquad 1.20 \times 10^{10}\ M^{-1}\ s^{-1} \tag{5.5.1.15}$$

$$HX + H_2O_2 \rightarrow H_2O + XOH \qquad 9.00 \times 10^{7}\ M^{-1}\ s^{-1} \tag{5.5.1.16}$$

However, the XOH also reacts with H_2O_2 and a competition is set up in the solution.

$$XOH + H_2O_2 \rightarrow O_2 + H_3O^+ \qquad 1.20 \times 10^{10}\ M^{-1}\ s^{-1} \tag{5.5.1.17}$$

In solutions with high organic contaminants that react with the XOH (e.g., benzene), it is possible that the overall effect would be beneficial. The effect of the XOH can be reduced by nearly 1000 if it is possible to adjust the pH to a rather high value (~ 11–12), where the reaction of the conjugate base, O^-, is substantially slower.

$$O^-X + H_2O_2 \rightarrow O_2^-X + H_2O \qquad 2.70 \times 10^{7}\ M^{-1}\ s^{-1} \tag{5.5.1.18}$$

The addition of scavengers may be beneficial (in lowering the dose required to meet treatment objectives and therefore the cost) and the potential advantages need to be determined on a case-by-case basis.

Kinetic Modeling

The underlying assumption for developing a kinetic model for the electron beam process is that it provides an easy tool to assist in optimizing the process and a "quick and dirty" way in which to determine the economic viability of the process prior to detailed experimental studies. In addition, when conducting large-scale experimental studies or on-site feasibility demonstrations, it serves as a guide to minimize the number of experiments to obtain the maximum information.

We have employed a computer code called MAKSIMA-CHEMIST, provided by the Atomic Energy of Canada (Carver et al., 1979), as the starting point for our kinetic model. This program uses a method based on the Gear predictor algorithm for integration. Further details of the integration algorithm (Gear, 1971), and validation tests where the model has satisfactorily predicted results for irradiation of water (Schwarz, 1962), have been reported elsewhere. The input to the kinetic model includes a list of all reacting species, their initial concentrations obtained from the experimental measurements and the rate constants (Table 5.5.1.5). The water residence time in the irradiated zone of the Miami EBRF has been estimated at 0.091 s (Kurucz et al., 1995). Taking into account the irradiation time, the empirically determined absorbed doses have been converted into dose rates (Table 5.5.1.6). In addition to the organic solutes, there are other solutes, such as O_2, and Cl^- and reaction by-products that also compete for the aqueous electrons and the other reactive species. The predictability of the model depends on the ability to account for all the existing reactions with proper rate constants and on the accuracy of the measured dissolved ion concentrations.

Several attempts to model single solute systems have met with reasonably satisfactory results. From experiments on $CHCl_3$, conducted at large scale (at the Miami EBRF), we have successfully predicted that the bimolecular rate constant that had been reported in the literature for $CHCl_3$ and e^-_{aq} was possibly incorrect (Mak et al., 1997). Upon reexamination of the rate, the literature value was found to be nearly three times too fast (Tobien et al., 2000a).

Another example of successful kinetic modeling of pollutant destruction is CCl_4, a compound that is not destroyed by traditional AOPs. The following equations summarize the reactions of CCl_4 with the various reactive species and subsequent reactions that are important in its destruction:

$$CCl_4 + e^-_{aq} \rightarrow CCl_3 + Cl^- \qquad 1.3 \times 10^{10}\ M^{-1}\ s^{-1} \tag{5.5.1.19}$$

$$CCl_4 + H\cdot \rightarrow CCl_3 + Cl^- + H^+ \qquad 3.2 \times 10^{7}\ M^{-1}\ s^{-1} \tag{5.5.1.20}$$

$$\cdot CCl_3 + O_2 \rightarrow CCl_3OO\cdot \qquad 3.3 \times 10^{9}\ M^{-1}\ s^{-1} \tag{5.5.1.21}$$

$$\cdot CCl_3 + \cdot CCl_3 \rightarrow Cl_3CCCl_3 \qquad 3.7 \times 10^{8}\ M^{-1}\ s^{-1} \tag{5.5.1.22}$$

We have shown that the kinetic model developed to describe the decomposition of the CCl_4 (for example, see Table 5.5.1.7 where data for a nominal concentration of 1000 μg/L is summarized) appears to be accurate over a number of concentrations and solution pH (Mak et al., 1997). In experiments conducted at large scale at the Miami EBRF, we showed that in the presence of methanol as an XOH scavenger, we were able to predict the effect relatively accurately (Table 5.5.1.8). The addition of methanol was convenient and it can be thought of as a general XOH scavenger. Further studies are in progress to improve the model, in particular for multiple solute systems.

We have chosen simple examples with well-known and simple destruction mechanisms. For more complex organic compounds and in particular high concentrations, a detailed reaction mechanism is very helpful to obtain good agreement between empirical and modeled results.

TABLE 5.5.1.5 The Reactions Describing Water Radiolysis (10^{-7} s after electron injection), the Reactions with Common Constituents of Natural Waters and the Disinfectant Monochloramine, and the Bimolecular Rate Constants

Equation	Reactants		Products	k (M^{-1} s^{-1})	
(1)	$COH + H_2$	→	$HC + H_2O$	4.00×10^7	Pure water reactions
(2)	$COH + H_2O_2$	→	$O_2\text{-}C + H_2O$	2.70×10^7	
(3)	$COH + HO_2\text{-}$	→	$H_2O + O_2\text{-}C$	7.50×10^9	
(4)	$COH + O_2\text{-}C$	→	$O_2 + OH^-$	1.10×10^{10}	
(5)	$COH + H_2O_2^+$	→	$O_2 + H_3O^+$	1.20×10^{10}	
(6)	$COH + HO_2C$	→	$O_2 + H_2O$	1.00×10^{10}	
(7)	$COH + COH$	→	H_2O_2	5.50×10^9	
(8)	$COH + OH^-$	→	$H_2O + O\text{-}C$	1.30×10^{10}	
(9)	$COH + O\text{-}C$	→	HO_2^-	2.00×10^{10}	
(10)	$O\text{-}C + H_2O$	→	$COH + OH^-$	9.30×10^7	
(11)	$O\text{-}C + HO_2^-$	→	$O_2\text{-}C + OH^-$	4.00×10^8	
(12)	$O\text{-}C + H_2$	→	$e^-_{aq} + H_2O$	1.20×10^8	
(13)	$O\text{-}C + H_2O_2$	→	$O_2\text{-}C + H_2O$	2.70×10^7	
(14)	$O\text{-}C + O_2\text{-}C$	→	$2OH^- + O_2$	6.00×10^8	
(15)	$e^-_{aq} + HC$	→	$H_2 + OH^-$	2.50×10^{10}	
(16)	$e^-_{aq} + e^-_{aq}$	→	$2OH^- + H_2$	5.50×10^9	
(17)	$e^-_{aq} + O_2$	→	$O_2\text{-}C$	1.90×10^{10}	
(18)	$e^-_{aq} + H_2O_2$	→	$COH + OH^-$	1.20×10^{10}	
(19)	$e^-_{aq} + O_2\text{-}C$	→	O_2^{2-}	1.30×10^{10}	
(20)	$e^-_{aq} + H^+$	→	HC	2.30×10^{10}	
(21)	$e^-_{aq} + H_2O$	→	$HC + OH^-$	8.90×10^2	
(22)	$e^-_{aq} + HO_2^-$	→	$COH + 2OH^-$	3.50×10^9	
(23)	$e^-_{aq} + COH$	→	OH^-	3.00×10^{10}	
(24)	$e^-_{aq} + O\text{-}C$	→	$2OH^-$	2.20×10^{10}	
(25)	$HC + O_2$	→	HO_2C	2.10×10^{10}	
(26)	$HC + O_2\text{-}C$	→	$HO_2\text{-}C$	2.00×10^{10}	
(27)	$HC + HC$	→	H_2	5.00×10^9	
(28)	$HC + COH$	→	H2O	7.00×10^9	
(29)	$HC + HO_2C$	→	H_2O_2	1.00×10^{10}	
(30)	$HC + H_2O_2$	→	$H_2O + COH$	9.00×10^7	
(31)	$HC + OH^-$	→	$e^-_{aq} + H_2O$	2.20×10^7	
(32)	$HC + H_2O$	→	$H_2 + COH$	1.00×10^1	
(33)	$HO_2C + O_2\text{-}C$	→	$O_2 + H_2O_2 + OH^-$	9.70×10^7	
(34)	$HO_2C + HO_2C$	→	$H_2O_2 + O_2$	8.30×10^5	
(35)	HO_2C	→	$H^+ + O_2\text{-}C$	8.00×10^5	
(36)	$H^+ + O_2^-C$	→	HO_2C	4.50×10^{10}	
(37)	$H^+ + HO_2^-C$	→	H_2O_2	2.00×10^{10}	
(38)	$H^+ + OH^-$	→	H_2O	1.43×10^{11}	
(39)	H_2O_2	→	$H^- + HO_{2-}$	3.56×10^{-2}	
(40)	H_2O	→	$OH^- + H^+$	2.60×10^5	
(41)	$HCO_3^- + COH$	→	$CO_3^-C + H_2O$	8.50×10^6	Alkalinity Reactions
(42)	$HCO_3^- + e–_{aq}$	→	PDTS	1.00×10^6	
(43)	$HCO_3^- + HC$	→	PDTS	4.40×10^4	
(44)	$CO_3^{2-} + COH$	→	$CO_3^-C + OH^-$	3.90×10^8	
(45)	$CO_3^{2-} + e^-_{aq}$	→	PDTS	3.90×10^5	
(46)	$CO_3^-C + COH$	→	PDTS	3.00×10^9	
(47)	$CO_3\text{-}C + O_2\text{-}C$	→	$O_2 + CO_3^{2-}$	6.50×10^8	
(48)	$CO_3\text{-}C + H_2O_2$	→	$HCO_3^- + HO_2C$	8.00×10^5	
(49)	$CO_3\text{-}C + HO_{2-}$	→	$HCO_3^- + O_2^-C$	5.60×10^7	
(50)	$CO_3^-C + CO_3^-C$	→	PDTS	2.00×10^7	
(51)	$DOC + e^-_{aq}$	→	PDTS	1.00×10^7	DOC reactions
(52)	$DOC + HC$	→	PDTS	1.00×10^7	
(53)	$DOC + COH$	→	PDTS	2.00×10^8	
(54)	$NO_3^- + e^-_{aq}$	→	NO_3^{2-}	9.70×10^9	Nitrate ion reactions
(55)	$NO_3^- + HC$	→	PDTS	1.40×10^6	

TABLE 5.5.1.5 (Continued) The Reactions Describing Water Radiolysis (10^{-7} s after electron injection), the Reactions with Common Constituents of Natural Waters and the Disinfectant Monochloramine, and the Bimolecular Rate Constants

Equation	Reactants		Products	k (M^{-1} s^{-1})	
(56)	$NO_3^{2-} + O_2$	→	$O_2^- + NO_3^-$	2.20×10^8	
(57)	$Br^- + H\cdot$	→	PDTS	2.80×10^7	Bromide ion reactions
(58)	$Br^- + \cdot OH$	→	PDTS	1.10×10^{10}	
(59)	$NH_2Cl + e^-_{aq}$	→	PDTS	**1.00×10^8**	Chloramine Reactions
(60)	$NH_2Cl + \cdot OH$	→	PDTS	**1.00e $\times 10^8$**	

Bolded bimolecular reaction rate constants have not been measured and these are estimates only.

TABLE 5.5.1.6 The Absorbed Dose and Dose Rate Conversion for the Electron Beam Research Facility, Assuming a Beam Residence Time of 0.091 s

Absorbed Dose (Mrad)	Dose Rate[a] (eV/L s)
0.025	1.71×10^{22}
0.050	3.43×10^{22}
0.100	6.86×10^{23}
0.200	1.37×10^{23}
0.300	2.06×10^{23}
0.400	2.74×10^{23}
0.500	3.43×10^{23}
0.600	4.12×10^{23}
0.700	4.80×10^{23}
0.800	5.49×10^{24}
0.900	6.17×10^{24}
1.000	6.86×10^{24}

[a] 1 Mrad = 6.24×10^{22} eV/L; therefore, using a beam residence time of 0.091 s, an absorbed dose of 1 Mrad yields a dose rate of 1.25×10^{24} eV/L/s

Disadvantages of the Electron Beam Treatment Process

There appear to be two disadvantages of the electron beam process that are severely limit its widespread application. The first one is that, although it has been shown to work, the capital costs make it difficult to rationalize. In cases in which there has been an economic analysis, even in cases where it is competitive with alternatives, engineers shy away from specifying a system that has large capital costs in the electron accelerator. Because, if it does fail, even after having completed on-site demonstrations, they feel that they will be stuck with an expensive accelerator. Simply put the financial and professional risks are too great to offset the potential benefits.

It should be pointed out that although the use of electron accelerators has not found application in the environmental field, they are the industry standard for many applications and have a proven operational and maintenance record for over 40 years. For example, the operational reliability of an insulated iron core-based accelerator (like the one at the Miami EBRF) is 97 to 99% on an annual basis. It is more likely that pumps will fail than the accelerator will experience a problem.

A second reason why the electron beam process has not found widespread acceptance in the environmental field is that it is an innovative treatment process. And again, the risk to the engineer of recommending an innovative process does not outweigh the possible benefits, no matter what the economic analysis has shown.

TABLE 5.5.1.7 Experimental Observations and Model Predictions of Carbon Tetrachloride Removal (%) from Solutions that were Nominally 1000 µg/L Before Treatment

pH	Dose (krad)	% Removed Experimentally	% Removed Kinetic Model	Error (%)
5	100	91	90	1
	200	97	99	–2
	300	99	100	–1
7	100	72	79	–7
	200	97	96	1
	300	98	99	–1
9	100	71	71	0
	200	93	99	–6
	300	96	100	–4

TABLE 5.5.1.8 Experimental Observations and Model Predictions of Carbon Tetrachloride Removal (%) in the Presence of Methanol as an XOH Scavenger

Methanol (m*M*)	Dose (krad)	% Removed Experimental	% Remove Kinetic Model	Error (%)
0.1	100	87	90	–3
	300	98	100	–2
	500	99	100	–1
0.4	100	88	94	–6
	300	98	100	–2
	500	99	100	–1
4.0	100	98	89	9
	300	98	100	–2
	500	99	100	–1

One of the major efforts that is needed is to develop lower cost accelerators. Once that has been achieved, the process is likely to find widespread application in environmental applications. Alternatively, a niche market must be found that only the E-beam process can solve. With time and operational success in this setting, the innovativeness of the process will be eliminated and additional opportunities will present themselves.

Summary and Advantages of the Electron Beam Process

The electron beam process has a number of advantages that make it a highly versatile treatment process. These advantages can be summarized as:

- The process is non-selective in the destruction of organic chemicals because strongly reducing reactive species (e^-_{aq}/H·) and strongly oxidizing reactive species (XOH) are formed at the same time and in approximately the same concentration in solution.
- Reactions of organic chemicals with the electron beam induced reactive species are very rapid and occur in less than 1 second. This allows the design of a flow-through system with good process flexibility at full scale in the event the flows vary with time.
- The formation of the reactive species is pH independent in the range 3 to 11. Therefore, any differences that exist in pH over time will not adversely affect the treatment efficiency.

- The process can effectively treat aqueous streams and slurried soils, sediments, and sludges, and gases. In fact, there are several large (800 kW) systems being installed for the oxidation of flue gases NO_x and SO_x to NO_3^- and SO_4^{2-} with scrubbing by ammonia to produce fertilizer. These are the first industrial-scale electron beam systems to be built.
- The process is temperature independent.
- The process produces no organic sludge.
- The process produces no air emissions.
- Because of the above, the electron beam process can be used efficiently and effectively as pretreatment for biological remediation.

There is one electron beam system in operation at a dye manufacturing site in Korea; it is owned and operated by Samsung Heavy Industries (Han, 1999).

With the limited successes currently in place and if the capital cost issues (and the fact that it is an innovative treatment process) can be overcome, it is likely that the process will see widespread use in the environmental area.

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5.5.2 High Energy Photons for Waste Treatment

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Introduction

The use of ionizing radiation to selectively decompose target pollutants in solution has only recently gained adequate appreciation. Radioisotope sources, especially ^{60}Co, are inexpensive and already used in other process applications. Most radiolysis research has been performed with Co γ-rays, often in anticipation that the results will be used for scale-up to process applications with electron beams (e-beams). For mixed wastes, regulated hazardous constituents are decomposed or precipitated. The matrix remains intact, and *radioactivity is not induced in the material being treated.*

The reactions resulting from γ-irradiation are the same as those of e-beam irradiation. The advantage of photons is that they carry no charge, allowing deep penetration into the irradiated medium prior to energy deposition. This makes possible the *in situ* treatment of the contents of drums and systems, and requires less demanding engineering for presentation of the matrix to the source. Alternately, machine-generated bremsstrahlung can be used in place of isotopic γ-rays. The use of photon sources fills a niche that complements the use of e-beams for waste treatment.

Fundamentals

The Interactions of Energetic Photons with Matter

For ionizing γ- and X-ray photons, the important interactions with the absorbing medium result in the production of electrons. Secondary electrons have considerable kinetic energy and cause further ionizations, resulting in a continuum of X-rays and electrons until the original photon energy has been absorbed. Because these photon energies are orders of magnitude higher than the energy of chemical bonds, the original energy is usually not crucial in determining the chemical effects of the event. The result is the generation of ionic and radical species characteristic of the irradiated medium. Because neutral reactive radicals are also produced, the ability to degrade the target is not necessarily proportional to only the free ion yield of the irradiated medium.

The reactive ion and radical species created by these events can diffuse away from the spurs in which they were generated, or they can undergo geminate recombination. Those that migrate into the bulk medium are available to react with other species present. The decomposition of target compounds by reactive species generated from the matrix is the essence of waste treatment by radiolysis. Direct interaction of the photon with the pollutant is rare, and can occur only as a function of that compound's abundance in the matrix.

Solution chemistry is thus a prerequisite for efficient radiolytic waste treatment. Direct irradiation of soil and of target compounds absorbed onto solid media have required prohibitively large amounts of radiation. However, in certain cases, the pollutant can be transferred by pretreatment to a solution suitable for radiolysis (see e.g., Curry et al., 1998).

The majority of solutions to be treated are aqueous and the ability to degrade a pollutant in water depends on the target's reactivity with the products of water radiolysis. Powerful oxidizing and reducing species are produced according to Equations 5.5.2.1 and 5.5.2.2 below (Buxton et al., 1988):

$$H_2O \rightarrow H_2O^+ + e_{aq}^- + H_2O^* \tag{5.5.2.1}$$

$$H_2O^+ + H_2O \rightarrow H_3O^+ + OH \tag{5.5.2.2}$$

The bimolecular rate constants (k) for the reaction of many compounds with these products have been tabulated (Buxton et al., 1988), and can be used to propose treatments for various compounds. The yields (G values) of the reducing electrons (e_{aq}^-) and oxidizing hydroxyl radicals (OH) are approximately equal, at 2.6 per 100 eV in neutral water. The electron yield drops off sharply at low pH due to scavenging by H^+. At high pH, OH dissociates to yield H^+ and O^-. A wide range of additional minor but important species are produced although waste treatment processes generally interpret their results with respect to reactions involving e_{aq}^- and OH.

Although the G values for the production of e_{aq-} and OH are nearly equal over the pH range 4 to 11, the electron is also captured in aerated solution according to Equation 5.5.2.3:

$$e_{aq-} + O_2 \rightarrow O_2^- \tag{5.5.2.3}$$

The superoxide anion product of Equation 5.5.2.3 is also a mild reducing agent, but has a low rate of reaction with many solutes. Thus, the radiolysis of air-saturated water produces a predominantly oxidizing system. However, reductive attack cannot be discounted for all targets because compounds with high electron affinity may still compete for electrons. The presence of other competing species can also not be ignored. They may seriously deplete the population of radicals necessary for target treatment. An important OH scavenger common to water is carbonate/bicarbonate alkalinity, shown in Equation 5.5.2.4:

$$OH + HCO_3^- \rightarrow H_2O + CO_3^- \tag{5.5.2.4}$$

The product of Equation 5.5.2.4 is the carbonate radical anion, which can also oxidatively attack some compounds.

Kinetics is important to process design. The rate of pollutant decomposition determines the energy required, and ultimately the cost of treatment. The removal of a target compound [T] by a free radical [OH] is governed by Equation 5.5.2.5:

$$d[T]/dt = k[T][OH] \tag{5.5.2.5}$$

where k is the bimolecular rate constant (in L/mol·s). In practice, target concentrations often decrease exponentially, resembling first-order kinetics. Several conditions may cause this behavior. If the radical species predominates, pseudo-first-order kinetics results and target decomposition can be modeled using Equation 5.5.2.6.

$$d[T]/dt = k'[T] \tag{5.5.2.6}$$

where k′ is a pseudo-first-order rate constant that can be determined empirically for a given set of conditions. Alternately, the radical concentration may be constant because it is continuously generated during irradiation. This can also be described by Equation 5.5.2.6.

Competition by scavengers can also cause exponential target decomposition. The ratio of the rate of target radical capture to scavenger radical capture is shown in Equation 5.5.2.7:

$$\frac{d[\mathrm{T}]/dt}{d[\mathrm{S}]/dt} = \frac{\mathrm{k}[\mathrm{T}][\mathrm{OH}]}{\sigma[\mathrm{S}][\mathrm{OH}]} \tag{5.5.2.7}$$

where [S] is the scavenger concentration and σ is the rate constant for its reaction with OH. If [S] >> [T], then $\mathrm{k}/\sigma[\mathrm{S}]$ reduces to a new constant k′, and the result again mimics first-order kinetics.

Other situations are possible, in which a combination of reactions mimics first-order kinetics. While exponential concentration decreases may reveal little about actual reaction mechanisms, they are common and useful for predicting dose requirements for target decomposition.

Target removal efficiency is thus often expressed conveniently in terms of k′, or as d, the dose constant which is expressed with respect to absorbed dose rather than time. Thus, dose requirements for many processes can be predicted using a modified first-order-rate law:

$$\mathrm{C} = \mathrm{C_o}\ e^{-\mathrm{dD}} \tag{5.5.2.8}$$

where D is the absorbed dose required to reduce the initial concentration $\mathrm{C_o}$ to a new concentration C.

The G value of traditional radiation chemistry represents a target decomposition rate at an instantaneous concentration during irradiation. This is not a disadvantage for describing pure water radiolysis, where the water concentration remains constant. It is not useful, however, for describing the exponential target concentration changes commonly found in waste treatment. Since G and d are both a measure of target decomposition with respect to dose, they are related if the target concentration decrease is exponential. This is shown in Equation (5.5.2.9):

$$\mathrm{G_o} = \mathrm{d}\ [\mathrm{T}]_\mathrm{o} \tag{5.5.2.9}$$

where $[\mathrm{T}]^\mathrm{o}$ is the initial concentration of the target compound. The G value here is expressed as the initial G value ($\mathrm{G_o}$) at zero absorbed dose. An example of a typical target decomposition curve, $\mathrm{G_o}$ and d determinations, are shown in Figure 5.5.2.1.

A further consideration when predicting dose requirements is the nature of the by-products. It is tempting to suggest that undesirable compounds are mineralized, but this is not usually, immediately true. Intermediate compounds may be less desirable than the starting material and any treatment (including non-radiolysis methods) that fails to address them should be viewed with skepticism. For example, the reaction of the OH radical with organic compounds usually results in hydrogen abstraction from saturated carbons, and OH radical addition to unsaturated sites. For halogenated organics, the addition usually occurs at an unsubstituted carbon. The conversion of the target to a hydroxylated chlorocarbon results in a measureable decrease in the original pollutant concentration, but is hardly mineralization to a nonhazardous product. In the absence of appropriate analytical measurements, the new compound can remain undetected. Fortunately, the by-product will often be an intermediate that is also susceptible to radiolysis. Thus, dose requirements for treatment should also consider decomposition of unwanted by-products.

The radiolysis of organic solutions results in a reducing system. Hydroxyl radicals generated from alcohol or trace water are rapidly scavenged and are unavailable for reaction with targets. The electron then becomes the most important reactive species, even in the presence of oxygen. Deaeration may then increase radiolysis efficiency. In special cases, other reactive species can act as electron transfer agents. The most important example is the well-known alkaline isopropanol system (Shimokawa and Sawai, 1977). Reducing systems are extremely efficient at dehalogenation, but do not appear to be capable of decomposing aromatic rings.

A sampling of the radiation chemistry literature follows, selected to provide examples of both oxidative and reductive reactions and an appreciation for the versatility of the process.

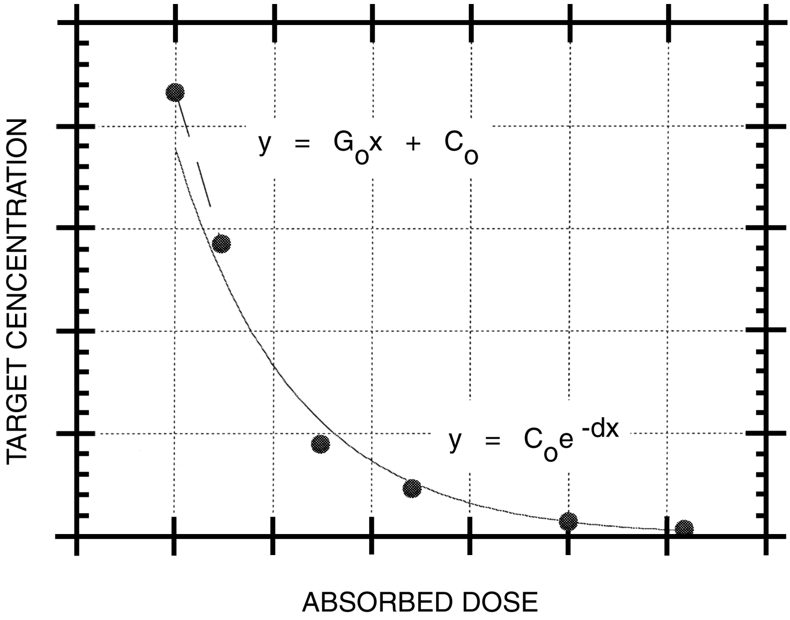

FIGURE 5.5.2.1 The exponential concentration decrease of an irradiated target compound with respect to dose may be modeled as a rate (G_o), or as a rate constant (d) the rate constant is useful for process calculations.

Applications

Aqueous Radiolysis of Organic Pollutants

Halogenated compounds are common contaminants of wastewaters, groundwaters, and drinking waters. This is due to contamination from industrial processes and intentional chlorination. An example of aqueous methylene chloride radiolysis is provided by Getoff (1989). Using ^{60}Co, inorganic chloride ion and formaldehyde were produced, at rates dependent on the methylene chloride concentration. The formaldehyde intermediate reached a maximum concentration, then decreased as it was mineralized by continued irradiation. Similar results were obtained for chloroform.

Bromo- and chloromethanes have been decomposed with γ-ray and e-beam irradiation (Cooper et. al., 1993). Inorganic halides and formaldehyde were produced stoichiometrically. Dehalogenation occurred due to a combination of reductive and oxidative processes; however, deoxygenated solutions showed reduced destruction efficiency. Thus, dechlorination mainly occurred oxidatively, as shown in Equations 5.5.2.9 through 5.5.2.11:

$$CHCl_3 + OH \rightarrow H_2O + CCl_3 \tag{5.5.2.9}$$

$$CCl_3 + O_2 \rightarrow CCl_3OO \tag{5.5.2.10}$$

$$CCl_3OO \rightarrow \rightarrow \rightarrow CO_2 + 3Cl^- \tag{5.5.2.11}$$

The product of Equation (5.5.2.10) is a peroxyl radical, which is an important intermediate in the oxidative decomposition of many organic compounds. Oxygen must be present for peroxyl radical formation, and many have reported that oxidative radiolysis is more efficient in oxygenated systems. The peroxyl radical hydrolyzes in Equation (5.5.2.11) (exact reaction mechanism unknown). The reported products are inorganic chloride, formaldehyde and CO_2. A d of 0.061 krad^{-1} (6.1 kGy^{-1}) was reported for bromoform and 0.013 krad^{-1} (1.3 kGy^{-1}) for chloroform (Cooper et. al., 1993).

The previous example shows that the oxygen concentration can affect radiolysis efficiency. Because γ-irradiations are often performed in sealed containers, the consumption of oxygen by electrons (Equation (5.5.2.3)) alters the system chemistry as the irradiation proceeds. The results of sealed irradiations must be interpreted with caution and are not desirable for oxidative treatments.

Trichloroethylene (TCE) and tetrachloroethylene (PCE) are two of the most common organochlorine compounds found in Superfund sites. Gehringer et al. (1988) and Proksch et al. (1987) have characterized, using ^{60}Co, the kinetics and mechanism of OH radical attack on TCE and PCE in aqueous solution. Trichloroethylene was readily decomposed in exponential fashion, with a reported G value of 5.4 molecules/100ev (d ~ 7 kGy^{-1}). A 10-ppm (76-μ*M*) solution was decontaminated with an absorbed dose of less than 600 Gy. One CO_2 molecule, one formic acid molecule, and three Cl^- ions were generated for each OH radical captured. These products were created by a series of at least nine reactions initiated by OH radical addition to the unsaturated TCE carbon (2.6×10^9 L/mol·s). The G values for TCE and PCE decomposition decreased with decreasing target compound concentration, similar to the methylene chloride irradiations of Getoff (1989).

Despite the very high bimolecular rate constant (1.2×10^{10} L/mol·s) for TCE capture of solvated electrons, Gehringer (1988) estimated that no more than 10% of the TCE was decomposed by reductive dechlorination. Reduction of TCE was limited by oxygen scavenging of electrons (Equation 5.5.2.3). Reductive dechlorination also produced inorganic chloride ion, and glyoxylic acid, rather than formic acid. The undesirable by-products (mono- and trichloroacetic acids) were not observed. Dichloroacetic acid was generated as an intermediate that disappeared upon continued irradiation. Dechlorination by a combination of oxidative and reductive radiolysis was shown to be stoichiometric. Aqueous TCE has also been irradiated by Getoff (1989), and Cooper (1993), who measured the same by-products. The presence of various radical scavengers, such as oxygen, carbonate, and nitrate, greatly reduced the treatment efficiency.

Tetrachloroethylene (PCE) at 10 ppm (60 μ*M*) behaved similarly, with a lower G values of 4.4 molecules/100ev (d Ý 7 kGy^{-1}) (Proksch et al., 1987). The lower G is expected because of PCE's lower rate constant (1.7×10^9 L/mol·s) for OH radical capture, although the molar concentrations were not identical. The decomposition was first order, trending toward zero order at the highest PCE concentrations.

Aromatic compounds are especially stable, and are therefore important pollutants. They include benzene, substituted benzenes, polyaromatic hydrocarbons (PAHs) which may be halogenated, (e.g., polychlorinated biphenyls [PCBs], which many pesticides. Aromatic rings are susceptible to OH radical attack. The oxidation is initiated by OH radical addition to the ring, which generates the hydroxycyclohexadienyl radical. Oxygen addition may then produce a peroxyl radical from the cyclohexadienyl radical, ultimately resulting in decomposition of the aromatic ring. However, irradiation of benzene with insufficient O_2 initially produces a more toxic solution due to phenol generation. Fortunately, phenol also is attacked by OH radicals, and continues to degrade. Continued oxidation in the presence of O_2 predicts mineralization of benzene to carbon dioxide, but various carboxylic acids are usually the reported products.

An example of aqueous phenol radiolysis is given by Getoff (1986), who used ^{60}Co γ-rays to produce polyhydroxybenzenes. Increased oxygen concentrations increased phenol radiolysis efficiency, presumably due to ring-opening reactions. The products were carboxylic acids.

The presence of various macroimpurities, as expected in actual wastewaters, reduces phenol radiolysis efficiency. Because the OH radical is known to be scavenged by carbonate/bicarbonate ions, the oxidative decomposition of aromatic compounds should be less efficient at higher pH. However, the rates of toluene and benzene decomposition remained the same in the pH range 5 to 9 (Nickelsen et al., 1994). It was theorized that carbonate radical anion (Equation 5.5.2.4) can also oxidatively attack the targets.

When 3 μ*M* methanol was used by Nickelsen to simulate the scavengers expected in waste water, the radiation needed for benzene removal increased by a factor of 15. Methanol capture of OH radical to produce the hydroxymethyl radical is shown in Equation 5.5.2.12:

$$CH_3OH + OH \rightarrow CH_2OH + H_2O \qquad (5.5.2.12)$$

which illustrates the dramatic impact of scavenger species on dose requirements for treatment of target compounds.

The presence of impurities can also alter reaction mechanisms. Nitrated species are produced from benzene in irradiated waters containing high nitrate concentrations (Cooper et al., 1996). In that study, by-product formation — including phenol, nitrophenol, and nitrobenzene — was measured. These products were destroyed by continued irradiation. These γ-ray results were used for scale-up to an e-beam application.

Radiolysis of aqueous trinitrotoluene (TNT) results in trinitrobenzoic acid (Schmelling et al., 1998). When a reducing system was created by N_2 sparging to remove O_2, and *t*-butanol addition to remove OH radicals (analogous to Equation 5.5.2.12), it was discovered that the rate of TNT radiolysis was higher. However, N_2 sparging in the absence of *t*-butanol did not have the same result. A probable explanation is that *t*-butoxy radicals undergo adduct formation with the TNT radical anion produced by electron capture. Adduct formation analogous to that shown for TNT in Equation (5.5.2.13) is known for many species irradiated in the presence of alcohol.

$$C_6H(NO_2)_3CH_3 + (CH_3)_3CH_2COH \rightarrow C_6H[(CH_3)_3CH_2COH](NO_2)_3CH_3 \qquad (5.5.2.13)$$

In the absence of *t*-butanol, TNT radicals were not converted into adducts, and probably decayed back to TNT. It was suggested that reductive irradiation of TNT may be preferred to oxidative irradiation due to the higher rate of TNT decomposition. However, this would only be true if the adduct is an acceptable product. In contrast, the oxidizing system allows for aromatic ring decomposition and eventual mineralization of TNT.

Polyaromatic hydrocarbons (PAHs) also react with OH radical. These compounds have limited water solubility and most studies have investigated gas-phase reactions. Napthalene was shown to be subject to a complex series of hydroxylations and peroxyl-induced ring-opening reactions leading to the production of organic acids (Bunce et al., 1997). Although conducted in the gas-phase, the products are similar to the aqueous-phase chemistry discussed here.

The PCBs, noted for their exceptional stability and ubiquitous environmental distribution, are representative of halogenated aromatic compounds. While extremely susceptible to reductive dechlorination by electron capture, they are not efficiently decomposed reductively in aerated, aqueous solution. They are attacked by OH radicals, forming intermediates of varying levels of hydroxylation (Sedlak and Andren, 1991). Presumably, these hydroxylated compounds would be susceptible to peroxyl radical formation and ring-opening reactions in the presence of oxygen; but due to their limited water solubility, few studies have examined the aqueous radiolysis of PCBs.

Nonaqueous Solution Irradiations

Many environmentally important pollutants have such limited water solubility that their aqueous chemistry is difficult to study. Among these are the PCBs, PAHs, dioxins, and many pesticides. While it has been shown that halogenated compounds can be oxidatively decomposed, the rate constants for electron capture predict more efficient reductive decomposition. Phenyl rings are not reductively decomposed, but a dehalogenated product may be sufficient for waste treatment purposes.

Organic solutions scavenge OH radicals and provide the opportunity to perform radiolysis in a purely reducing environment. Deaeration of organic solutions increases treatment efficiency.

Most nonaqueous radiolysis of halogenated compounds has been performed in alkaline isopropanol. This solvent produces G values orders of magnitude higher than in the neutral alcohol via establishment of a dehalogenation chain reaction with the hydroxyisopropyl radical as an electron transfer agent. This chain reaction is well-known, but most other alcohols do not sustain it. When chlorinated benzenes were irradiated in alkaline isopropanol, the products were less-chlorinated benzenes, chloride anion, and acetone (Shimokawa and Sawai, 1977). The acetone is a product of isopropanol radiolysis. Chlorophenylpropanols were also produced, probably by adduct formation analogous to the reaction in Equation 5.5.2.13.

While the radiolysis of pollutants in alcohols may appear to have limited utility, there are practical niches. Singh has suggested decontamination of drained PCB transformers in alkaline isopropanol (Singh et al., 1985). Pretreatment technologies can also be used to transfer pollutants from soil or debris to a solvent. While direct irradiation of contaminated soils is impractical due to high dose requirements, PCBs can be transferred from soils to solution for irradiation (Curry et al., 1998).

Polychlorinated biphenyls have also been irradiated directly in transformer and other oils (Mincher, 1998). The products were less-chlorinated PCBs and biphenyl. Adduct formation has also been shown. Dechlorinated alkane/PCB adducts are similar to compounds that are normal components of transformer oils, and thus may be an acceptable product.

As in aqueous radiolysis, solution constituents that compete for reactive species can severely suppress decomposition of the target compound. Mincher (1998) showed that hydraulic oils containing an unidentified impurity measurable by ECD gas chromatography had a PCB dose constant of only half that of clean oil with the same concentration of PCBs. A process wherein transformer oils are irradiated to selectively decompose PCBs and chlorobenzene has been recommended.

Radiolysis for Heavy Metal Treatment

The radiolytic precipitation of several heavy metals, including chromium, lead, and mercury, has been demonstrated (Chaychian et al., 1998). Ions were reduced by solvated electron or hydrogen atom reaction, and precipitated. Higher efficiencies were realized with N_2 sparging, and the use of alcoholic or acetic acid OH radical scavengers and buffering. Metals were also precipitated from their EDTA complexes.

Economics

Cleland et al. (1984) have examined the economics of waste treatment using isotopes such as ^{137}Cs and ^{60}Co, and compared them to e-beam irradiation. It was found that the economics of the process favors isotopes when dose requirements are low. When dose requirements become high, the large amount of the isotopes needed, coupled with replacement costs due to radioactive decay, favor machine-generated radiation. However, isotope sources will likely continue to fill the niche of being excellent experimental tools, and for specialized treatment applications.

Summary

The application of isotope sources of ionizing radiation for the decomposition of many compounds of environmental concern has been demonstrated. Decomposition of pollutants is the result of their reaction with free radicals produced by the action of radiation on the aqueous solvent. Thus, radiolysis has much in common with other treatment techniques that rely on radical generation. The mechanism and kinetics of these reactions are understood for many common pollutants and the by-products are known. While it is likely that process radiolysis will rely on e-beams, isotopes sources have a role to play in research and in specialized process applications.

Defining Terms

Ionizing radiation: For waste treatment purposes, electromagnetic radiation of sufficient energy to cause ionization. This may consist of γ-rays, X-rays, and electrons in the range of about 10 eV to 10 MeV.

Target: A matrix, medium, or individual compound that is irradiated with ionizing radiation.

Radiolysis: The chemical reactions that occur due to irradiation of a target. Radiolysis is synonymous with *radiation chemistry.*

Bremsstrahlung: X-rays produced by stopping an e-beam in an appropriate target.

Spurs: A volume of irradiated medium along the trajectory of a photon or electron that contains excited and ionized molecules.

Geminate recombination: The recombination of a radioltyically produced electron with its parent cation, preventing reaction of the electron with a target species.

G value: A measure of radiolysis, where G(X) is the number of molecules of X created or destroyed per 100 eV of energy absorbed. The SI units are mol/J, which equals 9.649×10^6 molecules per 100 eV.

Scavenger: A species that reacts with (or scavenges) one of the reactive species produced by radiolysis. Scavengers often interfere with desired reactions.

Dose constant: A measure of radiolysis efficiency, where d is the slope of the logarithmic plot of exponential target concentration vs. absorbed dose. The units are reciprocal dose.

Absorbed dose: The radiation energy absorbed by the target medium. The SI unit is the Gray (J/kg); the English unit is the Rad, and 1 Rad = 0.01 Gy.

Mineralization: The conversion of a target compound to its fundamental inorganic constituents, usually meaning CO_2, H_2O, and possibly inorganic halogen salts.

Adduct formation: Products of radical/radical addition, usually between the solvent radicals and target radical. This reaction sometimes competes with mineralization, especially in nonaqueous radiolysis.

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For Further Information

More detail on the topics discussed in this section can be found in *Applied Radiation and Isotopes*, published monthly by Pergamon Press, Bampfylde Street, Exeter EX1 2AH, England. The journal *Radiation Physics and Chemistry*, also by Pergamon Press, often contains articles related to this topic. This journal also publishes the papers of the biennial International Meeting on Radiation Processing, which hosts sessions on many aspects of the industrial uses of radiation.

The American Chemical Society journal, *Environmental Science and Technology*, 1155 16th St., N.W., Washington, D.C., has lately begun to carry articles on radiolytic waste treatment. The new *Journal of Advanced Oxidation Technologies*, Science and Technology Integration, Inc., 100 Collip Circle, Suite 110, London, Ontario, Canada N6G 4X8, contains many of the latest developments in this field. This is also the journal in which to find information on the International Conference on Advanced Oxidation Technologies for Air and Water Remediation.

An excellent source of current information on the uses of radiation for enviromental purposes is found in the new book *Environmental Applications of Ionizing Radiation,* edited by W.J. Cooper, R.D. Curry and K.E. O'Shea, John Wiley & Sons, 1988, New York.

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5.6

Phytoremediation Technologies

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Introduction

Phytoremediation is the use of green plants and their associated rhizosphere microflora to remove, degrade, or stabilize complex environmental contaminants. Most current phytoremediation applications take advantage of the integrated biological activities of both a plant and its associated microbial communities. Microbial communities in the rhizosphere, the adjacent soil or water, and on the plant surfaces (e.g., leaves and shoots) can play an important role in remediation events occurring in the plant-microbe system. Various types of vegetation, including trees, grasses, and aquatic plants, are used *in situ* to decontaminate air, soil, and surface and groundwater systems. The use of plants to treat contaminated environments is not a new phenomenon. Cunningham et al. (1995) briefly described the historical use of aquatic plants for water remediation and noted that the ability of other plants to "remove airborne contaminants is also well known." Many accepted agricultural techniques for cultivating, harvesting, and processing plant materials have been adapted for phytoremediation applications, as have many conventional or common methods used to treat traditional pollutants such as sewage, food industry wastes, and industrial effluents.

Although plants have been used for centuries to manipulate and/or treat the environment, phytoremediation technologies are presently undergoing serious evaluation as cost-effective alternatives for remediating sites contaminated with toxic metals, radionuclides, and hazardous organics at a fraction of the cost of many conventional treatment technologies. Overall, the application of phytoremediation is being driven by its innovative technical and economic advantages over conventional approaches, and an increasing level of acceptance by government agencies, the private sector, and the general public. A recent directive from the Office of Solid Waste and Emergency Response (OSWER) implemented a program that clearly supports the use of innovative phytoremediation technologies, as well as other technological approaches. Issued under the Superfund Reform Initiatives, the directive is designed "to encourage the demonstration and use of innovative technologies with the potential to lower costs and/or improve performance at a particular site and at other Superfund sites, and to document these early applications to assist future selection of response actions." The directive also supports the developers of promising technologies, especially small businesses, by "enhancing contracting opportunities with Principal Responsible Parties (PRPs)," and encourages PRPs to "assume a more active role in the development of new technologies for site remediation." (OSWER homepage http://clu-in.com/riskshar.htm, 1998).

Fundamentals (Working Definitions)

Flathman and Lanza (1998) listed current phytoremediation technologies as:

1. *Enhanced rhizosphere biodegradation.* Enhanced rhizosphere biodegradation takes place in the soil surrounding plant roots. Natural substances released by plant roots serve as substrates to the indigenous microflora in the rhizosphere. The result is an increased and more diverse microbial population capable of enhancing the rate of treating the contaminants present.
2. *Phytoextraction and rhizofiltration.* Phytoextraction is the uptake of contaminants, particularly toxic metals and radionuclides, by plant roots and the translocation of these contaminants into plant biomass, including shoots, leaves, and woody tissue. Specially selected plants, known as hyperaccumulators, can extract and accumulate exceptionally high levels of contaminants from soil. Current approaches to phytoextraction involve the transfer of contaminants from soil and/or water to plant biomass for recycling or other disposal, leaving soil water in place that meets regulatory levels.

   A process called rhizofiltration has been developed that uses plants that are raised hydroponically and then relocated to sites for the purpose of removing metal contaminants from aqueous wastestreams. Hydroponic plant roots suspended in contaminated water take up and accumulate contaminants. When the plants become saturated with the contaminants, they are harvested for disposal. One study reported a sunflower rhizofiltration system that removed ^{137}Cs and ^{90}Sr from a contaminated pond near the Chernobyl reactor in the Ukraine (Dushenkov et. al., 1995).
3. *Phytodegradation alone or with phytovolatilization.* Phytodegradation is the metabolism of contaminants within plant tissue. Plant root, stem, and leaf enzymatic metabolic activities can convert and detoxify contaminants removed from air, soil, and water. Plant physiological systems can hydrolyze and dealkylate contaminants to less toxic metabolites and may volatilize the metabolites during the normal transpiration processes of photosynthesis.
4. *Phytostabilization.* Phytostabilization is the use of plants along with agronomic techniques to stabilize contaminated sites (Bradshaw and Chadwick, 1980). Typically, soil amendments are applied to contaminated soil to reduce the bioavailability of contaminants, and the site is planted into vegetation which reduces off-site migration of the contaminated soil. For example, a variety of alkalizing agents, phosphates, mineral oxides, organic matter, and biosolids have been used as soil amendments to render lead more insoluble and unavailable to leaching, mammalian ingestion, or plant uptake. Studies have also demonstrated that plant roots can effectively immobilize stabilized lead contaminants in soil and, therefore, reduce risk to the environment (Cunningham et al., 1995). Plant varieties that can develop a substantial root biomass capable of binding and retaining toxic metals in contaminated soils without transporting metal to the shoots are good candidates for phytostabilization applications. Reduced shoot transport eliminates the necessity of treating harvested shoot residue as hazardous waste.
5. *Alternative cover (i.e., vegetative cover system).* Alternative cover technologies use vegetative cover systems at landfill sites and other contaminated areas to help contain toxic chemicals and reduce their movement to other sites. Vegetative cover systems are under study for their potential to reduce surface-water infiltration into a landfill, thereby decreasing leachate generation through transpiration. There is also the potential of reducing the toxicity of covered materials through basic phytoremediation processes.

Inorganic Contaminants

The remediation of inorganic contaminants requires the physical removal of the contaminant from air, water, or soil, or the conversion of the contaminant to a biologically inert or nontoxic form. Inorganic contaminants can be removed from a system by phytoextraction processes that translocate pollutants from the system to plant biomass (i.e., roots, shoots, leaves, blades). Phytoextracted contaminants can be disposed of by harvesting the biomass at the remediation site. After harvesting, the biomass can be reduced in volume and/or weight by thermal, microbial, physical, or chemical means, thus reducing the cost of handling, transportation, processing, and landfilling (Cunningham and Ow, 1996). For example, lead is a commonly encountered contaminant that can be removed from soil, sediments, and water using phytoextraction methods (USEPA, 2000). In the case of some economically valuable metals (e.g., nickel, zinc, and copper), biomass can be sent to smelters or other extraction facilities for recovery and reuse. Contaminant volatilization is another mechanism for the phytoremediation of inorganic contaminants. Volatilization of selenium by plants or a plant/microbe system has been reported (Banuelos et al., 1998; Terry and Zayed, 1994), and the phytoremediation of mercury and methylmercury contaminated soils has been recently demonstrated using genetically engineered plants (Rugh et al., 1996; Heaton et al., 1998).

Phytoremediation systems that use phytoextraction as the primary mechanism of inorganic contaminant removal depend on the use of plant systems that can take up and tolerate relatively high concentrations of pollutants. Plants typically take up large amounts of elements that are esential to their growth, reproduction, and maintenance and small amounts of elements that are toxic. Phytoremediation systems typically use soil manipulations to enhance the contaminant extraction process, including nutrient, oxygen, water, and chelation amendments (e.g., EDTA, hydroxyethylethylene diaminetriacetic acid). Plant systems capable of efficiently phytoextracting relatively high concentrations of inorganic contaminants are called hyperaccumulators and offer considerable promise as phytoremediation systems.

Organic Contaminants

The mobility and fate of organic contaminants in air, water, and soil systems are regulated by the chemical's concentration, relative solubility, vapor pressure, molecular size, charge, and the concentration of other organics present. In complex soil and/or sediment systems, the ability of the substrate to absorb/adsorb/desorb organic contaminants is directly associated with the organic matter content of the soil or sediment, the type and amount of clay present, the basic soil/sediment structure, cation/anion exchange capacity, pH, and the residence time and water flux of the contaminant through the soil and/or groundwater profile. Plant root systems absorb organics in nearly direct relationship to their relative lipophilicity. Although absorbed chemicals can follow a variety of fate and transport pathways, many chemicals are substantially bound into plant tissues in a form that is less biologically available and not amenable to normal chemical extraction methods. In sandy soils low in organic matter, phytoremediation processes for root absorption of contaminants and harvesting of plant biomass may be quite effective. Phytoextraction of organic contaminants from soil by root accumulation, zylem translocation, and volatilization from leaf surfaces is also possible at some contaminated sites. Organic contaminants differ from inorganic pollutants in that they can be biodegraded or mineralized by plants and their associated microflora (Cunningham and Ow, 1996). Hathaway (1989) demonstrated that plants have significant metabolic activity in their root and shoot components, and Schnoor et al. (1995) reported that some of these metabolic enzymes may be useful in chemical remediation outside of the plant root and rhizosphere areas.

Applications and Examples of Phytoremediation Approaches

Increases in phytoremediation efficiency are often driven by key variables affecting both contaminant behavior and plant system growth and physiology. Figure 5.6.1 provides a generalized conceptual model of major factors influencing contaminant removal and phytoremediation efficiency in different plant systems. The biological, physical, and chemical factors in Figure 5.6.1 can influence the movement, uptake, and degradation of many organic and/or inorganic contaminants and help to regulate the processes involved in the efficiency of contaminant removal in different types of phytoremediation systems.

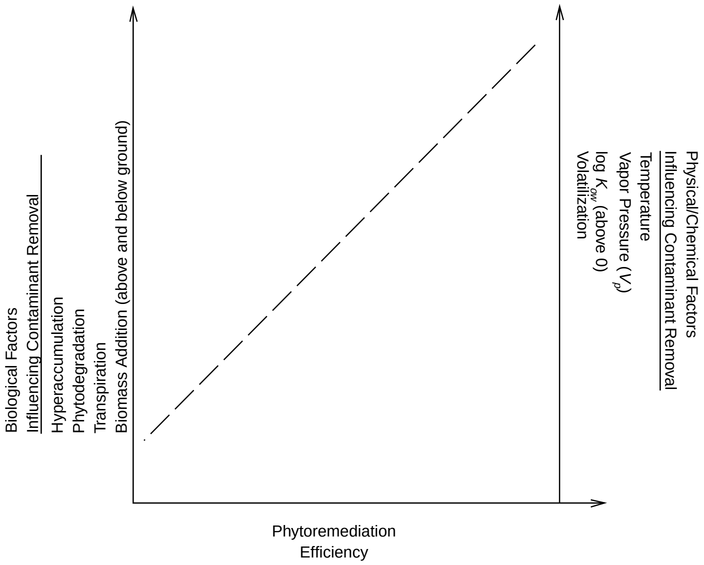

FIGURE 5.6.1 Generalized conceptual model — factors influencing phytoremediation efficiency.

Hyperaccumulation of Inorganic Contaminants

Plants classified as metal hyperaccumulators have special potential for wide-scale applications in phytoremediation (Baker and Brooks, 1989). Metal hyperaccumulation by plants is usually defined by the relationship between the concentration of a specific metal in the soil and the level of that metal accumulation in plant tissue. For example, plants that are classified as nickel hyperaccumulators typically take up 1000 μg of nickel in their stems and leaves to a final concentration of approximately 0.1% of their dry weight, while plants classified as zinc hyperaccumulators must absorb more than 1% zinc in their biomass on a dry weight basis. The reason for the difference is the fact that zinc has a higher soil background level than nickel and many other metals (Brown, 1995). Plants that can hyperaccumulate more than one type of contaminant are especially good candidates for development as treatment options for soils contaminated with complex mixtures of organic and inorganic chemicals and radioactive materials (i.e., mixed wastes). Brooks (1994) quantitatively characterized copper hyperaccumulation by plants by assigning a specific indicator value (s.i.v.). This approach may prove to be a useful method to characterize other types of inorganic contaminant hyperaccumulators.

$$\text{s.i.v.} = \frac{\text{HC} - \text{LC}}{\text{TSC}} \tag{5.6.1}$$

where

HC = Highest copper concentration in an individual plant sampled
LC = Lowest copper concentration in an individual plant sampled
TSC = Total soil copper concentration

(Modified from Brooks, 1994).

Good indicators of copper hyperaccumulation were plants with an s.i.v. of 4 or less. Brooks (1994) identified six copper hyperaccumulators using data describing maximum tissue copper concentrations (mg Cu/kg tissue) in the above-ground plant biomass as follows: *Ipomoea alpina* (12,300), *Lindernia perennis* (9322), *Haumaniastrum katangese* (8356), *Bulbostylis mucronata* (7783), *Pandiaka metallorum* (6260), *Gutenbergia cupricola* (5095) (Baker and Brooks, 1989).

Phytoextraction, Phytodegradation, and Phytovolatilization

Cunningham et al. (1995) reported that not all organic compounds are equally accessible to plant roots in the soil environment. Bell (1992) noted that plant roots have the inherent ability to absorb organic pollutants based on the relative lipophilicity of the compound. The relative lipophilicity of an organic contaminant can be characterized by measuring its relative partitioning between an octanol phase and a water phase expressed as the log of the partitioning coefficient or log K_{ow} where:

$$K_{ow} = \frac{[S]_{\text{octanol}}}{[S]_{\text{water}}} \tag{5.6.2}$$

where

S = Organic contaminant (the substance)
Square brackets [ ] = Concentrations of S in molarity or ppm units

Contaminants with log K_{ow} values above zero partition preferentially from a water phase into root biomass (Bell, 1992). Differences have been reported between roots, but generally the higher the contaminant's K_{ow} value, the greater the root uptake. In some soils, root uptake of contaminants followed by harvesting may provide a useful form of phyoremediation for organic contaminants (Cunningham et. al., 1995). In general, contaminants with K_{ow} values between 1.5 and 4.0 are the best candidates for phytoremediation. Contaminants with lower K_{ow} values would not be taken up by plant roots in significant amounts, and other plant mechanisms (e.g., water transpiration rates) might be better for manipulation as phytoremediation systems. Once a pollutant has been absorbed by the plant roots, it may be (1) sequestered in the root tissue, often in forms that are not available to extraction by solvents; (2) metabolized in the root tissue; and (3) transported out of the root and into the shoot either as parent material or in a slightly modified form (Cunningham et al., 1995). However, it is important to note that contaminant lipophilicity and K_{ow} can also lead to significant partitioning into soil humic matter and onto soil surfaces. Highly textured soils and soils with high levels of native organic matter could impede contaminant sorption by roots and make root harvesting difficult.

Phytovolatilization

Burken and Schnoor (1999) characterized the distribution and volatilization of selected organic contaminants using hybrid poplar trees clones (*Populus deltoides* x *nigra*, DN34) under experimental laboratory conditions. They reported a relationship between contaminant vapor pressure V_p and the volatilization of benzene, ethylbenzene, m-xylene, nitrobenzene, toluene, and TCE. Volatilization occurred from the leaf tissues. Activity from the root and stem portions of the trees were below detection limits. The authors reported the distribution and volatilization patterns of the contaminants and the volatilization of the contaminants as a function of contaminant V_p.

Benzene and TCE showed high volatilzation levels in these laboratory studies, with greater than 90% of the benzene and more than 70% of TCE volatilized from the leaf surfaces. The authors point out that the results of these experimental studies are based on relatively high chemical concentrations, different water uptake dynamics, and other conditions that are quite different than those encountered in most contaminated field sites. However, the general relationships between volatilization and the location of the contaminants in the plant tissue, and the volatilization of the contaminants as a function of vapor pressure, demonstrate the usefulness of bench-and pilot-scale studies in helping to predict the fate and transport for specific contaminants and plant species.

In contrast, field studies of TCE remediation with poplar trees over a 3-year period reported the greatest percent removal of TCE by plant tissue uptake and dechlorination, with less than 10% removal by volatilization (Newman et al., 1999).

Selection and Design of Phytoremediation Systems

The major considerations in selecting the best phytoremediation system for a specific site include (1) the type and location of the contaminated media, (2) the type and concentration of the contaminants, and

(3) the potential for the successful growth of the vegetation on site (e.g., climate, geomorphology). Table 5.6.1 outlines the phytoremediation technologies applicable to different types of contaminants. The appropriate phytoremediation technology should be selected using the basic parameters of media type (soil, water, air) and contaminant type or mix (e.g., radionuclide, heavy metal, PAH). Table 5.6.2 lists selected plants/trees either in use or under development as phytoremediation systems for inorganic and organic contaminants. Individual plants and/or mixtures of plants (e.g., trees and grasses; constructed wetlands) can be considered for different sites and contaminants. Table 5.6.3 provides criteria to assist the site remediation manager in selecting the appropriate phytoremediation system.

TABLE 5.6.1 Phytoremediation Technologies Applicable to Different Contaminant Types

	Phytoextraction		Rhizofiltration	Phytostabilization	Rhizodegradation	Phytodegradation
Technology Media	Soil	Water	Water	Soil	Soil	Soil/Water
Petroleum hydrocarbons	T				F	G
PAHs					F	
PCBs					T	
Pesticides					F	F
Chlorinated solvents	T				F	G/G
Munitions					G	G/F
Metals[a]	F	F	F	F		
Metalloids	T	F(Se)		T		
Non-metals	T					
Radionuclides[b]	G	F	F	G		
Nutrients			F[c]		G	F/F
Surfactants					T	

Note: The applicability of a particular method of phytoremediation to each contaminant type has been judged by the current state or stage of the application. This is indicated in the table by the following designations:

T = the application is at the theoretical stage;
G = the application has been researched in the greenhouse or laboratory;
F = the application has been researched using field plots or has been applied in full-scale field systems.

All contaminants can be controlled using vegetative cover systems. The vegetative cover system, riparian corridors, buffer strips, and hydraulic control are not included in the table because they can be considered combinations of the other phytoremediation technologies.

[a] Reeves and Brooks, 1983; Baker, 1995; Salt et al., 1995; Nanda Kumar et al., 1995; Cornish et al., 1995.

[b] Salt et al., 1995; Nanda Kumar et al., 1995; Cornish et al., 1995.

[c] In constructed wetlands.

Modified from USEPA, 2000.

McIntyre and Lewis (1997) outlined the major environmental and health risk assessment considerations in introducing plants into new environments for phytoremediation. They recommended considering the following elements as part of the risk assessment process:

1. Characteristics of the plant to be released, including information on its taxonomic identification, reproductive biology, and sexual compatibility with related species
2. Life history characteristics and ecological niche
3. Characterization of the ecosystem exposed or potentially exposed to the plant, including biotic and abiotic features and ecosystem processes
4. Potential environmental impacts of the introduction of the plant species at the genetic, population, and ecosystem levels; impacts include the potential of the plant to interbreed with related species in the ecosystem and nearby ecosystems
5. The potential of the plants or its hybrids to cause environmental degradation by disrupting ecosystem processes.

TABLE 5.6.2 Selected Plants/Trees in Use or under Development as Phytoremediation Systems for Contaminants

Plant Species	Contaminants
Alyssum montanum	Cu, Ni
Arabidopsis thaliana	Hg
Brassica juncea	Pb, U
B. napus	Se
B. nigra	Ni, Zn
Brassica spp.	Ni, Pb, Zn
Haumaniastrum katangese	Co, Cu
Helianthus annuus L.	L. Cd, Cr, Cs, Cu, Mn, Ni, Pb, Sr, Zn, U
Juncus spp.	Cu, Zn
Medicago sativa	Organics (PAHs)
Myriophyllum aquaticum	Organics (TNT)
M. spicatum	Cd, Cu, Ni, Pb, Zn
Panicum virgatum	Organics (PAHs)
Pelargonium sp.	Cd, Cu, Ni, Pb, hydrocarbons
Populus deltoides	organics (TCE)
P. tricocarpa x P. *deltoides* (line H 11-11)	B, Se, organics (TCE)
Prairie cascade	Organics (diesel range organics)
Salix viminalis, S. dasyclados	Cd, Zn
Salix spp.	(150 clones) Cd, Cu, Zn
Schizachyrium scoparium	Organics (PAHs)
Thiaspi alpestre	Pb, Ni Zn
T. caerulescens	Cd, Cs, Ni, Zn, U
T. rotundifolium	Ni, Pb
Typha spp	Al, Cd, Fe, Mn, Ni, Pb, U
Viola calaminara	Ni, Zn

Note: Data from Baker, 1981; Baker and Brooks, 1989; Black,1995; Brown, 1995; Kelly and Guerin, 1995; Dushenkov et al., 1995; 1997; Wang et al., 1996; Newman et al., 1997; Gordon et al., 1998; Heaton et al., 1998; Banuelos et al., 1999; IBC, 1999; Sobolewski, 1999.

Recently, the Phytoremediation Work Team of the Interstate Technology and Regulatory Cooperation Work Group (ITRC) produced a Phytoremediation Decision Tree to provide a tool that can help determine if phytoremediation can be effective at a given site (http://www.itrc.com). The authors suggest using the decision tree to compliment other phytoremediation documents such as the U.S. EPA's Introduction to Phytoremediation (U.S. EPA, 2000).

Large Field Site Demonstrations

The U.S. EPA's Office of Solid Waste and Emergency Response and Office of Research and Development (ORD) established the U.S. EPA's Superfund Innovative Technology Evaluation (SITE) Program. This program was formed in response to the 1986 Superfund Amendments and Reauthorization Act, which recognized a need for an "Alternative or Innovative Treatment Technology Research and Demonstration Program." The SITE Demonstration Program encourages the development and implementation of innovative treatment technologies for hazardous waste site remediation.

The U.S. EPA's National Risk Management Research Laboratory (NRMRL) in Cincinnati, Ohio, currently operates two SITE demonstrations on phytoremediation. The first involves a field demonstration initiated by the U.S. Air Force at Carswell AFB in Forth Worth, Texas, for the purpose of evaluating the effectiveness of eastern cottonwood trees in remediating a TCE-contaminated groundwater plume. The U.S. EPA is collaborating with the U.S. Air Force on this field demonstration, which involves periodic sampling and analysis of soil, groundwater, and the trees.

The second SITE is a phytoremediation project completed by Phytotech, Inc., of Monmouth Junction, New Jersey. Phytotech completed final soil sampling in the fall of 1998 for a 2-year SITE field demonstration to determine the ability of the Indian mustard, *Brassica juncea,* to phytoextract lead from soil. The process

TABLE 5.6.3 Phytoremediation System Selection Process (Selected Criteria)

1. Identify phytoremediation technology and remedial goals.
2. Gather site information.
    a. Location (also relative to plant/vegetation/ecosystem zones)
    b. Temperatures: averages, range
    c. USDA plant hardiness zone (range of average annual minimum temperature)
    d. Precipitation: amount, timing
    e. Length of growing season
    f. Amount of sun/shade
    g. Soil texture, salinity, pH, fertility, water content, structure (hardpans, etc.)
    h. Contaminant type, concentration, form
    i. Site-specific conditions or considerations
    j. Identification of plants growing in contaminated portion of site (optional):
        i. Do these provide a clue as to what plants to select?
        ii. If not, will these plants compete with the selected plant?
        iii. If the native plants do compete with the selected plant, are they easily removed?
    k. Identification of local plants and crops (optional):
        i. Do these plants provide a clue as to what plants to select?
        ii. Will a selected plant interfere with local plants?
3. Identify important criteria for plant selection.

    General:
    a. Disease resistance
    b. Heat tolerance
    c. Cold tolerance
    d. Insect tolerance
    e. Drought tolerance
    f. Salt tolerance
    g. Chemical tolerance
    h. Stress tolerance
    i. Legume/nonlegume
    j. Annual/biennial/perennial

    Culture requirements:

    Due to the added stress of a contaminated soil environment, the cultivation and maintenance factors may have to be carefully monitored.
        i. Seed pretreatment before germination (such as for some prairie grasses)
        ii. Planting method (seeds, sod, sprigs, whip, plugs, transplants), timing, density, depth (of seeds, root ball, or whips)
        iii. Mulching, irrigation, soil pH control, fertilization, protection from pests and disease.
        iv. Fallen leaves, debris
        v. Harvesting requirements
        vi. Labor and cost requirements (should not be excessive)
    k. Invasive, undesirable, or toxic characteristics
    l. Plant/seed source
    m. Establishment rate
    n. Reproduction method/rate
    o. Growth rate/biomass production
    p. Competitive or allelopathic effects
    q. Value of plant as cash crop

    Phytoremediation-related:
    r. Demonstrated efficacy of plant: The plant can take up and/or degrade contaminants, produce exudates that can stimulate the soil microbes, or possess enzymes that are known to degrade a contaminant. The potential for the success of phytoremediation can be increased by screening plants for useful enzymes (Fletcher et al., 1988).
    s. Phytotoxicity of contaminant: The contaminant should not be phytotoxic at the concentrations found at the site. Contaminant phytotoxicity and uptake information can be found in the phytoremediation and agricultural literature, or determined through preliminary germination and phytotoxicity screening studies.

        Databases such as PHYTOTOX or UTAB have been used to summarize and investigate phytotoxicity and uptake information (Fletcher et al., 1988; Nellessen and Fletcher 1993a; b).
    t. Root type: fibrous root system versus tap root system.

TABLE 5.6.3 (Continued) Phytoremediation System Selection Process (Selected Criteria)

  u. Root depth: the range of root depths of a given plant must be considered.
  v. Contaminant depth and distribution: The contaminant depth must be similar to root depth. The distribution of the contamination at various soil depths is also important in planning the plant type and planting method. The contaminant concentrations in the seed bed layer of the soil profile may have a strong effect on the ability to establish vegetation. A surface layer with minimal contamination underlain by greater contaminant concentrations might allow more successful seed germination than if the surface layer is heavily contaminated. Root growth into the more contaminated layer is then desired, and since it is not guaranteed, must be verified.

4. Make general decisions.
  a. Deciduous/nondeciduous: Deciduous trees will be dormant for part of the year, resulting in lowered transpiration rates.
  b. Monoculture vs. mixed species: The use of mixed species of vegetation can lead to more success due to the increased chance that at least one species will find a niche. However, there could be competition between plants for nutrients and space.
  A monoculture relies on just one plant type, possibly requiring more management to ensure its growth against adverse conditions. Despite this, a well-established stand of one plant that has been shown to be effective in phytoremediation could be the most efficient means of phytoremediation.
  c. Native vs. non-native: Native, nonagricultural plants are desirable for ecosystem restoration. In most applications, plants that are adapted to local conditions will have more chance of success than nonadapted plants.
  d. Growing season: Warm season and cool season grasses could be used in combination to address different seasonal conditions, prolonging a vegetative cover throughout more of the year.
  e. Sterile/male/female: The ability to reproduce is necessary for the long-term establishment of vegetation. In cases where the spread of the plant to surrounding areas is undesirable, however, the plants should be selected to prevent reproduction.
  f. Plant rotation; planned or natural plant succession: The long-term establishment of vegetation at a site is dependent on the project goals and future uses of a site. For long-term, no-maintenance vegetation establishment as part of ecosystem restoration, it is likely that there will be a succession of plants at a site. If so, this succession could be planned when considering the types and timing of vegetation. Plant rotation could conceivably be important when short-lived vegetation is used that does not reach remedial goals and that should not be replanted in the same place.

5. Match above criteria with list of available/proposed plants.
  a. Select all appropriate candidates (eliminate all inappropriate plants).
  b. Conduct detailed evaluation of remaining candidates against criteria in items 1 to 4 of this table.
  c. Conduct cost/benefit analysis of top candidates:
    i. Plant costs
    ii. Plant effectiveness in reaching goal
    iii. Plant value (cash crop)
  d. Conduct preliminary studies to assess germination, survivability, and biomass. It might not be possible to assess the success of some forms of phytoremediation (i.e., rhizodegradation) due to the insufficient time for preliminary testing. Because phytoremediation can be a long-term process, however, spending 1 or 2 years in preliminary trials will not substantially increase the overall remediation time.
    i. Germination screening studies for phytotoxicity
    ii. Small-scale greenhouse or laboratory chamber studies
    iii. Field plot trials

6. Select plant and implement phytoremediation.
  a. Monitor and evaluate plant growth and phytoremediation success.
  b. Reevaluate plant selection on basis of observations: Variability in phytoremediation efficacy in varieties, cultivars, or genotypes of a given species has been encountered in alfalfa for hydrocarbon rhizodegradation. A screening of cultivars/varities might be required.
  c. Reseed/replant as necessary with same or different plant.

Modified from USEPA, 2000.

uses chelators to make the contaminant more available to the grass. The site is the former Magic Marker facility in Trenton, New Jersey, and Phytotech has received considerable news coverage for its work at this Brownfield site, which is located in a residential/commercial area of the city. Battery manufacturing operations were thought to have been the source of the lead, which contaminated soil at concentrations ranging from 200 to 1800 mg/kg. The New Jersey residential standard for lead in soil is 400 mg/kg.

The SITE program is administered by ORD's National Risk Management Research Laboratory in the Land Remediation and Pollution Control Division (LRPCD), headquartered in Cincinnati, Ohio. By participating in the SITE program, both the U.S. Air Force and Phytotech are assisting the U.S. EPA in evaluating phytoremediation as a treatment alternative.

In 1992, the U.S. EPA created the Remediation Technologies Development Forum (RTDF) to identify what government and industry can do together to develop and improve the environmental technologies needed to address their mutual clean-up problems in the safest and most cost-effective manner. The RTDF fosters public and private sector partnerships to undertake the research, development, demonstration, and evaluation efforts needed to achieve common cleanup goals.

Selected Information Sources for Phytoremediation Technologies

1. *International Journal of Phytoremediation* (CRC Press, Boca Raton, Florida) http://www.aehs.com.
2. PHYTONET — http:// www.dsa.unipr.it/phytonet.
3. The SITE Program — http://www.epa.gov/ORD/SITE.
4. The RTDF Program — http://www.rtdf.org.
5. European Cost Action Program — http://www. belspo.be/cost, http://bewww.epfl.ch/COST837.

Market Potential and Costs of Phytoremediation Technologies

A recently published report on phytoremediation's current and future market potential reports that phytoremediation has made tremendous gains in market acceptance in recent years (Glass, 1999). The acceptance of phytoremediation is based on several factors, including its favorable economics, its compatibility with risk-based remediation, including natural attenuation approaches, and its potential versatility to treat a diverse range of hazardous materials in different contaminated media, such as soil, groundwater, wastewater, and landfill leachate. The 1998 U.S. market of $16.5 to $29.5 million was estimated to grow to $55 to $103 million by the year 2000, and to $214 to $370 million by 2005. Currently, the vast majority of the phytoremediation market is in the United States. However, international markets are forming and significant growth should occur in the very near future.

Cost comparisons of phytoremediation to other remediation technologies have recently become available. According to a recent survey of the literature, which includes several claimed cost ranges not necessarily substantiated by data, the consensus cost of phytoremediation has been estimated at $25 to $100 per ton ($28 to $110 per metric ton) for soil treatment and at $0.60 to $6.00 per 1000 gal ($2.27 to $22.71 per 1000 L) for treatment of aqueous wastestreams. In both cases, the remediation of organic contaminants can be expected to fall at the lower end of these ranges and remediation of heavy metals to fall at the higher end.

There is considerable economic data available for several different technologies for the remediation of organic contaminants from aqueous wastestreams, including phytoremediation. Drs. Victor F. Medina and Steven C. McCutcheon, at U.S. EPA's NERL in Athens, Georgia, used a mathematical model to estimate that treating TNT in constructed wetlands using the parrot-feather would cost ~$0.64 per 1000 gal (~$2.42 per 1000 L). Earlier published estimates noted by these authors were $0.40 to $1.00 ($1.51 to $3.78) for granular activated carbon (GAC), $1.00 to $3.00 ($3.78 to $11.36) for UV oxidation, $1.00 to $2.50 ($3.78 to $9.46) for supercritical water oxidation, and $1.00 to $5.00 ($3.78 to $18.92) for electron beam destruction per 1000 gal (1000 L) of water. Dr. Jerald L. Schnoor (University of Iowa, Iowa City, Iowa) reported unpublished data in 1997 from the U.S. Army Environmental Center, Aberdeen Proving Ground, Maryland, demonstrating that the use of canary grass in anaerobic wetlands remediated TNT at 30% the cost of GAC. Dr. Victor Medina (Washington State University, Richland, Washington) and Dr. Steven McCutcheon (U.S. EPA–National Exposure Research Laboratory, Athens, Georgia) reported data that compares well with modeled estimates for treating PCE using traditional technologies, such as $8.90 ($33.69) for pump-and-treat, $5.30 ($20.06) for an iron reactive barrier, $4.20 ($15.90) for a biological barrier, $1.80 ($6.81) for *in situ* bioremediation, and $1.20 ($4.54) for natural attenuation per 1000 gal (1000 L) of water.

There have been surprisingly few published estimates of the costs of phytoremediation systems using hybrid poplar trees despite the fact that their use is the longest standing and perhaps the most prevalent, commercial application of phytoremediation to date. Dr. Edward G. Gatliff (Applied Natural Sciences, Fairfield, Ohio), compared the total cost of remediating nitrate-contaminated groundwater with poplar trees against pump-and-treat using reverse osmosis. Phytoremediation, at a total 5-year cost of $250,000, was less than half the cost of the $660,000 cost for pump-and-treat systems.

According to 1997 U.S. EPA estimates, the cost of using phytoremediation in the form of an alternative cover (i.e., vegetative cover system) ranges from $10,000 to $30,000 per acre ($4000 to 12,000 per hectare), which is thought to be two- to fivefold less expensive than traditional capping. At a Chevron Corporation site, for example, the cost of an asphalt cap was estimated at $15 million. The cost for a vegetative cover system for that site was estimated at $4 million, which is a cost saving of almost 75% over the alternative.

Estimates from Dr. Evelyn Drake (Exxon Research and Engineering, Anandale, New Jersey), compared the costs of enhanced rhizosphere biodegradation of petroleum hydrocarbons with the costs of alternative technologies. Phytoremediation was estimated to cost $10 to $35 per ton ($11 to $38 per metric ton) with the cost for *in situ* bioremediation at $50 to $150 per ton ($55 to $165 per metric ton), soil venting at $20 to $220 per ton ($22 to $242 per metric ton), indirect thermal treatment at $120 to $300 per ton ($132 to $330 per metric ton), and soil washing at $80 to $200 per ton ($88 to $220 per metric ton). All other technologies in this comparison, including incineration, had ranges estimated to begin at or above $200 per ton ($220 per metric ton).

Obtaining credible, scientifically valid cost estimates of phytoremediation is a critical element in phytoremediation's acceptance in the market and should be a major goal of the demonstration projects now underway. This information is of importance to regulators, the consulting/engineering community, and the public.

Potential Limitations to Phytoremediation Technologies

Although phytoremediation is expected to become a widely used, cost-effective method for remediating environments contaminated with toxic metals, radionuclides, and hazardous organics, it does have limitations as a technology. Some disadvantages of phytoremediation are provided by McIntyre and Lewis (1997) and include: (1) hyperaccumulating plants may only accumulate one contaminant, and are often relatively rare taxa occurring in remote areas with restricted distribution; (2) many hyperaccumulators exist as relatively small populations with slow growth rates and low biomass production; (3) phytoremediation is frequently slower than traditional methods used for site clean up and may require several growing seasons; (4) phytoremediation may require that the site be large enough to accommodate traditional agriculture cropping techniques to remove the contaminants in biomass; (5) climate may be a limiting factor for plant growth and season length; (6) plants used for phytoremediation may provide an entry for the biomagnification of contaminants in food chains (e.g., herbivore grazing); (7) the methods for the disposal of contaminated biomass may have environmental impacts; and (8) genetically engineered phytoremediation systems may pose unacceptable ecological and environmental health risks.

Summary

In summary, the application of phytoremediation is being driven by its technical and economic advantages over competing conventional technologies. Phytoremediation systems are:

- Clean technologies, powered by solar energy
- Cost-effective, 10 to 50% of typical mechanical, thermal, or chemical treatment costs
- Effective at contaminant destruction or volatilization on site instead of relocation in a landfill
- Capable of generating a recyclable metal-rich plant residue
- Passive and *in situ*, causing minimal environmental disturbance
- High in public acceptance, and aesthetically pleasing

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Chapter Six

Stabilization and Solidification Technologies

6.1

Overview of Mixed Waste Solidification and Stabilization Methods

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Introduction

A variety of treatment methods exist for the various mixed waste types currently existing and being generated in both the government (e.g., the Department of Energy's nuclear weapons complex) and private sector (e.g., the medical and nuclear power industries). Fundamental treatment methods for mixed waste consist of thermal destruction, nonthermal destruction, chemical treatment, physical treatment, treatment for separating specific chemical fractions (radioactive and/or nonradioactive), and/or immobilization through stabilization that may or may not involve thermal or solidification methods. Specific technologies to accomplish these methods include, but are not limited to, incineration, plasma melting, wet air oxidation, acid digestion, pH adjustment, surface decontamination, filtration, evaporation, ion exchange, solvent extraction, and cement grouting.

In most mixed waste treatment applications, combinations of two or more of the above methods are required to produce mixed waste forms acceptable for final disposal. However, independent of which methods are selected, a low-temperature solidification/stabilization (S/S) process is usually required to accomplish a significant step in the overall mixed waste treatment train. Its popularity is a result of its simplicity and successful treatment history, because S/S has been effectively used in general waste treatment since the 1950s[1] and is presently identified by the Environmental Protection Agency (EPA) as the best-demonstrated available technology (BDAT) for 57 hazardous waste streams.[2]

Specifically for mixed waste, S/S methods are used as either the principal and primary treatment step, or are involved in treating the secondary waste produced by other mixed waste treatment processes. For example, incineration will destroy any hazardous or nonhazardous organics residing in the mixed waste stream, thereby greatly reducing its volume, but it will also generate potentially toxic and radioactive off-gases, fly ashes, bottom ashes, and spent off-gas scrubbing solutions. With the exception of the off-gas, these secondary streams will more than likely contain hazardous metals and radionuclides requiring further solidification/stabilization. Likewise, hazardous metals and radionuclides are routinely removed from mixed wastewaters to allow reuse of liquid streams. Such separation processes are frequently accompanied by an S/S stage to treat the concentrated mixed waste residue.

Before the final land disposal of a mixed waste that has been stabilized and/or solidified, the party responsible for the waste treatment must ensure that the final waste form meets requirements and criteria that have been independently established for both the hazardous and radiological constituents residing in the waste. For most situations, the hazardous constituents (characteristic and/or listed) will be regulated by the EPA, and will require treatment to meet the Land Disposal Restrictions (LDRs) as defined by the Resource Conservation and Recovery Act (RCRA). In addition, some disposal sites require that the radiological constituents be controlled by meeting guidelines that have been established for commercially generated low-level waste (LLW) as recommended by the Nuclear Regulatory Commission (NRC). Treatment requirements can be further complicated by the existence of special criteria established at specific disposal sites. As such, it is highly recommended that the desired disposal site be contacted before establishing S/S treatment paths to ensure that the final mixed waste form meets the specific set of specifications applicable to that site. Regardless of the disposal site, it is usually advantageous to create both highly durable and low-volume mixed waste forms, provided the chosen treatment process is both economical and practical. Low-temperature solidification/stabilization (S/S) technologies have proven to be effective in meeting these criteria without generating either off-gas emissions or significant secondary waste streams.

This subsection provides an introduction to low-temperature S/S methods as they apply to the *ex situ* treatment of liquid and solid mixed wastes (i.e., remediated and/or containerized wastes that are both RCRA hazardous and radioactive). Thermal stabilization processes, (e.g., vitrification), are partially omitted from the discussion. Unlike low-temperature methods, they create secondary wastes, produce off-gases, destroy organic constituents, and require complex equipment and control.

It is important to note that the information provided in this subsection is only relevant and correct for low-level mixed waste or waste that has *both* radioactive and hazardous components. As such, some of the information and conclusions provided in regard to economics, chemistry, physics, and regulations may not hold applicable for *only* hazardous waste.

This subsection provides a general description of S/S technology, along with definitions for the terminology associated with its use. Mixed waste applications and specific S/S technologies are discussed, as well as descriptions of the associated equipment. Sections addressing S/S produced waste form performance and S/S economical considerations are also provided. A reference section and bibliography are provided for those seeking additional information.

S/S Technology Descriptions and Terminology Definitions

Stabilization refers to the practice of employing various additives and/or binders for the primary purpose of rendering the hazardous and/or radiological constituents in the mixed waste less toxic, soluble, and/or mobile.[3] The additives and/or binders accomplish this through chemical and/or physical means. One of the most common methods of stabilization involves the addition of chemicals that lower the solubility of the hazardous and/or radioactive constituents in the mixed waste, thus substantially lowering its leachability to the environment. For example, nonhazardous sulfides, hydroxides, and phosphates are frequently used in binders and additives in an attempt to convert the highly soluble RCRA metal salts and oxides (e.g., $CdCl_2$ and $HgSO_4$) residing in the mixed waste to relatively insoluble metal compounds (e.g., $Cd\ (OH)_2$, and HgS).

Solidification refers to the use of additives, binders, and admixtures that transform the mixed waste from a sludge, semisolid, liquid, or particulate form into a solid (i.e., a form that holds it shape without a container) containing no free liquid. Usually, the primary goals behind mixed waste solidification are to convert the waste medium into one that is easier to handle and store, while at the same time minimizing the hazardous and radiological component leaching potential by reducing the surface area of the waste exposed to the environment.[3] In addition, solidified waste forms reduce the risk of waste particulate dispersion during handling, storage, transportation, and disposal, and therefore increase safety for both the workers and environment. Solidification also results in an increase in compressive strength and a frequent decrease in permeability relative to the original mixed waste condition. The solid formed through solidification can be either a monolithic block or a dense pellet. However, many liquid waste streams are solidified for acceptable disposal without formation of a monolith. The use of an absorbent, such as vermiculite, to bound free liquids is occasionally practiced to facilitate handling, but by definition is not considered an acceptable solidification or treatment step.

The term "chemical fixation"[1] is frequently used in the literature to define solidification or stabilization, or a combination of the two methods.[3] Usually the term is used to imply stabilization, but the available literature indicates use of the term to indicate solidification as well.

Collectively, the term "solidification/stabilization" (S/S) refers to mixed waste treatment processes that involve at least one, but preferentially both of the mechanisms described above.[2] For example, polymer-based encasement of mixed waste is considered more of a solidification method than a stabilization method, although it is frequently classified as an S/S method. Use of a molten polymer to encapsulate a mixed waste will result in a solidified waste form upon cooling; but without the use of specific additives (e.g., sulfides), the polymeric material alone does little to reduce the actual toxicity of the hazardous and/or radiological species residing in the original mixed waste. It does reduce the mobility and solubility of the contaminants by providing a physical hydrophobic barrier between the waste and the environment; however, if the barrier is compromised, a pathway is provided for leaching of the contaminants to the environment. In contrast, simple cement grouting of mixed waste is considered a solidification and stabilization method although it is more porous than polymeric substances. Hydration reactions that occur during setting and curing of the alkaline cement-waste grout mix create relatively insoluble hazardous and radioactive metal hydroxides, chemically lowering the leachability of some of the constituents in the waste. In addition, cement-based S/S methods reduce the mobility of inorganic compounds by forming insoluble metal carbonates and silicates, substituting the metal into a mineral structure, and physically encapsulating the waste. Thus, even if the internals of the cement waste form are exposed to the environment directly, the waste contaminants retain a resistance to any leaching. However, over time, the reserve alkalinity of the cement waste form may be comprised, which will eventually increase the leachability of some of the toxic metals. Additionally, many of the cement bonding mechanisms are limited in their ability to retain or chemically fix certain radionuclides (e.g., ^{60}Co).

Solidification/stabilization (S/S) processes are broadly classified as either inorganic or organic, although some methods have recently been developed that incorporate both classes of materials. Traditional inorganic methods such as simple portland cement, natural/man-made pozzolans, or low-temperature ceramics involve complex hydration and/or simple acid-base cement chemistry to both solidify and stabilize. Because these methods require hydration reactions, they can be used for treating both aqueous and solid wastes. On the other hand, traditional organic-based/polymeric methods (e.g., polyethylene solidification) simply encapsulate the waste and inherently do not mix well with aqueous wastes. Thus, these methods are not generally applicable to liquid wastes because they usually involve a closed extrusion process. However, if a direct mixing process is utilized, certain organic-based methods, such as those employing polyesters, are applicable to aqueous wastes. Macroencapsulation using organic-based material results in waste forms that are coated on only the outside surface, resulting in a polymer jacket around the original solid mixed waste. The use of sealed plastic containers to contain mixed waste debris for disposal is also currently in practice, and for some specific applications is considered acceptable macroencapsulation. In contrast, microencapsulation involves a homogeneous mix of both the polymer and the solid mixed waste. As a consequence, macroencapsulation is frequently used for large debris waste or lead monoliths, and microencapsulation is employed for mixed waste particulate, soil, sludges, and crushed debris.

For mixed waste organic-based solidification applications, polymers can broadly be classified as either having thermoplastic or thermosetting properties. Thermoplastics, such as low- and high-density polyethylene, are usually noncross-linked linear polymers that melt and become viscous at a specific transition temperature. They can be melted, reworked, and returned to their original form upon cooling. They require no reaction to solidify, and the mixed waste material does not interact with the polymer chemistry. Basic microencapsulation operations involve simply mixing the waste with the polymer in the melting phase of an extruder, and pouring the homogenous polymer-waste mix in a disposal drum for cooling and hardening. Thermosetting polymers, on the other hand, cannot be reworked, reformed, or remelted. They are usually cross-linked, rely on polymerization reactions to solidify, and decompose upon overheating. Unlike thermoplastic resins, the waste can react and interfere with the thermosetting resin reactions. Polyester resins, as well as epoxies, are classified as thermosetting.

Over the past 15 years, a considerable mixed waste S/S development effort has been expended toward enhancing or replacing the baseline S/S methods of cement grouting and polymer encapsulation. The majority of these development activities have focused on increasing the actual mass-based waste loading and/or decreasing the volume of the final waste form. This objective is usually based on the perception that reduced final waste form volumes, usually produced as a consequence of increased waste loading, translate into an overall more economical S/S process. For many applications, this assumption is valid because the volume-sensitive costs associated with the handling, shipping, and especially disposal of the final mixed waste form usually have a larger impact on the total S/S life-cycle cost in comparison to other S/S expenditures (i.e., labor, capital, material, and design). However, each S/S application is unique and the economics are dependent on many variables and factors, including the original mixed waste volume. Savings (or increased costs) realized through the development of alternative S/S methods that achieve higher waste loadings and/or greater volume reductions are directly proportional to the amount of a given homogenous mixed waste inventory to be treated. Established baseline technologies may already be adequate for relatively low waste volumes because insufficient waste inventories may not achieve the savings required to recover the costs associated with developing and deploying an alternative method. Additionally, higher waste loadings are often accompanied by increased contaminant leaching over time and/or result in poor-quality waste forms with inferior physical properties. Although a decreased product quality may still be within the criteria established for disposal, the potential for decreased public trust and acceptance is also a “cost” that must be weighed accordingly.

Some confusion and inconsistency have arisen in regard to methods used to compare the waste loading and volume reduction of competing S/S methods. Mixed waste loading is usually calculated as a *dry* mass/weight percent of the final waste form as determined by Equation (6.1.1):

$$[M_W/M_{WF}] \times 100 = \text{Waste Loading } (\%)_m \tag{6.1.1}$$

where M_W is the *dry* mass of the original mixed waste just before the solidification/stabilization step, and M_{WF} is the mass of the final waste form containing M_W.

Volume reduction is the percent difference in volume between that of the original mixed waste and that of the final waste form, which for many S/S applications has experienced some level of compaction and densification. Except for situations in which the original mixed waste volume is of a particulate form with a high void fraction and low bulk density, the volume of the final waste form is rarely less than that of the original waste. Therefore, the objective is to select an S/S method that minimizes the amount of volume increase from waste to waste form. Volume reduction (i.e., the negative value of the volume increase) is normally calculated via Equation (6.1.2):

$$100 \times [V_W{}^0 - V_{WF}]/[V_W{}^0] = \text{Volume Reduction } (\%)_V \tag{6.1.2}$$

where $V_W{}^0$ is the volume of the original, uncompacted unstabilized mixed waste before any pretreatment (including that of evaporation), and V_{WF} is the volume of the final, usually densified and compacted, waste form. An example indicating the differences in calculating waste loading and volume reduction during S/S is provided below.

Example Problem

In a HEPA filtered laboratory hood permitted for waste storage and treatment, 50 kg of a dry, radiologically contact-handled mixed waste sludge (characteristically RCRA hazardous for cadmium metal only) occupies 45 L in an open 55-gal standard waste barrel. In an effort to exit RCRA and dispose of the barrel in a Department of Energy (DOE) low-level waste (LLW) landfill, cement-based and pozzolanic stabilizing agents, along with the appropriate amounts of water, are added to the waste and the mix is allowed to set and cure. Toxicity Characteristic Leaching Procedure (TCLP) results on a crushed 100-g sample of the treated waste form confirm that the cadmium leach levels pass Universal Treatment Standards (UTS) for land disposal. Department of Transportation (DOT) shipping forms required for transport of the barrel to the LLW disposal site document that the net weight of the waste barrel is 90 kg and the cement compacted monolith inside it occupies ~ 40 L. Calculate the waste loading and waste form volume reduction.

Solution:
Because the waste is defined as already "dry," the waste loading is simply determined as [100 × 50 kg/90 kg = 55.55 wt%], and the volume reduction is calculated as [100 × (45 L – 40 L)/45 L = 11.11 vol%].

Usually mixed waste inventories that are amenable to (or are candidates for) low-temperature S/S methods have been poorly characterized and/or were generated from complex processes involving a multitude of physical, thermal, and/or chemical steps. As a consequence, the mixed waste may have unknown properties (e.g., high pH) and/or contain species (e.g., excess oils, reactives, excess salts, nuisance metals, specific radionuclides) that will interfere with the selected S/S options and/or deteriorate the waste form over time. To avoid costly large-scale S/S deployment failures, prescreening and small-scale testing of candidate S/S methods, followed by appropriate performance testing of the resultant waste form, is almost always recommended. In addition to identifying the most optimum S/S method for deployment, the prescreening and small-scale testing will establish the necessity of any pretreatment steps. If the testing is performed with small samples of the actual mixed waste, it is usually designated to the EPA as a "treatability study." As detailed in 40 CFR sections 261.4 Parts e and f, the treatability study designation provides exemption from many RCRA permit requirements, and allows the prescreening test to occur more readily as long as the proper notifications are made, the amount of mixed waste treated is less than 1000 kg (10,000 kg for soil waste), and the treatability study residues are properly managed. Prescreening through surrogate testing may be the only option if the radiological levels are excessive, but extreme care must be taken when using simulated wastes to determine the performance of candidate S/S methods. The omission of even the most inconsequential species in the surrogate, as a result of incomplete mixed waste characterization, can lead to failure.

Low-Temperature Mixed Waste S/S Applications

Numerous mixed waste types are suitable for solidification/stabilization based on operating experience and/or testing with both actual mixed waste inventories and surrogates. Low-temperature *ex situ* S/S methods are most suitable for inorganic, radiologically contacted-handled mixed waste consisting of a liquid or a solid medium that is homogeneous and/or particulate, such as soils and dry sludges. The classes of mixed waste that have been frequently and effectively immobilized via S/S methods include contaminated soil, baghouse dust, collected particulate, wastewater treatment sludges/residues, evaporator bottoms, scrubber blowdown generated from the treatment of off-gases, incinerator bottom and fly ashes, various pond sludges, concentrated aqueous wastes, and transuranic homogeneous solid waste. Specific waste streams consist of paint chips, paint sludges, ion exchange resins, mixed waste sludges resulting from the treatment of high level wastes, unconcentrated salt wastes, and previously unsuccessfully stabilized waste forms. S/S treatment is also applicable to inorganic/organic absorbents, inorganic chemicals, low reactive metal chips and turnings, crushed glass, and crushed ceramic. Various debris waste, if properly sized, are candidates for S/S, especially micro- or macroencapsulation techniques.

As a general rule, S/S methods are not applicable to mixed wastes containing significant quantities (e.g., >10% by mass) of large debris, oily sludges, organic liquids, high concentrations of salts, reactives, and/or explosives. Although limited S/S methods are available for mixed wastes containing nonhalongenated, halongenated, semivolatile, and/or volatile organics, nonpolar and hydrophobic organics do not consistently react well with many inorganic or organic binders. The best demonstrated available technology (BDAT) for organic-based mixed waste is still incineration or its equivalent.

Salts (defined as the reaction product generated when a metal ion replaces the hydrogen ion of an acid) are highly soluble. As a consequence of this characteristic, mixed wastes containing appreciable salts can sometimes affect the set and cure rate of inorganic, cement-based binders, and/ or result in waste forms that are susceptible to deterioration over time due to the salt mineral expansions in the macropores of the waste form microstructure. This deterioration may lower the durability and strength of the stabilized waste form and create pathways for the hazardous and radiological constituents to be released from the immobilized waste over time.[4] Because a considerable number of past DOE processes involving the formulation of nuclear materials required the use of metals and acids, a significant inventory of mixed waste containing salts was produced. As introduced in the preceding subsection, considerable development has therefore occurred to validate S/S methods for this mixed waste class. Most of the successful development has centered on the use of redox chemistry during pretreatment or stabilization to help immobilize and lower the leachability of the hazardous constituents, despite the long-term detrimental effect of the salts on the waste form structure.

Low-Temperature Mixed Waste S/S Methods

The most common inorganic-based, low-temperature, *ex situ* S/S additive for mixed waste, as well as hazardous and/or low-level waste (LLW), is simple portland cement. The use of ordinary portland cement as a waste solidification and stabilization medium has been in practice for decades. Because cement hydration reactions occur at low temperatures, generate no off-gases, chemically bind aqueous wastes to the matrix, and are relatively inexpensive, they are excellent choices for providing the S/S treatment of many mixed waste types.

Dry, basic, portland cement clinker is manufactured by calcining natural limestone ($CaCO_3$) and clay materials at 1400 to 1500°C and then subsequently crushing it to a powder. The resultant cement binder product usually consists of specific combinations of the following three basic oxides: silica (SiO_2), lime (CaO), and alumina (Al_2O_3). At a minimum, the specific oxide combinations consist of the following three crystalline compounds:

- Tricalcium silicate: $3CaO\text{-}SiO_2$
- Dicalcium silicate: $2CaO\text{-}SiO_2$
- Tricalcium aluminate: $3CaO\text{-}Al_2O_3$

For most cements, these three compounds make up ~80% of the dry matrix, and their proportions determine which of the eight American Society of Testing and Materials (ASTM) standard types of portland cements are formulated. Sulfur-containing gypsum ($CaSO_4$) is also added when making portland cements. The role of the gypsum is to slow down the cement setting during hydration (i.e., the addition of water). The tricalcium aluminates and gypsum react with water to form a mineral (i.e., ettringite) and gel that coats the remaining unhydrated cement clinkers. Setting is slowed because the water must diffuse through this mineral barrier to hydrate the remaining cement components. This extends the time the cement waste mix is workable before complete setting. Under normal conditions, the rate of hydration is such that after 28 days, only two thirds of the cement has reacted with water. However, the rate and extent of hydration and curing are greatly dependent on the type of contaminates in the waste, as well as the amount of water added to the waste-cement mix.

The hydration reactions between the dry cement powder, the mixed waste, and any added water can be complex, and even the most simple cement hydration mechanisms are not yet fully understood. In general, the bulk of the crystalline calcium silicates in the cement reacts with water to form amorphous hydrated calcium silicates (also known as tobermorite gels or $3CaO\text{-}2SiO_2\text{-}3H_2O$), and crystalline slaked lime [also known as calcium hydroxide ($Ca(OH)_2$) or portlandite]. The tobermorite gel, which causes setting, is the main cementing component of the waste form and the presence of the soluble slaked lime in the pores causes the cement form to be basic (i.e., pH ~11.5). As a favorable consequence of the high pH, the acetic acid solution used as an extract in the RCRA required Toxicity Characteristic Leaching Procedure (TCLP) test can be immediately neutralized and will lose its ability to leach any hazardous RCRA metals. The presence of the hydroxide will also result in the favorable conversion of any RCRA hazardous metals present in the waste to their less-soluble hydroxide form. Other portland cement-based stabilization reactions include formation of carbonates, silicates, and substitution of the metals into cement hydration products. The slaked lime is also somewhat soluble, and over long time periods in a wet environment will diffuse through the pores and leach out of the cement waste form. Because the Ca $(OH)_2$ can constitute over 30% of the waste form, its slow removal from the waste monolith over extremely long time periods can seriously degrade it. However, the benefit that $Ca(OH)_2$ provides in buffering the leachability strength of any acidic solutions that the waste form is exposed to substantially exceeds any long-term negative consequences of this degradation.

During cement hydration and the onset of setting, some of the tobermorite gel is formed from a sol (i.e., a homogeneous dispersion of fine solids in a liquid) that follows the principles of colloidal chemistry. According to these principles, the formed tobermorite sol coagulates into floccules or gel substances. The gel then precipitates to cementing solids once the static charge is lost. Because this precipitation or setting step is greatly affected by the ionic strength of the sol, the presence of salts in the mixed waste can significantly impact the cement's setting rate in either direction (i.e., accelerate or retard the set). Once all the gel has settled, it begins to dry and crystallize in what is designated as the "cement hardening" or "curing" phase. During this curing phase, crystalline slabs and needles are created that decrease the porosity and increase the strength of the waste form.[5]

In addition to simple portland cement grouting, inorganic S/S methods for mixed waste include — but are not limited to — methods involving mixtures of portland cement and various other binders or additives, such as extra gypsum, clay, lime, soluble silicates, and other natural or man-made pozzolans. For some applications, these various binders and additives can also stand-alone as a S/S method.

Pozzolans are siliceous and/or aluminous material. They are substances, naturally occurring or produced as industry by-products, that acquire some cement-like characteristics when activated by calcium hydroxide. As such, the use of these additives is cost-effective because a special manufacturing step is not required, as in the case of portland cement. The fly ash generated from coal combustion and other pozzolans contain a glassy silica phase that reacts with the slaked lime in cements during hydration to form a calcium silicate hydrate (CSH) gel, which is the main setting agent of cement.

Blast furnace slag, another popular pozzolan, is produced as a by-product of the iron and steel industry. Its earthly constituents come from iron ore processing and it consists of the same oxides as portland cement, but in different proportions. Immediately after its production, the slag is usually quenched for rapid cooling in a process known as granulation. The granulation results in a reactive amorphous glass and avoids any crystallization. Like portland cement, blast furnace slag also reacts with water (i.e., is hydrated) to form hydrated calcium silicates or tobermorite gels. However, unlike simple portland cement, it forms this critical cementing agent (tobermorite gel) by consuming the slaked lime, $Ca(OH)_2$, provided by the hydration of the portland cement. Removal of some of the slaked lime is advantageous because less of it in the waste form will lead to less dissolution of the lime over time, and consequently less long-term waste form degradation. In addition, there will be less slaked lime available to potentially react with salts, and thus produce undesired expansive and destructive minerals in the future. Blast furnace slags also routinely contain sulfides that react with and lower the solubility of many hazardous metals in the mixed waste.

In addition, it has been postulated that because blast furnace slag is amorphous and not crystalline, it hydrates to tobermorite gel without forming the colloidal solutions commonly observed for the calcium silicates in simple portland cement. Because sols are not formed, the ionic nature of the salts may not affect the tobermorite gel formation or set rate of the waste form.

Sulfur polymer cement (SPC) is another inorganic-based S/S method recently developed for application to mixed waste. Specifically, the use of SPC as a mixed waste S/S method has been investigated by the DOE's Brookhaven National Laboratory, Oak Ridge National Laboratory, and the Idaho National Engineering and Environmental Laboratory. Originally, SPC was developed by the U.S. Bureau of Mines in an attempt to use waste sulfur in materials that may serve as commercial alternatives to construction cement. The development resulted in a high-strength, quick-setting cement substitute, which is currently only manufactured by Martin Resources of Odessa, Texas. SPC is manufactured by reacting solid sulfur with small amounts of the inexpensive chemical modifiers di- and monocyclopentadiene.[6] The presence of sulfur makes it especially attractive to mixed wastes containing mercury because sulfur tends to readily amalgamate with hazardous mercury, thus lowering its leachability. Unlike other inorganic S/S methods, heated SPC exhibits thermoplastic properties and thus has a low enough melting point and viscosity to be used in a manner similar to that of organic or polymeric methods (i.e., deployment equipment consisting of heated and stirred vessels). Deployment of the SPC process on the mixed waste market to date has been limited. However, a commercial mixed waste treatment and disposal facility may implement the SPC S/S method developed at Brookhaven National Laboratories.

Although not as widely deployed as inorganic-based methods, organic-based S/S methods are experiencing increased use for mixed wastes. For more than 20 years, various organic polymers have been used to encapsulate hazardous and low-level waste materials because their chemically inert properties usually allow for higher waste loading than that achievable with cements. Polymers in general have moderate to excellent resistance to the acids, bases, and organics present in many mixed waste streams. Both the thermoplastic and thermosetting polymeric stabilizing materials are normally formed through either chain- or condensation-type polymerization reactions involving one or several types of monomers. In most waste solidification operations, the waste media is mixed with a melted thermoplastic preformed polymer or gets microencapsulated during a controlled polymerization reaction involving a thermosetting plastic. The inherent resistance of organic polymers to water favors the low leachability potential of a final waste form, but also presents challenges in encapsulating wastes with high water contents. However, the development and use of water-extendable polymers and emulsifiers has led to the encapsulation of many aqueous wastes.

The most prevalent organic-based thermoplastic polymer in use for both the macro- and microencapsulation of mixed waste appears to be polyethylene. Polyethylene's natural resistance to chemical, microbial, and solvent attacks, as well as its increased performance in high-radiation fields, makes it suitable for most dry and homogeneous mixed waste streams. Manufactured via the polymerization of ethylene gas, polyethylene is an inert crystalline/amorphous substance with a relatively low melting point. High-density polyethylene (e.g., 0.95 g/cm^3) contains little branching, as opposed to low-density polyethylene (e.g., 0.92 g/cm^3). Low-density polyethylene is the preferred type for waste encapsulation because it also has a lower melt temperature (e.g., 120°C) and viscosity.[6]

Thermosetting microencapsulation techniques involving polyesters, urea formaldehyde, epoxies, polyurethane, polybutadiene, ester-styrene, and polysiloxane have also been demonstrated on surrogate and/or actual mixed wastes. Bitumen, generated from the distillation of petroleum crude, has been widely used in Europe and Japan as another organic-based material for mixed waste encapsulation. However, its use in the United States has been limited as a result of fire safety concerns. Additionally, numerous tests with unique, low-temperature, microencapsulation techniques involving sol-gels (e.g., polycerams) and novel thermosetting polymers indicate that greater waste loading (i.e., greater than those achievable with conventional portland cement) may be possible with even the troublesome salt-containing mixed wastes. The sol-gel polycerams consist of inorganic and organic compounds linked together by strong silicon oxide bonds. The inorganic and organic liquid precursors are intimately mixed with the waste in a sol, which then gels to a solid waste form following a series of hydration and condensation reactions.

Although potentially more costly, there are many other mixed waste S/S technologies at various stages of development and/or deployment that could be considered as competing with or as adequate as the well-established baselines of portland cement grouting or polyethylene encapsulation. Mixed waste stabilization methods currently in the later stages of development by the DOE include enhanced concretes using proprietary additives, phosphate-bonded ceramics, and several methods provided by commercial vendors.

The chemically bonded phosphate ceramic (CBPC) S/S process, developed at Argonne National Laboratory, is one of several phosphate-based, low-temperature waste S/S processes available. CBPC is unique in that it is formed at room temperatures like a portland cement, but has some properties of a ceramic. The ceramic strength of CBPC is derived from its acid/base chemistry, which produces strong covalent bonds. Acid/base cements have been in existence for over 50 years, but their application as a mixed waste S/S method has only recently been evaluated.[7]

As given by Equation (6.1.3) below, low-temperature stabilization of mixed waste with CBPC is based on the acid/base exothermic reaction between magnesium oxide (MgO) and monopotassium phosphate

(KH_2PO_4) binders. The binders are ground to a powder and blended. The MgO is also frequently calcined beforehand to reduce its reactivity. The reaction produces $MgKPO_4$, hydrated by six moles of water. Additionally, pozzolanic Class C or F fly ash is routinely added to the binders and waste to increase waste form strength and integrity. Under most conditions, heat from the reaction causes a temperature increase up to less than 80°C, until the waste form starts cooling upon curing.

$$MgO + KH_2PO_4 + 5H_2O \rightarrow MgKPO_4 \cdot 6H_2O) \rightarrow MKP\cdot 6H_2O \tag{6.1.3}$$

The hard, insoluble, stable, and dense ceramic of $MKP\cdot 6H_2O$ acts as a crystalline host matrix for the mixed waste. The RCRA hazardous heavy metals and radioactive contaminants in the waste also react with KH_2PO_4 to form insoluble phosphates. In addition, the phosphate minerals (e.g., monazite) formed are natural hosts to radioactive elements and are also insoluble. The final waste forms routinely have compressive strengths greater than 2000 psi and porosities less than those fabricated of cement. The density of the ceramic waste form (~1.8 g/cm^3) is also routinely less than that of a cement form (~2.4 g/cm^3).

A 50 wt% concentrated phosphoric acid (H_3PO_4) solution can be substituted for the KH_2PO_4 binder to form the insoluble newberyite, $MgHPO_4\cdot 3H_20$, ceramic. However, the MKP system is usually perferrred over the acid system because testing has indicated that it generates less heat and improves leachability performance.

Although considered high-temperature methods, alternatives involving nonvitrification, thermal sintering techniques may also lead to acceptable waste forms with considerably more volume reduction compared to that achievable with grouts, polymers, or low-temperature ceramics. Thermal-based stabilization involving sintering methods differs from vitrification in that only melting at grain phase boundaries occur without the complete amorphous restructuring that takes place in glass formation. Like vitrification, sintering occurs at temperatures above 1000°C and can emit volatile hazardous metals. Although densification is possible for some additional volume reduction, slight volume increases usually occur. However, a waste loading as high as 80% is possible. The equipment for sintering is less complex than vitrification, but more complex than grouting or microencapsulation. For a typical sintering process, grinding, mixing, and extruding equipment are required, as well as ovens, calciners, and off-gas treatment systems. For most waste streams, sintering methods will require an extensive process development effort involving statistically designed experiments.

Testing to date indicates that none of the above-described alternative S/S technologies clearly outperforms the others or the baselines. Potential end users will need to consider factors other than waste form performance in choosing an alternative. These factors include but are not limited to — the issue of "stabilization versus encapsulation," the availability of equipment, previous operating experience, the applicability of the technology to other types of waste media, the cost of development, and issues involving both safety and stakeholder concerns.[8]

S/S Equipment

Equipment systems for mixed waste S/S methods are not unlike those that have been used in the hazardous waste industry. Designers of mixed waste S/S processing systems must account for the presence of radioactive fields and protect the worker accordingly. Although most applications will result in "contact-handled environments," advanced shielding and remote operations may be necessary.

Operational systems for deploying most inorganic-based mixed waste stabilization processes involve simple, readily available equipment. Basic equipment components of any system will involve: waste feed, binder, and additive hoppers; waste feed transfer equipment; a mixer; and a mixing vessel and/or disposal containers. Either additives are preblended with other binders and fed from a designated single feed hopper, or dedicated feed hoppers for each additive and/or binder are installed and employed. Hopper weighing scales are used in most systems to ensure the mixing of accurate amounts of waste and additives.

In-container or inline mixer systems are applicable for inorganic-based binder processes. Many existing systems in the non-DOE hazardous waste industry are inline, where the inorganic binders, additives, waste, and water are added to a dedicated mixer and then transferred to a final disposal container before the onset of hardening. Most common are 55-gal batch systems, but continuous operations are possible for consistent and homogeneous mixed waste streams. To ensure disposal compliant waste forms and quality control, samples of the mix are usually taken when transferring from the mixer to the final disposal container.

In-container systems are those that mix the binder, any additives, water, and mixed waste in the same drum to be used for disposal. They include drum tumblers, disposable mixers, and removable mixer systems. A popular removable mixer system involves a 55-gal drum-scale planetary mixer in which hydraulics are used to lower and raise the mixing blades to enable drum placement and removal. Mixing is initiated with the addition of waste and binders and then terminated when the amperage rate on the mixing blades increases sufficiently to indicate the onset of grout setting. Regardless of the chosen system, high-shear, high-speed mixers are recommended.

Operating procedures sometimes involve the addition of premeasured amounts of binders and additives to the drum mixer, followed by alternating additions of waste and water to control heat evolution. However, binders and additives are frequently added to previously charged waste to control mixing and ensure the best waste loading. Mix times are usually an hour, followed by several days of setting and curing before disposal.

Organic-based or thermoplastic polymeric mixed waste processing is routinely carried out in externally heated screw extruders. The extruders can posses either single or double screws. If the extruder contains two screws, they can be either co-rotating or counter-rotating with nonintermeshing or fully intermeshing vanes. Extrusion processing of mixed waste occurs over three distinct zones: feed, transition, and metering.

In the feed zone, the channel is deep and the screw flights are long to allow for sufficient mixing of the waste and the solid pure polymer. This zone frequently contains a circulating coolant to prevent premature melting of the feed materials. In the transition zone, external heat is applied and the channel volume narrows to produce the shear friction needed to melt the polymer. The waste-molten polymer combination in this zone pressurizes and the mix is propelled down the screw. This zone frequently contains a vent for releasing the pressure of any vaporized moisture and volatiles. After an increase in channel volume, the volume is abruptly decreased again in the last zone to obtain the high pressure needed to pump out the homogeneous polymer-waste mix. The molten waste form is usually metered through the extruder die into a disposal container for cooling and curing.

Alternative polymeric processing systems, such as a proprietary kinetic mixer, are able to microencapsulate the high-moisture, high-organic streams unsuitable for extruders. These processes use high-intensity flux, high blade speed mixers that drive off volatiles before they become trapped in the polymer matrix.[6]

Waste Form Performance

Once a mixed waste has been stabilized/solidified, samples of the waste form are subjected to a series of performance tests before final disposal. Depending on the waste acceptance criteria (WAC) imposed by the selected disposal site, the type and extent of these performance tests can vary significantly. For non-DOE, commercially generated mixed waste, the requirements for an NRC-licensed, low-level waste disposal facility must always be satisfied (i.e., DOE-generated mixed waste is not subject to NRC requirements unless it is disposed of in an NRC-licensed disposal facility). Except for mixed waste radiologically classified as transuranic (i.e., TRU), testing to ensure that the RCRA land disposal restrictions (LDRs) have been met will also be required as a minimum. This verification is accomplished through a common EPA leachability test conducted according to the Toxicity Characteristic Leaching Procedure (TCLP). If the TCLP test results indicate that specific contained metals and other RCRA hazardous substances leach at levels below distinct values, the waste may exit RCRA or, as a minimum, be acceptable for land disposal.

In some instances, such as those involving disposal locations regulated by the NRC and accepting commercially generated mixed LLW classified as NRC types B or C, a disposal site may require that the final mixed waste form exhibit a minimum performance in regard to radionuclide retention and migration. If required, long-term radionuclide leachability is frequently determined through completion of the standardized leach test described in ANSI 16.1. This method establishes the leachability of any constituent in the mixed waste form, radiological or nonradiological, and is conducted over a significant time period (e.g., 90 days). Performance results are reported as a leach index, which is the negative log of the diffusivity constant for the specific waste constituent whose leachability is being determined. Higher values are therefore desired, and a value greater than 6 has been recommended by the NRC for most hazardous and radioactive constituents.

Some disposal sites, especially those accepting commercially generated, mixed low-level waste (LLW), require performance data in regard to waste form compressive strength, permeability, and free water content. Limits for these parameters are frequently established in the WAC of specific disposal locations, and the NRC has provided acceptable levels for these and other waste form performance parameters for non-DOE class B and C wastes. Compressive strength is routinely determined via standard method ASTM D1633, and there are numerous other performance tests available to determine and measure its change as a result of wet/dry cycling, freeze/thaw cycling, and exposure to high radiation fields over time. Although rarely specified, performance data is also obtainable by completing standardized tests to determine biodegradation of the waste form.

The type and extent of mixed waste form performance testing are not exclusively dictated by the requirements imposed by the chosen disposal site's WAC. Frequently, extensive performance testing is completed in the S/S development stage to distinguish between competing S/S technologies for both DOE and commercially generated mixed waste.

Recommendations have been made to establish consistent disposal criteria and performance tests for stabilized/solidified DOE mixed waste, in a similar manner that the NRC has established them for commercially generated mixed waste.[10] In particular, tests and methods to establish the long-term durability of S/S mixed waste forms are needed because the TCLP test only establishes the waste form's short-term resistance to leaching.

S/S Economical Considerations

Potential end users of mixed waste S/S processes must consider economics at two distinct decision levels. First, the end user must decide between low-temperature S/S methods and other alternative, thermally based S/S treatment and disposal options. If low-temperature S/S is selected, a second decision must be made: selecting among the numerous S/S binder alternatives available. Usually and obviously, the optimal alternative is the one that provides the most favorable life-cycle economics with regard to the specific end user's unique mixed waste application.

If mixed waste volumes are relatively low, low-temperature S/S is generally the better economical choice over vitrification and plasma melter systems. Melter systems are capital equipment extensive and require expensive control and off-gas treatment. However, for large volumes of waste, the increase in the waste form disposal volume that is generally inherent in low-temperature S/S technologies can negatively affect the overall economics. At this point, vitrification technology may become competitive as a result of the excellent volume reduction and waste form durability it produces. Conversely, for very specific mixed waste applications, pretreating to achieve some of the properties inherent to vitrification (e.g., dehydration, denitration) and then applying a low-temperature S/S technology can provide the similar volume reduction and durability offered by vitrification at a fraction of the cost and complexity. This economic dependency on volume holds accurate for only mixed waste, because the disposal costs for mixed wastes are distinctively greater in contrast to nonradioactive RCRA or CERCLA wastes. For many hazardous-*only* wastes, low-temperature S/S methods may be the economical choice, regardless of volume.

Relative to melter or plasma technology, and regardless of the low-temperature S/S method, the operating, labor, material, and equipment costs among alternative low-temperature S/S technologies for mixed waste are low. As a consequence, these costs are not usually compared when selecting among low-temperature alternatives. End users routinely compare the waste loading and volume reduction among applicable S/S methods because these parameters frequently affect disposal costs more significantly. However, the end user's unique situation and specific requirements do not usually lend themselves to such a simple evaluation method. Factors including complexity of the process, robustness of the equipment, waste pretreatment requirements, and secondary waste generation can be and usually are considered in the selection of the S/S process. Other critical factors include operating experience, throughput potential, level of development, ease of permitting, stakeholder issues, and safety concerns.[9] Any one or a combination of these factors can influence the final S/S technology selection, regardless of cost.

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For Further Information

Technologies now available for the solidification and stabilization of applicable mixed wastes are obviously either an extension of or identical to long-established S/S methods applicable to either low-level radioactive or RCRA hazardous only wastes. The literature indicates that S/S methods for hazardous or low-level only wastes have been in practical use for over 40 years. They were developed with the fundamental objective of primarily immobilizing either the hazardous or radiological component, and are therefore logical initial choices for mixed waste.

Considerable information on LLW stabilization information is collectively available in two reports published by the International Atomic Energy Agency (IAEA). One is entitled "Improved Cement Solidification of Low and Intermediate Level Radioactive Wastes" (No.350/1993). The other is "Immobilization of Low and Intermediate Wastes with Polymers" (No.289/1988). The information in these publications is based on extensive experience with the treatment of LLW generated by the nuclear power industry. Technologies and actual processes deployed are described in detail, as well as waste form performance and descriptions of the types of waste treated. Additional information on these publications is accessible by consulting the following Web site: http://www.iaea.org/worldatom/publications/nfcwm/waste.html.

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Over the past 8 years, considerable development by the DOE has been performed in an attempt to identify and qualify alternative S/S methods for troublesome and challenging mixed waste streams. In particular, the DOE's Mixed Waste Focus Area of the Office of Science and Technology has sponsored research and development on S/S technologies involving polyethylene micro/macroencapsulation, sulfur polymer cement, polyesters, enhanced concretes, polysiloxane, phosphate-bonded ceramics, sol-gels, and sintered ceramics. Details on the specifics of these mixed waste S/S methods have been published in a series of Innovative Technology Summary Reports (ITSRs). These ITSRs are available through the following Web site: http://wastenot.inel.gov/mwfa/sadoc.html.
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6.2

Chemical Fixation and Stabilization

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Introduction

Stabilization is a technology for treating hazardous, radioactive, and mixed wastes, debris, and contaminated environmental media. The objective is to reduce the hazard (solubility, leaching, toxicity) of specific contaminants so that the resulting waste forms can be disposed of in approved/licensed facilities. In general, the stabilization chemistry and technologies that are applied to hazardous and low-level radioactive wastes are also applicable to mixed wastes. However, innovative technologies are required for unique processing requirements/limitations and for some specific waste streams. Treatment technologies related to chemical stabilization and fixation include vitrification (high-level mixed wastes), sintering, hydrothermal processing, and hot isostatic pressing. These processes have the same objective as stabilization/fixation but are carried out at higher temperatures and require rigorous off-gas controls. Most stabilized waste forms are processed at ambient temperatures and have ventilation controls appropriate for the radioactive and chemical contaminants present in the waste.

Stabilization of mixed waste results in a waste form that requires disposal. The U.S. Environmental Protection Agency (EPA) in conjunction with state agencies regulates treatment and disposal of the hazardous contaminants in stabilized mixed waste forms. The EPA has identified stabilization as the best developed available technology (BDAT) for several specific hazardous waste types, which are assigned Resource Conservation and Recovery Act (RCRA) listed waste codes. Unless delisted, stabilized listed hazardous and mixed wastes must be disposed of in a hazardous or mixed waste disposal facility (RCRA Subtitle C Facility). Stabilization is also identified as one technology for achieving performance-based standards (leaching limits) for wastes that display the RCRA characteristic of toxicity. In contrast to treated listed hazardous/mixed wastes, characteristically hazardous and mixed wastes can exit RCRA regulation if treatment (stabilization) results in the waste form no longer displaying the original characteristic(s).

Treatment and disposal of the radioactive contaminants in mixed wastes are regulated by either the Nuclear Regulatory Commission (NRC) (commercially generated waste) or by the U.S. Department of Energy (DOE) (waste generated at federal facilities). The NRC has licensed specific stabilization technologies for treatment of commercially generated low-level radioactive wastes (Class A/B/C). Commercially generated mixed wastes, debris, and contaminated environmental media such as soils, pond sludges/sediments must meet the applicable EPA/RCRA and NRC requirements, in addition to processing and transportation requirements and the waste acceptance criteria for the intended disposal facility. Stabilized mixed waste forms generated at federal facilities must meet the EPA/RCRA, DOE, transportation, and disposal facility requirements for disposal.

Terminology

The terms “fixation,” “solidification,” “immobilization,” and “encapsulation” (micro and macro) are, at times, used interchangeably with stabilization. However, these terms have unique technical as well as regulatory meanings. In this discussion, stabilization and fixation refer to chemical alteration of the contaminants to a less soluble, mobile or toxic form. The physical nature and handling characteristics of the waste are often but not necessarily changed by stabilization/fixation. An exception to this definition is encountered in landfill or tank stabilization applications. In these cases, treatment is intended to achieve physical stability; that is, to prevent subsidence of the overburden and closure cap. *In situ* stabilization of waste in a tank refers to chemical treatment/fixation of the contaminants in this material.

Solidification refers to physical alteration of the waste to a new physical form, such as converting a liquid, sludge, or slurry into a solid or converting a fine particulate waste into a granular or monolithic waste form. As a result of this treatment, liquid wastes are made “spill proof” and particulate wastes are made “dust proof.” A solidified waste form may be a monolithic block (rigid solid), a clay-like material (plastic solid), or a granular solid. Reducing the surface area also reduces the extent of direct contact between the waste and the environment. Solidification may or may not result in chemical interaction between the contaminants/waste and the treatment reagents. However, stabilization processes often result in some degree of physical solidification.

Encapsulation is usually applied to a process in which the waste particles are physically entrapped and completely surrounded by inert material. Solid particles in the waste and particles formed as a result of the stabilization reactions are often referred to as being microencapsulated in the waste form matrix or binder. Technologies based primarily on encapsulation and immobilization of waste particles and debris in organic and inorganic media are discussed in detail in subsequent subsections.

Vitrification, sintering, and metal melting accomplish the same general objectives as stabilization and fixation and are described in subsections. Although these high-temperature processes usually result in lower leaching and lower volume waste forms, there are many instances in which cost and the management of secondary wastes (off-gas and spent equipment) do not warrant their selection.

Waste Form Selection and Design

Selection and design of a stabilization/fixation treatment process and/or final waste form require detailed characterization of the starting material, processing requirements (production rate, capacity, shielding, etc.), and a listing of the regulatory requirements and waste acceptance criteria (WAC) for the intended disposal facility. A working knowledge of the commercially available products and processes will facilitate comparing technologies and selecting the most cost-effective, technically acceptable option. Several excellent reference books on the subject of hazardous waste stabilization are available (Conner, 1990; Conner and Wilk, 1997; Adaska et al., 1998).

Both processing properties and cured properties must be specified and controlled for quality assurance. Some of the properties that are often specified, along with the relevant test methods, include:

1. Workability: the ability to mix the ingredients (mixing tests, pilot-scale tests)
2. Rheological properties: viscosity/yield strength/consistency (rheometer measurements), slump (ASTM C-143), flow (ASTM D-6103)
3. Gelation time, gel point: time after mixing at which the slurry/paste stops flowing in response to stress (rheometer measurements)
4. Set time: time after mixing at which the waste form displays the properties of a rigid solid (ASTM C-403)
5. Bleed water: water that accumulates on the surface of waste forms as the result of phase segregation/gravity settling of the solids in the slurry/paste (ASTM C-232)
6. Air content: volume of air voids in the waste form (ASTM C-231)
7. Unit weight: density after casting the waste form (ASTM C-138)

8. Temperature rise: temperature rise of the waste form if it is cured under adiabatic (insulating, mass pour) conditions (adiabatic calorimeter)

Cured properties that are often specified include:

1. Compressive strength: (ASTM C-39, C-109, D-2166, D-1633)
2. Free standing/drainable liquid (not the same as bleed water): drainable water is determined prior to disposal; bleed water is determined soon after setting (ANSI/ANS 55.1)
3. Hydraulic conductivity: (U.S. EPA Method 9100-SW846 or modified ASTM tests for soil or rock)
4. Leaching limits for RCRA metals: EPA Toxicity Characterization Leaching Procedure (TCLP); limits are set by EPA and/or governing state agencies.
5. Leaching limits for radionuclides: ANSI/ANS 16.1 (American Nuclear Society, 1986; Fuhrmann et al., 1990).
6. Durability if applicable: (U.S. Nuclear Regulatory Commission, 1991)
7. Irradiation stability: (NRC protocol)
8. Thermal cycling: (ASTM B-553 modified per NRC protocol)
9. Freeze-thaw: (ASTM D-4842)
10. Wet-dry cycling: (ASTM D-4843)
11. Biodegradation: not required for Portland cement/lime waste forms

A summary of other relevant physical tests, chemical testing procedures, and technology screening protocols is provided elsewhere (U.S. EPA, May 1989).

In general, treatability studies are performed with both surrogate and actual waste samples to evaluate stabilization/fixation reagents and to develop the process flow sheet. Treatability studies are typically performed at the bench scale. For a new process or waste stream, pilot-scale testing is often necessary to confirm unit operations, portions of a treatment train, or the entire flow sheet.

In many cases, the radioactive contaminants in the waste or other properties of the waste make the commercial processes and fixation/stabilization reagents unacceptable. This is especially true for unique mixed waste streams encountered in the DOE complex. For several years, the DOE has been coordinating development, demonstration and deployment of innovative technologies for mixed waste stabilization (Mayberry and DeWitt, 1983). Several of these innovative technologies are described in this chapter section.

Applications

Aqueous waste streams (slurries and sludges), fine particulate wastes, high salt wastes, and high-volume environmental media are candidates for stabilization. In practice, stabilization and the related technologies defined above are considered as treatments for mixed waste and debris when the contaminants of concern (COC) — typically metal species — cannot be recovered for reuse, separated for special treatment, or destroyed. This is illustrated in Figure 6.2.1. Stabilization is also applicable to wastes for which ambient temperature or low-temperature treatment is advantageous due to release of contaminants in the off-gas at higher temperatures.

Waste types that are not suitable for stabilization include materials that are dimensionally unstable in the chemical environment of the waste form matrix (Glasser et al., 1988) and/or surrounding environment. For example, ion exchange resins may shrink and swell in response to changes in ionic strength of associated fluids, the presence of competing ions, or fluctuations in moisture content. Consequently, many resins are not compatible with hydrated cement waste forms. Metals or alloys, which react with water (pyrophoric or subject to extensive corrosion), are also unsuitable for stabilization in hydrated waste forms. For example, aluminum metal corrodes under alkaline conditions and generates hydrogen gas. Wastes containing hazardous organic contaminants are not typically treated by stabilization. The organics are usually treated/destroyed by oxidation. Several commercially available products contain reagents to emulsify and/or chemically bind non-hazardous organic contaminants in hydrated waste forms. Activated carbon is also used as a reagent to chemically sorb organic compounds/contaminants.

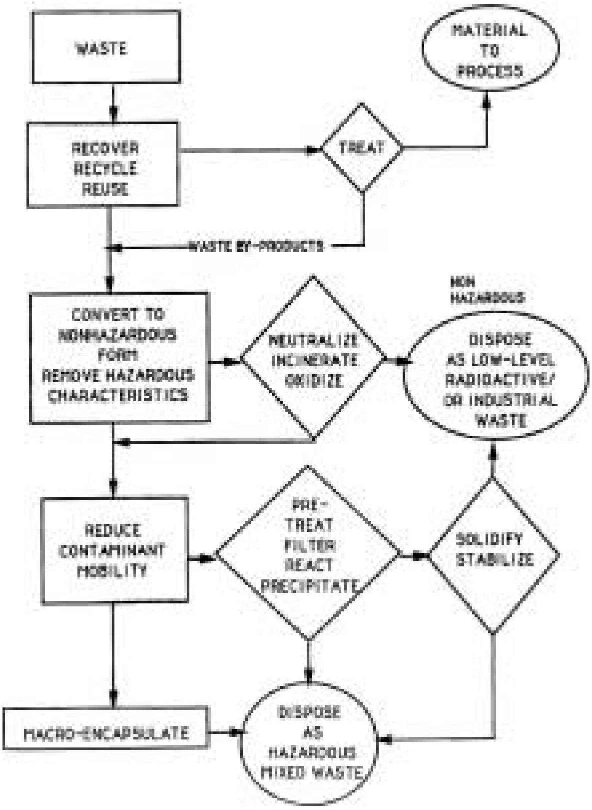

FIGURE 6.2.1 Flowchart illustrating the logic of selecting a stabilization/fixation mixed waste treatment.

Flexible processing at ambient temperatures is a feature of most chemical fixation/stabilization technologies. For example, wastes can be mixed with the reagents in-container, in-line, or in a mixer. A facility can be operated as a batch or as a continuous process. Low-volume mixed waste streams are often treated in-drum. Large-volume streams are typically processed on a repetitive batch or continuous basis using in-line mixers.

Treatment trains can be designed to include single or multiple pretreatment step(s). Alternatively, waste forms can be designed so that the contaminants are treated *in situ* by reacting with the compounds which form the matrix phases or by reacting with special additives included in the formulation. Examples of three treatment trains for an aqueous mixed waste include:

1. Treat with fixation chemicals → Dewater → Package solid material for disposal and evaporate or discharge water
2. Concentrate → Pretreat (pH Adjustment + Precipitate contaminants) → S/S with cement
3. Evaporate (optional) → Cement stabilize *in situ* → Cure

In the first example, the reagents for chemically fixing/stabilizing the contaminants are added to the aqueous waste and then dewatered (evaporation or filtration). The stabilized contaminants are converted to a solid form (particulates, filter cake, monolith, etc.) and can then be tested and packaged for disposal. Wastewater generated in this process can be evaporated or further treated for discharge. In the second example, the aqueous waste is concentrated to minimize process feed volume and pretreated if necessary to ensure cement reactions will occur. Pretreatment can also address chemical fixation of one or more contaminants. The concentrated solution slurry is then solidified with or without additional stabilization in a cement matrix. In this example, the wastewater is used to hydrate the binder reagents. In the third example, all of the contaminants of concern (COC) are treated by reactions with chemicals/compounds inherent to or blended with the stabilizing/solidifying reagents. Much of the water associated with the waste is used to hydrate the binder reagents. Systems engineering studies are used to determine the best technical, operational, and cost-effective approach.

Chemical Fixation and Stabilization Mechanisms

Hazardous metals and radionuclides cannot be destroyed in non-nuclear waste treatment processes. Removal and reuse is also not practical because trace quantities of radionuclides are usually associated with the recovered material. The contaminants in mixed waste that require treatment are typically present as soluble chlorides, hydroxides, nitrates, nitrites, oxides, phosphates, silicates, or sulfates. The objective of chemical fixation is to convert the dissolved species or soluble precipitates to low-solubility compounds or forms. Waste with dissolved contaminants are easier to treat than those containing leachable solids because the aqueous contaminants can be precipitated directly as low-solubility phases. In contrast, leachable solid particles must either be dissolved and then reprecipitated, or alternatively coated with insoluble reaction products. The most effective surface treatments typically involve reactions with the soluble species. For example, wastes containing particulate lead oxide can be reacted with soluble phosphate (PO^{4-}) to form a low-solubility lead phosphate hydrate layer on the particles.

- Mechanisms for chemical fixation of hazardous metals and non-metals and radionuclides include:
- Precipitation or co-precipitation (aluminate, carbonate, hydroxide, oxide, phosphate, sulfate, sulfide, silicate, titanate)
- Solid solution formation
- Sorption
- Chemisorption
- Ion exchange

Some of these mechanisms are inherent to the hydration of the primary binder phases. Others can be induced by changing the contaminant concentration, adjusting the alkalinity (pH), controlling the redox potential (E_h), or including appropriate reagents. A systematic description of chemical fixation mechanisms and reagents for treatment of the RCRA hazardous metals and other inorganic and organic contaminants is presented elsewhere (Conner, 1990).

Chemical Stabilization/Solidification Technologies

Chemical stabilization/solidification (S/S) technologies are classified according to the ingredients/reagents that form the solid matrix/binder phases. S/S reagents and mixtures of reagents that react with water to form solid binders are referred to as cements. Examples of inorganic cement systems, commercial products, and associated waste forms are listed in Table 6.2.1.

Stabilization reagents can be purchased in bulk or as prepackaged mixes. They can be customized for specific waste streams and/or performance requirements. The bulk compositions of the common ingredients in hydraulic cement waste forms are illustrated in Figure 6.2.2. Proprietary formulations typically contain mineral and chemical additives that are included to reduce leachability of both hazardous and radioactive contaminants and to improve processing. Patented products for stabilizing mixed wastes are also available from several manufacturers.

Hydraulic Cement Waste Forms

Reagents and Specifications

When hydraulic cements (Portland cements, lime cements, kiln dust cements, etc.) are mixed with water or aqueous wastes, the compounds in these materials react to form an alkaline slurry or paste with an initial pH of about 11 to 12.5. Portland cement hydration is the result of anhydrous calcium silicate phases reacting with water to form amorphous calcium silicate hydrate phases. The reactions involved and the properties of the resulting material are described in detail elsewhere (Conner, 1990; Taylor, 1997). A special subset of

TABLE 6.2.1 Inorganic Cement Systems, Commercial Products, and Associated Waste Forms

Inorganic Cement System	Product Trademarks or Waste Forms[a]
Calcium silicate hydrates	
Portland cement	WV Cement Waste Form, SR Ashcrete
Portland cement-pozzolan (slag, fly ash, etc.)	SR Saltstone, SR Reducing Grout
Portland cement-soluble silicates	SR Naval Fuels Saltcrete
Portland cement-pozzolan-Clay	OR Hydrofracture Grout, HF Saltcrete
Portland cement/lime-soluble silicates	Delaware Custom Materials waste form
Lime-pozzolan	Phoenix Ash™
Aluminum silicate hydrates	
Clays, modified clays, cement/clay mixtures	Aquaset™, Petroset™ (Fluid-Tech Inc.)
Complex silicate hydrates	
Slag/Alkali hydrates	Super Cement™ (ATG Inc.)
Calcium aluninate hydrates	
Calcium aluminate cement	Fondu™ (LaFarge Cement Co.)
Calcium sulfate hydrate	
Gypsum	Envirostone™ (US Gypsum Inc.)
Magnesium phosphate	
Magnesium phosphate cement	Ceramicrete™ (Argonne National Lab)

[a] Indicates U.S. DOE facilities where technology was/is used. HF = Hanford, Washington; OR = Oak Ridge, Tennessee; SR = Savannah River, South Carolina; WV = West Valley, New York. Calcium aluminate cements and calcium sulfate cements are not used extensively for mixed waste treatment. Magnesium phosphate cements are discussed in a later chapter section

this system is made up of the slag cements in which alkali hydroxides (NaOH, KOH), or alkaline earth oxides/hydroxides (CaO, $Ca(OH)_2$ are used as set activators. Again, the reaction products of the glassy slag, alkaline compounds, and water are insoluble, amorphous silicate hydrates (Chandra, 1997). Another subset consists of the lime-pozzolan mixtures. The lime or hydrated lime reacts with water and amorphous silicate/aluminate phases (pozzolans) to form insoluble matrix phases similar to those in Portland cement pastes. The lime S/S systems are widely used in environmental restoration projects to reduce leaching/mobility of the same hazardous and radioactive contaminants as found in mixed wastes.

Specifications for the various types of Portland cements, hydraulic slags, and pozzolans manufactured in the United States are provided by the American Society for Testing and Materials standard methods, ASTM C-150, C-989, and C-618, respectively (ASTM, 1997). Portland cement Type I (general purpose), and Type V (sulfate resistant), are most often used in waste form application. Type I Portland cement is often referred to as ordinary Portland cement (OPC). Type III, a high early strength, is occasionally used to minimize settling and bleed water.

Leaching Properties

In general, cement waste forms meet the NRC low-level waste leachability index requirements of ≥6 for radioactive contaminants (Atkins et al., 1986). However, additional additives are often incorporated in the mixed waste forms to achieve chemical fixation of specific radioactive and hazardous contaminants. Examples include:

- Reducing agents, such as sodium thiosulfate are used to lower the valance state of contaminants, such as Cr^{6+} and Tc^{7+} to Cr^{3+} and Tc^{4+}, thereby causing them to precipitate as low-solubility hydroxide compounds in basic systems (Barnes et al., 1988; Gilliam et al., 1987).
- Chemical reagents, such as soluble sodium silicate and ferrous phosphate react with most RCRA metal contaminants to form low-solubility precipitates.
- Reactive agents, which sorb contaminants onto surfaces include clay minerals, such as illite (Gilliam et al., 1987), modified clays, such as heat-treated attapulgite, metal hydroxides such as iron hydroxide or iron filings, and activated carbon (Spence et al., 1993) are used to sorb cesium, strontium, and other radionuclides and RCRA metals.

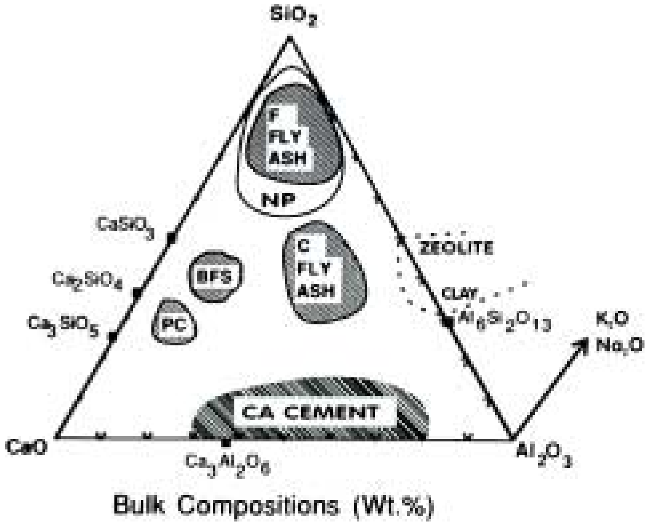

FIGURE 6.2.2 Bulk compositions of materials used in inorganic hydraulic cement waste forms. CA = calcium aluminate cement, BFS = blast furnace slag, and PC = portland cement. Zeolites and clays contain water. The compositions shown in this figure are projected onto the anhydrous portion of the phase diagram.

- Ion exchange materials, such as natural zeolites (clinoptilolite and phillipsite have been tested for cesium stabilization) and synthetic zeolites, can also used as additives in mixed waste forms.

Physical Properties

The compressive strengths of cement waste forms range from about 0.5 to greater than 20 MPa, depending on the type and amount of cement and pozzolan, water content, additional stabilizing reagents, waste loading, type of waste, and age of the sample. Compressive strength is relatively simple to adjust over the range stated above and is usually not a limiting property in the overall design and production of waste forms. Adjustments in compressive strength are typically achieved by modifying the above parameters. For example, lowering the water to cement ratio results in an increase in compressive strength (Taylor, 1997).

The majority of the matrix phases in Portland cement waste forms are amorphous silicate hydrates, which have a high surface area. Cement waste forms have a high porosity (about 40 vol% voids) and are typically at least partially saturated under normal disposal conditions. The pores are interconnected and range in size from gel pores (10^{-8} cm) to capillary pores ($10^{-4 \text{ to } -5}$ cm) to air voids ($>10^{-2}$ cm) (Taylor, 1997).

The hydraulic conductivities and compressive strengths of Portland cement waste forms depend on the formulation and, in particular, on the water to total cementitious solids ratio (w/c_{total}). Pozzolans are usually included as cementitious material if the physical properties of the waste forms are evaluated or predicted after long-term curing. Saturated hydraulic conductivities of cement waste forms typically range from 10^{-7} cm/s to $<10^{-12}$ cm/s for $w/c_{total} = 1.0$ to 0.30, respectively (Walker, 1999). Reducing the hydraulic conductivity is typically accomplished by lowering the $w{:}c_{total}$ ratio. By adding dispersants, such as polycarboxylic acids or lignosulfonates, this ratio can be usually be lowered to about 0.3 for pumpable mixtures. A summary of the performance properties for stabilized low-level waste forms is presented elsewhere (Mayberry and DeWitt, 1993).

Processing Properties

Pozzolans and inert fillers are often used to adjust processing properties, such as set time, bleed water, workability, slump, and pumpability, and thermal transients resulting from the exothermic hydration reactions. Workability, pumpability, gel time, and set time can be modified by incorporating dispersants, fluidifiers, set accelerators, retarders, and anti-bleed additives. A detailed description of commercially available processing aids is presented elsewhere (Ramachandran, 1984).

The ratio of water to cement (or total cementitious materials) is usually specified in the Portland cement and related systems to achieve both the processing requirements and the final waste form properties. Waste forms, which are designed to be pumpable, are often referred to as grouts or slurries. Waste forms that are mixed in the disposal container or in a mixer discharging directly into a container are referred to as either pastes or grouts. Several types of in-container mixing systems are used for small batch processes. In-drum disposable paddles/mixers and reusable overhead mixers are most common; however, drum tumbling is also used. In-line vane or auger/screw mixers are typically used for high-volume waste streams.

The water can be added as mixing water or it can be part of the waste, as in the case of sludges, slurries, and brines. Waste loading can be reported either in terms of the weight percent waste (specify if the weight of the water is or is not included) of the waste form or the volume increase (i.e., the volume of the final waste form compared to the volume of the actual waste). Because inorganic silicate-based cements have a higher specific gravity than the phosphate and aluminate cements and organic binders, comparisons made on the basis of weight percent waste do not correlate with comparisons made on the basis of volume increase. Disposal costs are usually a function of disposed volume. However, transportation costs are calculated on a volume and weight basis.

Recent Innovations: In-Tank Waste Stabilization

Innovative strategies for stabilizing wastes in tanks have recently been developed. Complete retrieval/removal of the residual/incidental material or "heals" in empty mixed waste tanks can be very difficult and expensive due to the associated radioactivity. Consequently, innovative technologies have been applied to in-tank mixing of waste sludges/slurries and stabilizing reagents. Single and multiple point jet grouting equipment has been designed and successfully tested to intimately mix waste and the stabilizing materials.

Another approach that has been used at full scale relies on a sparging action to intimately mix the residual waste and reagents. In both cases, the reagents are delivered to the tank in the form of a premixed slurry. These slurries can be formulated to contain one or more reactive reagents for stabilizing specific contaminants in addition to reagents such as Portland cement which hydrate to form the matrix phases. A third technique recently used in the closure of high-level waste tanks at the DOE Savannah River site involved encapsulation or "sandwiching" of a small amount of residual mixed waste sludge in between successive grout placements. The initial grout pour was used to displace the sludge off the bottom of the tank due to density differences. The soluble contaminants in the sludge liquid were then stabilized with a "top dressing" of dry reagents. The stabilized/solidified residual waste was then encapsulated with a successive layer of grout. Stabilizing reagents, sodium thiosulfate and ground blast furnace slag, were used to chemically reduce Tc^{7+} to Tc^{4+}, which was subsequently precipitated as TcO_2. The same stabilizing reagents were also present in the grout used for this encapsulation (Caldwell et al., 1998). The grout mixes designed for this application were self-leveling and flowed over 10 meters without segregation or bleed water formation.

Chemical Fixation and Solidification

Alumino-Silicate Waste Forms

Alumino-silicate-based treatment agents contain clays, modified clays, and often additives to control the hydration of the clays. Zeolites can also be used in these systems. Mixtures of different clays, sodium bentonites, calcium bentonites, attapulgite, illites, and modified clays are formulated to enhance the stabilization/fixation of the specific contaminants of concern. Chemical stabilization occurs by adsorption, chemisorption, or incorporation into the crystal structure of the mineral reagents.

These systems are typically used for treating aqueous-based mixed waste streams with a high water content. Similar to the cement systems, the clay systems also bind the water and render the waste form a solid. The alumino-silicate systems are very versatile and are used for treating waste containing high concentrations of dissolved salts and organic contaminants.

Alumino-silicate waste forms have a wide range of physical properties, which can range from soft, clay-like soil (plastic) to a granular soil-like material to a hard solid. A cement component is commonly added to the alumino-silicate systems to achieve stronger materials. The soil-like properties of some of these systems are ideal for disposal scenarios in which the treated wastes are compacted in the field to maximize space utilization in a landfill.

Summary

Fixation/stabilization is one of the most widely used technologies for treating low-level radioactive mixed waste. Cement waste forms are typically based on Portland cement and hydraulic slags (hydrated calcium silicate binders). Mineral systems are typically based on clays (hydrated alumino-silicate minerals). Chemical fixation/stabilization is widely used because it offers flexible treatment trains, ambient temperature processing, a wide range of physical and processing properties, compatibility with a wide variety of wastes, excellent radiation stability and chemical durability, and low materials and processing costs. Additives are often used to immobilize specific radioactive and/or hazardous contaminants.

A large amount of information on fixation/stabilization of hazardous and radioactive wastes is available in the open literature, in government reports, and in vendor reports. Much of the data can be directly applied to mixed waste treatment. Technology development in this field is primarily related to processing and placement needs associated with unique mixed waste applications such as in-tank mixing of waste and stabilization reagents.

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For Further Information

A good introduction to cement-based waste form design is presented in *Chemical Fixation and Stabilization of Hazardous Wastes,* by J.R. Conner. The author provides background information of cement hydration, waste form processing and contaminant stabilization.

The monthly journal *Waste Management* is an international journal of industrial, hazardous and radioactive waste management science and technology. This journal is a forum for new developments in stabilization treatments.

The U.S. DOE and the USEPA Office of Solid Waste and Office of Research and Development have also published many useful reports on general and specific mixed waste stabilization technologies.

6.3

Chemically Bonded Phosphate Ceramics for Stabilization and Solidification of Mixed Waste

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Introduction

Approximately 250,000 m^3 of mixed low-level waste resides within the U.S. Department of Energy (DOE) complex.[1] It exists in various forms in the following proportions: 39% aqueous liquids, 17% inorganic sludges and particulates, 25% heterogeneous debris, 3% soils, and 5% organic liquids. The volume will increase to 1,200,000 since 1994. In addition, the DOE's treatment plans currently show a significant number of waste streams that require solidification and stabilization.[1] Thus, there is a significant need for a room-temperature stabilization technology.

The low-level mixed wastes contain both hazardous chemical and radioactive species. Stabilization of such wastes requires that contaminants be immobilized effectively. Often, the contaminants are volatile and hence cannot be treated effectively by high-temperature processes.[2] These volatiles are usually in the form of chlorides or fluorides of heavy metals and actinides. Fluorine and chlorine are introduced in the wastes from the production processes or plastics such as polyvinylchloride. In a conventional vitrification or plasma hearth process, such contaminants may be captured in secondary waste streams such as scrubber residues, or off-gas particulates that need further low-temperature treatment for stabilization. It may not be viable to continuously recycle these secondary waste streams in the feed stream of the high-temperature process because of the buildup of contaminant levels. These secondary waste streams will therefore require low-temperature treatment to meet existing Land Disposal Restrictions (LDRs). Also, some waste streams may contain pyrophoric materials that ignite spontaneously during thermal treatment, potentially causing hot spots that may require expensive control systems and equipment with demanding structural integrity.[2] Some sites do not allow thermal treatments. Therefore, there is a critical need for a low-temperature treatment-and-stabilization technology that will effectively treat the secondary wastes generated by high-temperature treatment processes and wastes that are not amenable to thermal treatment; this was the main objective in the development of chemically bonded phosphate ceramics (CBPCs). Now developed, CBPCs have found their niche applications in treating most difficult wastes such as salts, ashes, liquids, and sludges.

Transuranic (TRU) wastes contain incinerated residues such as ash, ash heels (i.e., ash calcined to get rid of loss-on-ignition fraction for safe transportation), and Pu-contaminated crucibles are stored at several DOE sites.[3] Some of these wastes contain as much as 17 wt% Pu and require stabilization for their safe transportation, safeguarding, and storage at facilities such as the Waste Isolation Pilot Plant (WIPP). Earlier attempts to stabilize such waste streams[4,5] employed thermal treatments that were based on encapsulating wastes in a dense, hard ceramic or glass matrix. Such heat treatment of TRU wastes is generally expensive. Formation of a good monolithic glass may also be difficult because flaws develop in the matrix due to pyrophoric components during processing of the waste streams. In addition, if the TRU wastes also contain hazardous components, the release of off-gases containing volatile species must be treated to meet permit requirements. CBPC technology was successfully demonstrated for these wastes.

Chemically Bonded Phosphate Ceramics

CBPCs are fabricated by acid-base reactions between an inorganic oxide and either phosphoric acid solution or an acid-phosphate solution. Kingery[6] conducted preliminary studies of phosphate bonding in refractories at low temperatures and identified several phosphate systems that form hard ceramics. The acid-base process has the advantage that it can be used to treat both acidic and alkaline wastes. In addition, because the process employs solid powder and phosphate solution for the reactions, both solid and liquid wastes can be treated. Solid wastes can be crushed and mixed with a starter powder and then reacted with liquid; liquid waste can be mixed with the phosphoric acid or acid-phosphate solution and then reacted with the inorganic-oxide powder. After the acid solution and base powder are mixed, the slurry can be transferred into molds for setting. Because of the acid-base reaction, this technology is applicable to systems within a wide pH range. These advantages broaden the applicability of this technology. Their low-temperature-setting characteristics, good strength, and low porosity make these phosphates suitable for the stabilization of mixed wastes that cannot readily be treated by current technologies.

Previous work at Argonne National Laboratory (ANL)[7-10] and that of others[11,12] on the development of the CBPCs demonstrates the inherent favorable properties of these materials for containment of mixed wastes. Some of these properties are summarized below.

- *Natural analogs of radioactive and rare earth elements.* Monazites ($[Ce, La, Y, Th]PO_4$) and apatites ($Ca_5[PO_4]_3$) are ores of U and Th and are natural host minerals of rare earths and radionuclides. These natural analogs suggest the suitability of phosphate systems for incorporating actinides.[13]
- *Extreme insolubility.* Phosphates are extremely insoluble[14] in groundwater, which ensures that the phosphate-based final waste forms will protect groundwater from contamination by the contained waste. A study by Sliva and Scheetz[12] shows good performance of the waste forms that simulated wastes from the Idaho Nuclear Technology and Environmental Center; retention of Cs and Sr was excellent. Long-term leach tests conducted at ANL on Mg-phosphate systems showed that these phosphates are essentially insoluble in water and brine.[7-10] These examples indicate that phosphate complexes are most suitable for containment of mixed waste.
- *Phosphates can be used in solid form at room temperature.* As solidifying agents for low-level mixed waste, $MgKPO_4$ has been used exensively.[6]
- *Nonflammable compounds.* Phosphate-bonded ceramics are nonflammable inorganic materials and hence are safe during transportation and storage.
- *Minimal secondary waste streams and heat generation.* Because the final waste form is synthesized at a low temperature, volatilization is not a risk. Furthermore, because there is no thermal treatment of the waste streams, the fabrication steps and processing equipment needs are simple. In addition, the entire stabilization reaction occurs within hours. The short setting time is particularly advantageous because it minimizes worker exposure when radioactive waste is treated.
- *Low overall processing costs.* The raw materials required for fabricating the waste forms are readily available at comparatively low cost. In addition, the fabrication technology is simple, very similar to cement stabilization, and uses the similar equipment that is used to stabilize cement. The

stabilized product has a volume tht is nearly the same as that of the waste due to densification. This also reduces the disposal costs.

- *Other favorable properties.* The radiation stability of magnesium ammonium phosphate is excellent.[15] Changes in the mechanical integrity of the material were not detected after gamma-irradiation to a cumulative dosage of 10^8 rads. Also, aluminum phosphate is known to be a molecular sieve, and zirconium phosphate has a large ion-exchange capacity.[16] Such properties make phosphates excellent host materials for radioactive isotopes.

Synthesis of CBPC

CBPCs are formed by reaction between magnesium oxide (MgO) and monopotassium phosphate (KH_2PO_4) in solution. The reaction is governed by the reaction:

$$MgO + KH_2PO_4 + 5H_2O \rightarrow MgKPO_4{\cdot}6H_2O \tag{6.3.1}$$

This reaction yields the hard, dense ceramic of magnesium potassium phosphate hydrate, $MgKPO_4{\cdot}6H_2O$ (MKP), which acts as a crystalline host matrix for the waste. During the reaction, the hazardous and radioactive contaminants also react with KH_2PO_4 to form highly insoluble phosphates. The bulk ceramic then microencapsulates the reacted contaminants in the dense crystalline matrix of MKP. The crystallinity of the CBPC and overall phase formation may be seen in the scanning electron microscopy (SEM) microphotograph and X-ray diffraction output in Figures 6.3.1 and 6.3.2, respectively.

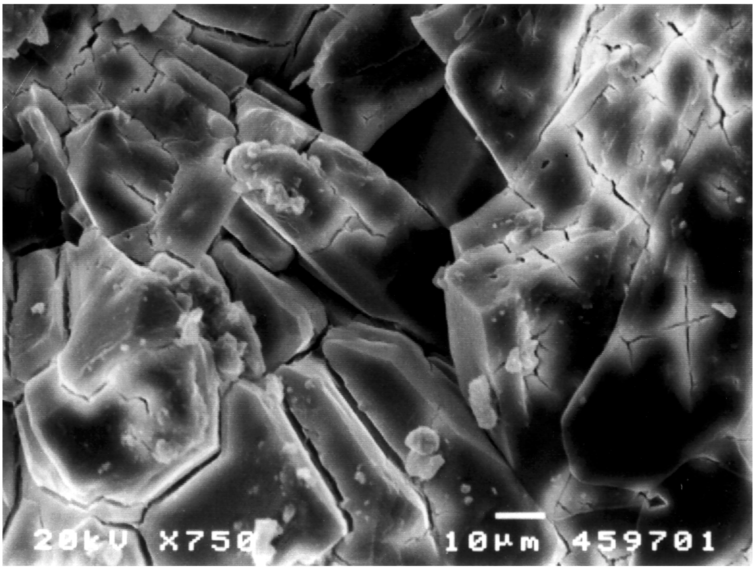

FIGURE 6.3.1 SEM photomicrograph of CBPC matrix.

CBPC waste forms are fabricated by slowly stirring a mixture of the waste, MgO, and KH_2PO_4 in water. Because of the dissolution of the KH_2PO_4, the solution contains ions of potassium phosphates and protons (H^+) and is therefore acidic. The acidity of the solution increases the solubilities of MgO, oxides of hazardous metals, and to some extent, radioactive contaminants, and leads to the dissolution of the MgO and the contaminants. This, in turn, leads to the release of Mg^{2+} and metal ions of the contaminants. These cations subsequently react with the aqueous phosphate ions to produce phosphates.

To form a ceramic of MKP, it is necessary that Mg^{2+} react slowly with the phosphate ions. On the other hand, it is necessary that the hazardous metals and radioactive components react rapidly so they can be encapsulated in the MKP matrix. If the metals and radioactive components react at a rate that is

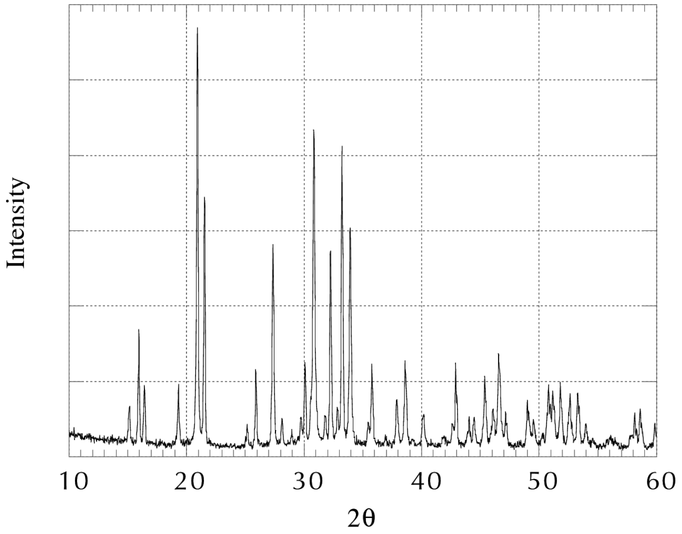

FIGURE 6.3.2 X-ray diffraction output of CBPC matrix. All peaks have been identified as those of $MgKPO_4 \cdot 6H_20$.

slower than the formation of the MKP matrix, sufficient phosphate anions will not be available for them to react and they will not be fixed by the matrix as phosphates. Thus, for superior stabilization, it is necessary that contaminants be converted to phosphates rapidly.

The setting reaction given by Equation 6.3.1 can be quantitatively formulated by studying the thermodynamics of dissolution and overall reactions of the oxides in the KH_2PO_4 solution. The KH_2PO_4 has high solubility and its dissolution is described by:

$$KH_2PO_4 = 2H^+ + KPO_4^{2-} \tag{6.3.2}$$

where the superscripts represent the ionic charge. This reaction is endothermic and occurs before other components dissolve. When an alkaline oxide such as MgO is stirred into the acidic phosphate solution, the pH of the solution slowly rises because the acid is neutralized. Initially, the pH of the KH_2PO_4 is Ý4, but dissolution of the oxide neutralizes the acid, which leads to the formation of ceramics at a pH of Ý8.

In the presence of the $2H^+$ released by the KH_2PO_4, MgO dissolves by the reaction:

$$MgO + 2H^+ = Mg^{2+}(aq) + H_2O \tag{6.3.3}$$

where (aq) means the ion is aqueous. Equations (6.3.1) through (6.3.3) form the basis for binder development in the CBPC process. The ions from Equations (6.3.2) and (6.3.3), along with five additional moles of water, react to form the matrix material $MgKPO_4 \cdot 6H_2O$ as given in Equation (6.3.1).

The reaction between the ions in Equations (6.3.2) and (6.3.3) is exothermic; the heat is partially offset by the cooling provided by the dissolution of KH_2PO_4. This can be seen in Figure 6.3.3, where we have plotted the temperature of the slurry vs. time. As the dissolution of KH_2PO_4 occurs, the slurry becomes acidic and cools (see the inset in Figure 6.3.3). Within Ý10 min, due to this cooling, some condensation was observed on the sides of the 55-gal drum in which the stabilization was carried out for soils.[10] In this acidic solution, MgO starts to dissolve according to Equation (6.3.3) and then reacts with the phosphate ions to produce the matrix material and heat; thus, the temperature of the slurry starts to rise. At 55°C, the slurry thickens rapidly and solidifies almost instantaneously. The temperature of the newly formed monolithic solid continues to rise, which indicates that the reaction is not complete and continues. The maximum temperature observed in a full drum was 82°C. This temperature profile indicates that the slurry will not boil during formation of the ceramic and hence the process is safe for treating waste streams at full scale (i.e., even in 55-gal drums).

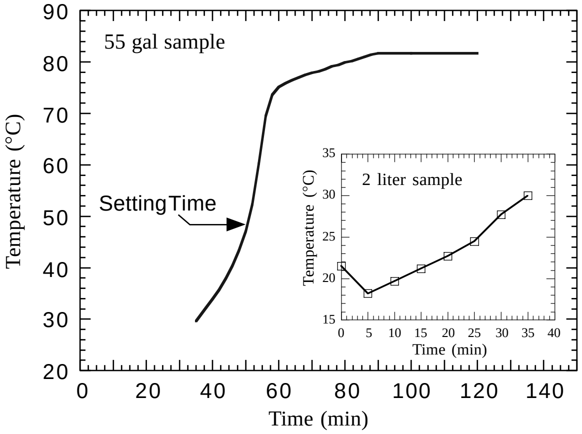

FIGURE 6.3.3 Variation in temperature with time, which reflects pH (see text), during setting of soil in CBPC process at 55-gal and 2-L scales.

Contaminant Stabilization

The solubility of hazardous, radioactive, and fission product contaminants in the CBPC pH range of 4 to 8 plays a key role in the stabilization of these contaminants. Therefore, it is necessary to study the solubility of the contaminants in detail.

The solubility product constant *K*, which is the ionic concentration of solubilized products normalized to the initial concentration of the reactants, is related to the net change in Gibb's free energy[17] ΔG for a dissolution reaction by the following:

$$K = \exp \beta(-\Delta G) \tag{6.3.4}$$

where $\beta = 1/RT$, and R and T are, respectively, the gas constant and the absolute temperature of the system. It is customary to report *K* as:

$$\mathrm{pKsp} = -\log K = -\beta\Delta G/(2.301) \tag{6.3.5}$$

Using the values of ΔG for each of the solubilization reactions of the hazardous metal oxides, Pourbaix[18] calculated pKsp values of various hazardous contaminants and plotted them as a function of pH. These plots are reproduced in Figure 6.3.4. These plots provide some insight into the solubilization behavior of the oxides of hazardous contaminants and their stabilization characteristics, which are given below.

- The solubility increases at low pH. Thus, in the acidic solution of KH_2PO_4, the contaminant oxides are easily dissolved. With KH_2PO_4, the minimum solubility is beyond the pH range of stabilization (4 to 8) which ensures better solubilization of these contaminants and this reaction with the phosphate.
- Except for As_2O_3 and HgO, all the other oxides generally show minimum solubility at alkaline pH. Only Cr_2O_3 shows a minimum solubility at slightly acidic pH. These findings imply that the CBPC process, in which pH ranges from 4 to 8, the solubility is initially high and the contaminants readily solubilize and react with the phosphate and are then stabilized. Even Cr_2O_3 will initially have a significant solubility and will readily react before the pH reaches that of minimum solubility.
- The solubilities of As_2O_3 and HgO are constant in a wide range of pH centered on neutral, and increase only at very low and very high pH.
- Among the divalent oxides, overall, HgO exhibits a constant low solubility in much of the acidic range and entire alkaline range.

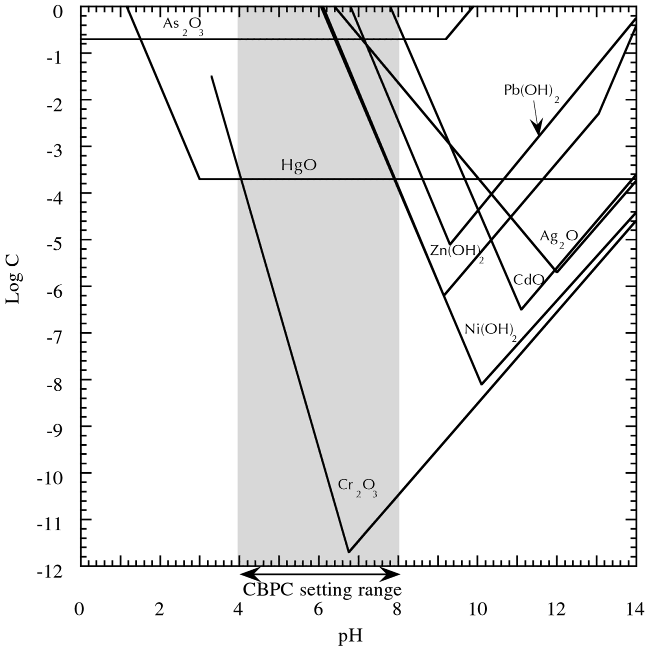

FIGURE 6.3.4 Solubility pKsp (shown as log C) of hazardous contaminants as a function of pH. Adapted from Pourbaix.[18]

These observations imply that stabilization of As_2O_3, Cr_2O_3, and HgO can be difficult in the CBPC or any other chemical process such as cement stabilization. These three oxides may require additional stabilizers, such as a source of sulfides, to make them very insoluble. This will be demonstrated in relation to specific waste streams in later subsections.

Commercially available MgO reacts too rapidly and does not support formation of a ceramic and hence development of CBPCs was elusive for a long time. We have been able to calcine MgO sufficiently to reduce its solubility. When MgO is first stirred in, MgO dissolves in the acidic solution. This raises the pH of the solution. As the pH approaches the neutral range, MgO dissolves slowly and supports the formation of a ceramic.

As Figure 6.3.4 reveals, the solubility of the contaminants changes within the pH range of 4 to 8 (shown by shaded area), where the CBPC matrix is formed. The contaminants that will react rapidly have positive logarithm of the solubility in this range. All of the contaminants that have a positive logarithm will react rapidly at pH 4. Those contaminants will require additional stabilization. Oxides of Ag, Cd, Ni, Pb, and Zn lie on the right-hand side of the line at pH 4, and will spontaneously dissolve in the phosphate solution, whereas oxides of As, Cr, and Hg will not dissolve spontaneously and hence may not readily react.

As will be seen in the case studies presented in later subsections, stabilization of contaminants, except for As, Cr, and Hg, has been reliable. In the laboratory tests, stabilization of As and Cr in small concentrations (ppm) were not a problem, partially because the Toxicity Characteristic Leaching Procedure (TCLP) limits for these substances[19] are high enough (i.e., 5 and 0.19 mg/L, respectively), and partial chemical stabilization and microencapsulation of these contaminants by the phosphate matrix could effectively reduce their leaching. However, satisfactory stabilization of Hg is very difficult because the TCLP limit is very stringent (0.0025 mg/L); hence, an additional stabilization step is required. Certain mining wastes of As and Cr contain high levels of these contaminants, usually in a few percent. When As and Cr are in such high concentration in the waste, for example, or when they occur in higher leachable oxidation states as arsenates and chromates, their stabilization is also difficult and they require additional stabilizers in the binder.

In the CBPC process, the problematic oxide components of Hg, As, and Cr are treated by a small addition (<1%) of a sulfide such as K_2S, which is added to the binder. Sulfidation of the oxides converts them into insoluble sulfides, which are then microencapsulated in the CBPC matrix. The oxides that are in higher oxidation states (e.g., Cr^{6+} or As^{5+}) can be reduced to lower oxidation states by the addition of reductants to the binder; they are then stabilized.

Sometimes, contaminants exist in high concentrations and the phosphate ion concentraton is not adequate for satisfactory stabilization. A good example of this is that of the Waste Experimental Research Facility (WERF) ash from Idaho National Engineering and Environmental Laboratory (INEEL). The Zn concentraton in this ash was very high. Thus, the Zn was competing with other contaminants to form phosphate, and some metals were not stabilized. The problem was remedied by adding a small amount of phosphoric acid to stabilize these contaminants.

Thus, while the CBPC process is simple to operate, it does require a detailed understanding of the waste stream composition and the stabilization mechanism. Sulfidation, reduction mechanisms, or pH adjustments make the process highly successful in treating a very wide range of waste streams.

Oxides of tetravalent actinides, such as ThO_2, UO_2, PuO_2, and AmO_2, are inherently insoluble in groundwater. The values of pKsp for some of these oxides[20-23] are provided in Table 6.3.1, and the actual solubility of $Pu(OH)_2$ as a representative of actinide pksp is compared with $Mg(OH)_2$ and $PbHPO_4$ in Figure 6.3.5. One notices that actinide solubilities are several orders of magnitude lower than the pKsp values of Mg or the hazardous contaminant oxides discussed in the preceding subsection. Thus, because of their extremely low solubility, actinide oxides, for immobilization purposes, can be simply micro- or macroencapsulated in a dense matrix of phosphates. If actinides exist at a lower oxidation state and exhibit a higher solubility, they are fully oxidized to the tetravalent state in the oxidizing environment of the phosphate solution and insolubilized before encapsulation.

TABLE 6.3.1 Solubility Product Constants of Phosphates of Radioactive and Related Materials

Phosphate	pKsp	Ref.
Radioactive contaminants		
$(UO_2)_3(PO4)_2$	46.7	20
UO_2HPO_4	10.69	20
UO_2KPO_4	23.11	21
$Pu(HPO_4)_2 \cdot xH_2O$	27.7	20
$Th_3(PO_4)_4$	78.6	20
$Th(HPO_4)_2$	20	20
Matrix phases		
$MgKPO_4 \cdot 6H_2O$	10.6	22
Newberyite	5.8	23
Surrogate waste form		
Monazite as $CePO_4$	23	20

During encapsulation of these oxides in the CBPC matrix, these insoluble oxides are not expected to react with the matrix components, even in an acidic solution.[9] This can be seen in the solubility diagram shown in Figure 6.3.5,[24] which plots the solubility of $PbHPO_4$, $Pu(OH)_4$, and $Mg(OH)_2$. In the pH range of the reaction slurry (4 to 8), the solubility of $Pu(OH)_2$ is the lowest, with a value of 8.5; hence, it is the most insoluble. On the other hand, $Mg(OH)_2$ will solubilize readily in this pH range and form the matrix to encapsulate $Pu(OH)_2$. Such microencapsulation has been demonstrated for PuO_2 by SEM, as discussed.

The four fission products Cs, Sr, Ba, and Tc have solubility characteristics in the acidic phosphate systems different from those of other contaminants and hence must be considered separately. Cesium occurs as readily soluble compounds (e.g., CsCl), which are regarded as salt wastes that need not only

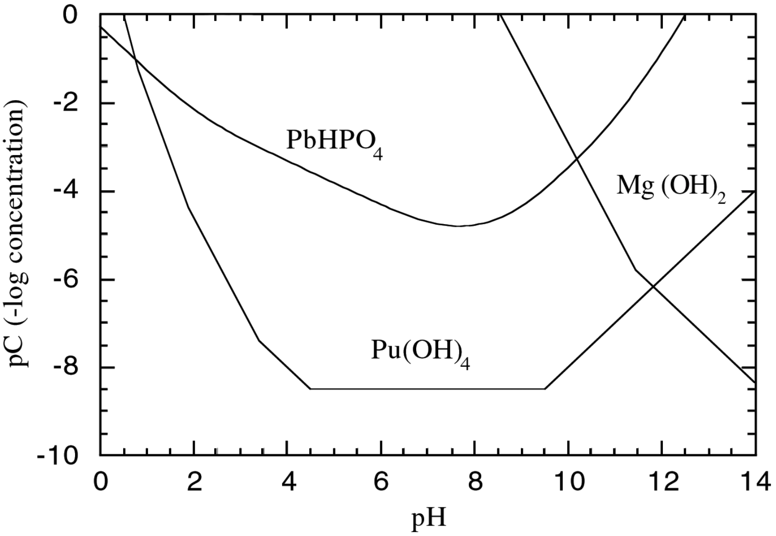

FIGURE 6.3.5 Dissolution characteristics of $Pu(OH)_4$, $PbHPO_4$, and $Mg(OH)_2$ in acid-base reaction of CBPC process. (From Puigdomenech, I., and Bruno, J., 1991. Plutonium Studies, Tech. Report 91–04. Swedish Nuclear Fuel and Waste Management Co., Stockholm. With permission.)

chemical immobilization but also must be supplemented by enhanced physical macroencapsulation. We will discuss this in the context of salt waste stabilization. Sr and Ba behave more like the other hazardous metals discussed above. Each of them will dissolve easily, react to form insoluble phosphates, and then become microencapsulated in the phosphate matrix.

Technetium is more complex[25]; it normally exists in the tetravalent state, but tends to oxidize when disposed of as pertechnate (Tc^{7+}), which is easily leachable. To retain it in the tetravalent state in the phosphate-bonded ceramic waste form, the CBPC process has been modified. Its performance is discussed below.

Demonstration of the Process with Actual Wastes: Case Studies

Several case studies were conducted to demonstrate the superior performance of the CBPC waste forms as treatment of DOE waste streams. Below some of the major case studies that show various advantages of the process, including (1) leach resistance of the waste forms, (2) their long-term durability, (3) removal of pyrophorocity from the waste streams, (4) minimal gas generation, (5) nonflammability of the final waste forms, and, most importantly, (6) the ability of the process to treat a very wide variety of waste streams that cannot be handled by other methods.

Stabilization of Low-Level Waste

The CBPC technology was deployed to treat and dispose of low-level mixed waste at the ANL-West facility.[26] Two debris wastes that contained hazardous metals and low-level fission product contaminants were treated:

1. *Hg-contaminated crushed light bulbs.* Visual inspection of this waste revealed that 90 vol% was <60 mm in size; thus, it could not be classified as a debris waste.[26] Typical sizes of the crushed glass ranged from 2 to 3 cm long by 1 to 2 cm wide, down to fine particulates. Chemical analysis indicated an Hg concentration of Ý2.5 ppm. In addition, emissions from isotopes of ^{60}Co, ^{137}Cs, and ^{154}Eu were 1.1×10^{-5}, 4×10^{-4}, and 4×10^{-6} μCi/g, respectively.
2. *Radioactive contaminated lead-lined gloves.* This waste was essentially Pb-lined gloves used in various hot-cell operations. Radioactive contamination in the gloves was ^{137}Cs (Ý5×10^{-7} μCi/g).

To stabilize this waste, the gloves were first cryofractured in liquid nitrogen with a high-speed blender. Typical debris size from this operation ranged from powder to pieces as large as a few millimeters.[26] Chemical analysis indicated that Ý11.3 wt% Pb is present in the waste.

CBPC waste forms were fabricated in 5-gal drums. Typical waste loading ranged from 35 to 40 wt%. For glass waste, small amounts of potassium sulfide were added to the binder mixture to stabilize Hg by converting it into its least-soluble cinnabar (Hg_2S) form. After mixing for Ý30 to 35 min, the resulting slurries were allowed to set in drums. This procedure produced dense, hard ceramic waste forms.

TCLP test results (Table 6.3.2) showed excellent stabilization of both Hg and Pb in the waste forms. Hg levels of 0.05 ppb in the leachate were well below the Environmental Protection Agency's (EPA's) Universal Treatment Standard (UTS) of 25 ppb, whereas the level for Pb was <0.1 ppm, compared with the UTS limit of 0.37 ppm. The principal advantage of this technology is that immobilization of contaminants is the result of both chemical stabilization, and subsequent microencapsulation of the reaction products. Overall, Ý22 kg of the waste was treated, removed from the inventory, and sent to the Radioactive Waste Management Complex at the INEEL for disposal.

TABLE 6.3.2 TCLP Results on CBPC Waste Forms

Source	Loading (wt%)	Contaminant Conc. in Waste Form	TCLP Results on Source	TCLP Results on Waste Form	Regulatory Limits
Hg waste	40	Hg, 1000 ppb	24.4 ppb	0.05 ppb	25 ppb
Cryofractured Pb-lined gloves	35	Pb, 4 wt%	328 ppm	<0.1 ppm	0.37 ppm

Stabilization of Fission Products

Technetium-99, present in DOE high-level waste as a by-product of fission reactions, poses a serious environmental threat because it has a long half-life and is highly mobile in its soluble Tc^{7+} form. Because of the volatility of ^{99}Tc, wastes that contain this material must be treated at low temperatures. CBPC process fulfills this need.[26]

The actual waste stream tested was ^{99}Tc that was partitioned from simulated high-level tank waste, such as Hanford supernatant, using a complexation-elution process developed by Los Alamos National Laboratory (LANL).[27] A typical composition of the waste solution generated in the complexation-elution process is 1 M NaOH, 1 M methylenediamine, and 0.005 M Sn(II). The technetium concentration in the waste was as high as 150 ppm.

Waste forms were fabricated by first precipitating ^{99}Tc from the waste stream using a reduction process[28] and subsequently solidifying the precipitated Tc-oxide in the CBPC. Tc loadings in the waste forms were as high as 900 ppm. The performance of the waste forms was evaluated with various strength, leaching, and durability tests. Long-term leaching studies, as per the ANS 16.1 procedure, showed that leachability indices (defined as the negative logarithm of the diffusion constant) for ^{99}Tc under ambient conditions ranged between 13 and 14.6 (see Table 6.3.3). The normalized leach rate for ^{99}Tc determined by the Product Consistency Test[2] was as low as 1.1×10^{-3} g/cm^2-d (see Table 6.3.4) under ambient conditions. The compressive strength of the waste forms was Ý30 MPa, which showed that the waste forms were durable in an aqueous environment. Superior containment of ^{99}Tc in the CBPC matrix is believed to be due to a combination of appropriate reducing environment (determined from E_h-pH measurements) and microencapsulation in a dense matrix.

Pu-Containing Combustion Residue Waste

A feasibility study was conducted on the use of CBPCs for stabilization of the combustion residue of TRU wastes.[7] Using the CBPC matrix, we made waste forms that contained 5 wt% Pu to satisfy the safeguard termination limits of the WIPP.

To test the feasibility of incorporating Pu in the CBPC waste forms, we first conducted a detailed leaching study with Ce as a surrogate for Pu and then made bench-scale samples. The samples were tested for compressive strength and short- and long-term leaching by TCLP and 90-day immersion,

TABLE 6.3.3 ANS 16.1 Results for CBPC Specimens Fabricated by Precipitating ^{99}Tc by Reduction Process and then Solidifying Precipitated Tc Oxide in CBPC

Method of Preparation	^{99}Tc Conc. (ppm)	Leachability Index
MKP + $SnCl_2$ + Precipitated ^{99}Tc	41	14.6
MKP + $SnCl_2$ + Precipitated ^{99}Tc	164	13.3
MKP + $SnCl_2$ + Precipitated ^{99}Tc	903	14.6

TABLE 6.3.4 Product Consistency Test Results for CBPC Specimens Fabricated from Reduction-Treated, Precipitated ^{99}Tc

Method of Preparation	Test Temperature (°C)	Tc Conc. (ppm)	Normalized Leach Rate (g/m²·d)
MKP + $SnCl_2$ + Precipitated ^{99}Tc	25	40	3.9×10^{-3}
		164	8.5×10^{-3}
		903	1.1×10^{-3}
MKP + $SnCl_2$ + Precipitated ^{99}Tc	90	40	$7.2 \times 10–^{-2}$
		164	1.1×10^{-1}
		903	3.6×10^{-2}

respectively. With satisfactory results from the surrogate waste forms, we selected three actual waste streams, which are described in Table 6.3.5. The U-Pu oxide mixture was the result of corrosion of a U-Pu alloy. The TRU combustion residue, which was originally obtained from Rocky Flats, was fully calcined for safe transport to ANL. Therefore, all organics and combustibles were completely incinerated and the Pu concentration was enhanced. Thus, to produce samples that were suitable for the study of the radiolysis effects of the organic components in the wastes, it was necessary to add a polymer to the waste. This was accomplished by adding Bakelite mounting compound to the waste and thus produced the third waste.

TABLE 6.3.5 Origin, Characteristics, and Pu content of Test Waste Streams

Waste Stream	Origin and Characteristics	Content of Pu and Other Actinides (wt%)
Mixture of U and Pu	U-Pu alloy, an ANL inventory item, fully oxidized and formed into fine powder.	U = 75; Pu = 25
TRU combustion residue	Originally from Rocky Flats; subsequent operations led to high Pu concentration; fine powder residue	Pu = 31.8 as PuO_2, with minor reduced phase of Pu. ^{241}Am = 0.1, ^{39}Pu = 90, ^{240}Pu = 8.4, ^{241}Pu = 1
TRU combustion residue with addition of Bakelite mounting compound	63.7 wt% mounting compound added to combustion residue; waste form contained 10 wt% organics	Pu =19.4 as PuO_2 in combustion residue, with minor reduced phase of Pu; ^{241}Am = 0.06, ^{239}Pu = 90, ^{240}Pu = 8.4, ^{241}Pu = 1.3

The surrogate waste forms displayed high leaching resistance for both hazardous metals, and Ce. Using Ce_2O_3 as a surrogate for pyrophoric Pu_2O_3 and U_2O_3, Wagh et al.[9] also demonstrated that such components oxidize within the matrix and produce nonpyrophoric components such as CeO_2. Here, we concentrate on the detailed study conducted on radiolytic gas generation from the actual waste forms. Hydrogen generation due to alpha-radiation from Pu at its high concentration (5 wt%) was a major concern because $MgKPO_4{\cdot}6H_2O$ is the CBPC matrix material, and contains six moles of water for every mole of magnesium potassium phosphate. Radiolytic decomposition of this water and any organic

TABLE 6.3.6 Yield of H_2 from Samples Investigated in Gas Generation Studies

Sample	wt% Pu	$G(H_2)$ Value (Molecular H_2/100 eV)
CBPC with U-Pu oxide mixture	5.245	0.13
CBPC with TRU combustible residue	7.87	0.10
CBPC with TRU combustible residue	5.00	0.231
CBPC with TRU combustible residue and Bakelite compound	31.8	31.8

Note: $G(H_2)$ observed for >0.83 × 10^{22} eV of total released decay energy. An average of 0.57 molecular H_2/100 eV was observed for 0 to 0.83 × 10^{22} eV of total released decay energy. All G values were calculated assuming that 100% of decay energy is deposited into entire mass of sample.

compounds in the waste form may pressurize the containers during shipping and storage of the waste forms. The results of the actual study of the waste form conducted to test this are given in Table 6.3.6.

Table 6.3.6 gives the H_2 yield of samples subjected to gas generation studies. The H_2 yield is represented in terms of a $G(H_2)$ value, which is defined as the ratio of the radiation chemical yield to the energy absorbed, expressed in terms of the number of molecules generated per 100 eV. The observed $G(H_2)$ values for the various CBPC samples compare well with the $G(H_2)$ values reported in the literature for alpha- and gamma-radiolysis in similar waste forms. They are comparable to a $G(H_2)$ value of 0.6 molecules of H_2/100 eV investigated for solidification of tritiated water, 0.095 ± 0.005 total molecules/100 eV for the total gas production in FUETAP concrete, and 0 to 0.43 total molecules/100 eV (combined alpha- and gamma-radiolysis) for simulated Hanford current acid waste and double-shell slurry wastes immobilized in a cement-based grout.[29] Siskind[30] summarized the $G(H_2)$ values reported in the literature for cement-solidified low-level waste exposed to gamma-radiation; these $G(H_2)$ values range from 0.03 to 0.35 molecules of H_2/100 eV. Draganic and Draganic[31] reported $G(H_2)$ values for the radiolysis of pure liquid water as a function of the linear energy transfer. For ^{239}Pu, $G(H_2)$ is 1.6 moleculars H_2/100 eV. The values given in Table 6.3.6 for waste streams without organics compare well with these reported $G(H_2)$ values. These observations indicate that the gas yield is minimal and will not lead to pressurizing the waste containers unless the waste contains very high levels of organics. Such a situation is unlikely because most of the Pu wastes are calcined to oxidize Pu to its fullest extent to make it stable in the waste stream.

Figure 6.3.6 shows the SEM back-scattered image of PuO_2 that is physically microencapsulated. It is physically immobilized in the dense, strong matrix. In addition, the fact that it is present in its fully oxidized state as PuO_2 ensures that pyrophoricity is removed and leaching resistance is maximized. The high leach resistance is due to the very low solubility of PuO_2 and superior microencapsulation. These superior results, even at a concentration of 5 wt% Pu, indicate that the waste forms satisfy the current Safeguard Termination Limit for storage of TRU combustion residues.

Stabilization of Salt-Containing Waste

One of the key features of the CBPC process is that, unlike conventional cements, the phosphate binder sets even in the presence of salts such as nitrates and chlorides. This was demonstrated by producing monolithic solids of the binder through the use of sodium nitrate and sodium chloride solutions in place of water.[32,33] The solids represented waste streams at DOE sites such as Hanford.

This demonstration was conducted with surrogate salt waste. The surrogate waste in this work represented the salt waste inventory within the DOE complex. Both chloride and nitrate waste contained Fe_2O_3, $Al(OH)_3$, Na_3PO_4, synthetic calcium silicate, and water as the major components; NaCl, $CaSO_4$, and $NaNO_3$ as the salts; and Pb, Cr, Hg, Cd, and Ni (up to 800 to 900 ppm) as the heavy metals in each of the contaminant oxides. Trichloroethylene was added to investigate whether setting of the ceramic was

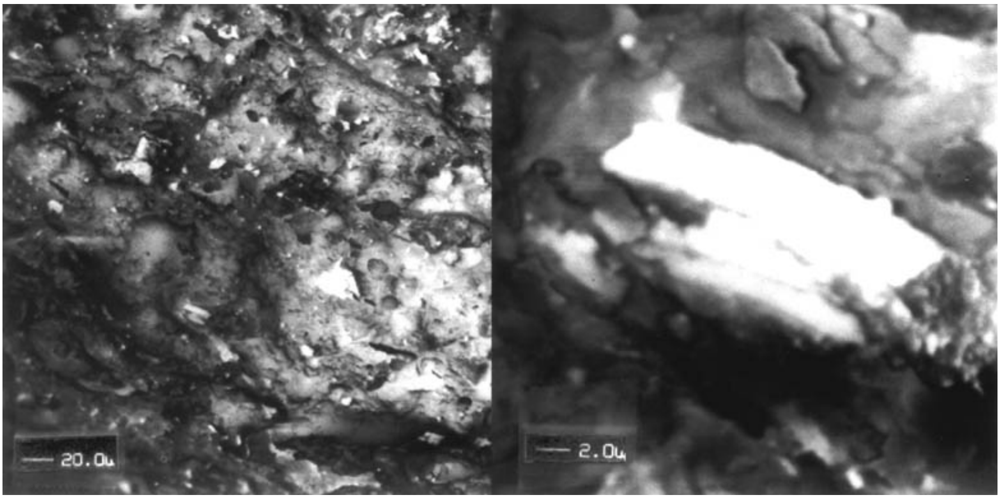

FIGURE 6.3.6 Backscattered images of stabilized Pu waste form: (a) low magnification, and (b) high magnification.

in any way affected by residual organics in the waste. Waste forms were fabricated with two waste loadings (58 and 70 wt%) for each of the waste streams.

The hazardous contaminants were chemically immobilized and physically encapsulated in the matrix of the CBPC; thus, the TCLP leaching results were excellent. The density of the final waste forms ranged from 1.7 to 2.00 g/cm^3 and compression strengths ranged from 1400 to 1900 psi for both the chloride and nitrate waste forms. These values are significantly higher than Nuclear Regulatory Commission LDR of 500 psi for cement-based waste forms.[9] Thus, CBPC salt waste forms at extremely high loadings are relatively dense, hard materials and are suitable for salt waste stabilization. The TCLP performance was also excellent. The results showed that the leaching levels were well below the EPAs UTS limits for all of the contaminants.

To arrest leaching of $NaNO_3$ and NaCl, a macroencapsulation technique (in which a coating is applied to the waste forms) was investigated and appropriate coating materials were identified for successful retention of the anions.[34] Using this macroencapsulation technique, we fabricated specimens and tested them for nitrate and chloride leaching using the ANS 16.1 standard test. Table 6.3.7 provides the leachability index of the various specimens and shows that the leaching levels of the anions are significantly reduced by the coating. The leaching index of 12.6, obtained with the coating, is one of the highest for the nitrate waste forms.

TABLE 6.37 Results of ANS 16.1 Test for Various Waste Forms

Waste Forms	NO_3/Cl in Waste Form (ppm)	Fraction of NO_3/Cl Leached	Effective Diffusivity (cm^2/s)	Leachability Index
Uncoated NO_3 samples, waste loading 58 wt%	218,700	0.33	6.31×10^{-8}	7.2
Coated NO_3 samples, waste loading 58 wt%	218,700	0.0169	6.87×10^{-13}	12.6
Uncoated Cl samples, waste loading 60 wt%	46,535	0.0669	1.26×10^{-9}	8.9
Polymer coated Cl samples, waste loading 60 wt%	46,535		Readings mostly below detection limit	Readings mostly below detection limit

The efficient retention of the anions in the macroencapsulated waste forms can be attributed to the sealing of the pores on the surface of the waste forms by the coating material. To verify this, we investigated the microstructure of the cross-section of one of the macroencapsulated waste forms by SEM. Figure 6.3.7 provides the photomicrographs obtained at low and high magnification.

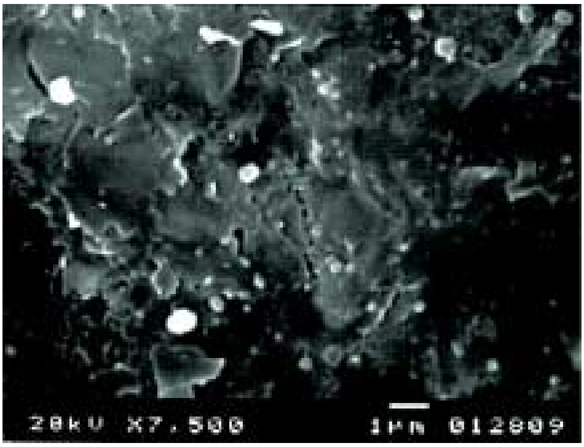

FIGURE 6.3.7 SEM photomicrograph of the cross-section of coated nitrate waste form.

As one can see in Figure 6.3.7, the polymer seeps into the connected porosity of the phosphate waste forms very efficiently. As one moves from the top to the bottom of the photomicrographs, the polymer fraction is reduced. At the top, the coating is continuous where the surface porosity of the samples was greater. As the coating penetrates into the sample, it plugs all of the pores and forms an impermeable coating that arrests leaching of the anions. In addition, this penetration helps to develop a durable physical bond between the sample and the coating.

To test the durability of the waste forms after 90-day-immersion leachability testing, we conducted compression strength measurements on the nitrate waste forms. Three nitrate waste form specimens were immersed in deionized water for 90 days. Compression strengths of the three specimens were determined at the end of the test period. The average compressive strength of the three waste forms was 770 psi for 58% waste loading and 640 psi for 70% waste loading. Once again, these values are higher than the minimal LDR of 500 psi.

Because nitrate waste is ignitable, it is necessary that the waste form be nonflammable for safe transportation and storage. To demonstrate that CBPC waste forms comply with this requirement, an oxidation test was conducted on the nitrate waste forms. Using the procedure recommended by the EPA,[34] we prepared a mixture of the waste form powder and soft-wood dust (sawdust) in a weight ratio of 1:1 and ignited it by passing an electrical pulse through a Kanthal loop with a radius of 2 cm that was embedded in the pile of the mixture. The time taken for the flame to consume each of several mixtures was recorded and is presented in Table 6.3.8. The table shows that the time required to burn mixtures of sawdust and known flammable salts (e.g., potassium bromate and ammonium persulfate), was extremely short (19 to 197 s), whereas the time required to burn the waste form-and-sawdust mixtures was >480 s (>8 min), which is much longer than the combustion time of ammonium persulfate, the minimum time for passing the test. This result implies that salt waste solidifed in CBPCs will not require any special packaging because the CBPCs are inorganic ceramic-type materials that assist in inhibiting the spread of flames and can be excellent solidification media for flammable salt waste.

Packaging of Radium-Rich Fernald Silo Waste

Fernald Silo I and II wastes are radium-rich. Radium (Ra) disintegrates into radon (Rn), which is a gas. Therefore, the wastes need to be suitably packaged for disposal and transportation. For this reason, a demonstration of their packaging in the CBPC matrix was conducted at bench scale.[35] The waste received from the Fernald Environmental Management Project (FEMP) contained As^{5+}, Ba, Cr^{6+}, Ni, Pb, Se^{5+}, and

TABLE 6.3.8 Combustion Time for Various Mixtures of Waste Form Powder and Sawdust Subjected to Oxidation Test

Mixture	Combustion Time (s)
1:1 Potassium bromate and sawdust	19
1:1 Ammonium persulfate and sawdust	49
1:1 Surrogate waste and sawdust	87
4:1 Surrogate waste and sawdust	197
1:1 Waste form and sawdust	>480

Zn as the hazardous contaminants. The total specific activity of all the isotopes in the waste was 3.85 μCi/g; radium alone accounted for 0.477 μCi/g of this activity. This indicated that Rn, as a daughter product of the Ra in the waste, could pose a serious handling problem during this study. Waste-form samples were prepared in a glovebox with an actual Fernald waste loading of 66.05 wt% and subjected to the TCLP test. The results given in Table 6.3.9 show excellent stabilization of all contaminants. Actual levels detected in the leachate were well below the EPA's most stringent UTS limits and in almost all cases were one order of magnitude below this limit.

TABLE 6.3.9 TCLP Results (mg/L) on Stabilized Samples of Fernald Waste and UTS Limits (mg/L) for Various Contaminants

	Contaminant									
Level/Limit	As	Cd	Ce	Cr	Co	Cu	Ni	Pb	Se	Sr
Level in leachate	0.22	<0.1	<.05	0.05	0.55	0.01	2.31	<0.1	0.82	0.13
UTS limit	5.0	0.2	—	0.85	—	—	13.6	0.75	5.7	—

Table 6.3.10 gives the specific α, β, and total activities of the TCLP leachate. Although Ra activity in the waste was 0.477 μCi/g and the total specific activity of all the isotopes was 3.85 μCi/g, activity in the leachate is very low. In particular, because Ra is water soluble, the leachate could provide it with a pathway. The fact that the activity in the leachate is at the pCi/mL level implies that Ra and most of the other isotopes are stabilized in the waste forms. This is possible because Ra would form a phosphate that is insoluble in the leachate. Thus, the CBPC process is a good way to arrest leaching of radioactive contaminants.

TABLE 6.3.10 Specific Activities (μCi/g) in Various Stabilized Samples of Fernald Waste

Sample Code	Alpha	Beta	Total
As-received waste			
Total specific activity	—	—	3.85
Specific activity of Ra^{226}	—	—	0.477
Waste form calculated activities			
Total specific activity	—	—	2.06
Specific activity of Ra^{226}	—	—	0.255
Specific activity in TCLP leachate (pCi/L)	25 ± 2	98 ± 10	221 ± 22[a]

Note: We have assumed gamma activity Ý beta activity.

Solidification of Radioactive Incinerator Waste

The incinerator at the DOE Savannah River Site (SRS) burns low-level mixed waste. Ash and scrubber residues are generated during the incineration process. Tests were conducted to verify whether the ash and scrubber waste streams can be stabilized by the CBPC method. Acceptance criteria for the solid waste forms include leachability, bleed water, compression strength testing, and permeability. Other tests on the waste forms include X-ray diffraction and SEM.

TABLE 6.3.11 Composition of Blowdown Salts (mg/L)

Component	Concentration	Component	Concentration
Al	541.5	Cl	19,618
Ca	600.3	Nitrite	230
Fe	545.3	Nitrate	274
Mg	178.0	Sulfate	40,274
Na	32,126.8	Oxalate	<10
F	639	Phosphates	646
Formate	<10	Phosphates	646

The composition of the incinerator blowdown is presented in Table 6.3.11. The quench system is operated to produce blowdown that contains Ý10% total solids. The blowdown samples that were used in this study contained 1.5% suspended solids, mostly SiO_2 and $Zn(OH)_2$. The dissolved solids content, usually NaCl and Na_2SO_4, was 8.2%. The pH of the blowdown was 8.77 and the water content, 90.3%.

Based on X-ray diffraction, the blowdown contained cristobalite as SiO_2, other forms of silica, anorthoclase $(NaK)(AlSi_3O_8)$, magnetite (Fe_3O_4); and hematite (Fe_2O_3). The ash, which was wet-quenched, contained 45 ± 15% quench water; the pH of the water in contact with the ash was 10.55. Ash and blowdown used for sample preparation were generated at SRS by incineration of diatomaceous earth filter rolls.

CBPC waste forms with various proportions of ash, blowdown, and combinations of ash and blowdown were fabricated.[36] The test matrix of the waste form composition is given in Table 6.3.12. The blowdown solution was evaporated to achieve higher salt waste loadings in the waste form while maintaining the same amount of water. The samples were cured in sealed containers for 28 days before testing.

TABLE 6.3.12 Test Matrix for SRS Waste Treatment

Sample No.	SRS Ash (g)	Blowdown (g) 10%	Blowdown (g) 20%	Binder (g)	Coal Ash (g)	Blowdown (wt%)	SRS Ash (wt%)
1	0	0	0	41.4	50	0	0
2	0	10	0	71.2	0	12	0
3	0	0	36.1	93.8	0	28	0
4	40	0	0	49.0	0	0	33
5	50	0	0	43.5	0	0	42
6	60	0	0	38.4	0	0	51
7	16.5	25	0	66.4	0	23	15
8	48	0	16	55.6	0	13	40

Compressive strength estimates with a concrete penetrometer gave readings >700 psi, which exceed the specification criterion of 500 psi. Permeability testing of the nonradioactive blank sample with a Permeameter (Model # K-670A, ELE Int., Lake Bluff, IL) gave a reading of 1×10^{-4} cm^2/s. This permeability was higher than the acceptability criteria decided by SRS, which implies that there is room for improvement in the CBPC waste forms. A sample of ash that was not solidified passed the TCLP leachability limits; thus, so no further TCLP tests were needed on stabilized waste forms.

Initially, the blowdown solution contained <0.01 ppm Hg, <0.025 ppm Ag, 2.56 ppm As, 0.12 ppm Ba, 0.211 ppm Cd, 2.11 ppm Cr, 0.325 ppm Pb, and 0.65 ppm Se. Results for Hg, Ag, Ba, Cd, and Pb were below the detection limit and only As, Cr, and Se levels were measurable; these are given in the Table 6.3.13. The detection limits for the various elements were as follows: Cr, 0.0056; As, 0.045; Se,

TABLE 6.3.13 TCLP Results for SRS Incinerator Waste Forms (mg/L)

	Sample No.						
Element	1	2	3	4	5	6	7
As	0.406	0.082	0.099	0.067	0.068	0.069	0.089
Cr	0.014	0.115	0.016	0.016	0.008	0.005	0.011
Se	0.084	—	0.028	Below detection limit			0.048

0.0045; Ba, 0.0051; Cd, 0.0044; Ag, 0.0073; Pb, 0.0159; and Hg, 0.00035 mg/L. Overall, all of the contaminants passed the TCLP limits assigned by the SRS.[36]

In summary, the CBPC waste forms showed excellent performance. The only test that failed was the test for permeability of a blank that was made from phosphate ceramic that was above the minimum SRS acceptability criterion. Since this case study, excellent nonpermeable CBPCs have been developed; they must now be tested with actual waste streams.

Conclusions

CBPC is a novel stabilization and solidification technology, developed at Argonne, that can treat a very wide variety of mixed waste that contains low-level radioactivity, fission products, TRUs, and salt waste. The case studies used to demonstrate this technology address several issues faced at DOE sites. These issues include high TRU concentrations and the gas generated by them; most leachable salts, for which CBPC is a unique technology; occurrence of most leachable contaminants, such as Tc^{7+}, that require reduction during stabilization; and Ra-containing silo waste that cannot be easily handled and treated. CBPC technology is a solution for each of these cases.

Schwinkendorf and Cooley[37] have conducted an economic evaluation of various technologies that are available for the treatment of mixed wastes in the DOE complex. They concluded that CBPC technology is one of the most economical methods to treat these wastes. Because this technology has been demonstrated in 55-gal trials, its superior performance and cost effectiveness puts it in the forefront for treatment of DOE and commercial wastes in the millennium.

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6.4

Polyester Resin Microencapsulation

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Introduction

This section summarizes the current state of mixed waste stabilization/solidification (S/S) using polyester resins. The polyester resin binder forms a microstructure of closed cells around the waste constituents and utilizes solidification as the primary technique of waste contaminant immobilization. The resulting monolithic solid has high structural integrity, but the matrix does not necessarily involve a chemical interaction between the waste and the solidifying reagents. Contaminant migration is restricted by drastically decreasing the surface area exposed to leaching and/or isolating the waste within an impervious capsule.

Polyester resins have been used in several countries for treating spent ion-exchange resins generated in commercial nuclear power plants (Subramanian and Mahalingam, 1979; IAEA, 1988). Additionally, the U.S. Nuclear Regulatory Commission (NRC) has approved topical reports for two proprietary waste solidification methods using vinyl ester resin, a specific type of polyester. The successful application of polyester resins in nuclear waste treatment has led to recent evaluations pertaining to the treatment of large U.S. Department of Energy (DOE) inventories of salt-containing mixed waste (DOE, 1999).

Three types of unsaturated polyester resins (orthophthalic, isophthalic, and vinyl ester) were used in these recent studies (DOE, 1999) to evaluate the S/S of salt-containing mixed wastes. In another study, orthophthalic and vinyl ester resins were successfully used to immobilize and reduce the leachability of heavy metals and other contaminants in asbestos brake lining dust (Chan et al., 1999a). Results from all these studies are summarized in this section.

Chemistry

Polyester resins are one in a class of thermosetting polymers and they have seen wide use in the manufacture of fiberglass-reinforced plastics (FRP). A simple ester, R′C(O)OR, is usually formed via a condensation reaction between an organic alcohol, R′OH, and an organic acid, RC(O)OH. During the reaction, water is formed — hence the term "condensation." The symbols R and R′ can represent any unsaturated or saturated aliphatic or cyclic hydrocarbon group, C_XH_Y. To form a chain-like or "poly" ester compound, diols (i.e., dialcohols and glycols), such as HO-R′-OH, and diacids (i.e., anhydrides), such as HO(O)C-R-C(O)OH, are frequently used as starting monomers to provide condensation-type polymerization reactions on both ends of the monomer molecule. Thus, the backbone of the resulting unsaturated polyester has three basic types of structural units, each contributing to a specific desirable characteristic. The unsaturation provides the sites for crosslinking, the saturation determines the degree of spacing or concentration of the unsaturated acid molecules along the polyester chains, and the glycols form the ester groups bridging the dibasic acids to form the polymer.

For the three polyesters studied in a recent DOE-funded evaluation (DOE, 1999) R and R′ either represent hydrocarbon cyclic/ring (phthalic) compounds, $–C_6H_4–$, or the double bond vinyl group, –HC=CH–. Upon completion of the condensation polymerization reactions, each phthalic or vinyl compound is attached to two ester groups, –C(O)O–, for each link in the polymer chain. The position of the ester group on the cyclic compound further classifies two of the polymers studied. Orthophthalic polymers have ester groups attached to the ring adjacent to each other, whereas iso (or meta) phthalic polymers have an unsubstituted ring carbon between the two attached ester groups. Orthophthalic resins, made from phthalic anhydride, comprise the largest group of polyester resins. Isophthalic resins are synthesized by substituting phthalic anhydride by isophthalic acid to enhance mechanical and thermal performance and improve corrosion resistance.

The fourth resin studied in the recent DOE evaluation was an unsaturated water-extendible polyester (WEP) specially formulated to allow for the preparation of water-in-polymer emulsions. The WEP allows aqueous wastes to be dispersed as fine droplets to form a stable emulsion. To the contrary, the other three polymers are only applicable for wastes that are sufficiently dry. All four polymers were provided in a preformed condition by the Ashland Chemical Co. (Columbus, Ohio), under the trade names or codes listed in Table 6.4.1.

TABLE 6.4.1 Trade Names of Ashland Chemical Co. Resins

Polymer	Trade Name/Code
Orthophthalic	S2293
Isophthalic	Aropol™ 7334
Vinyl ester	Hetron® 922-L25
Water extendible	Aropol™ WEP 662P

Basic polyester chains are preformed as described above before blending the mixed waste into the resin. The polymeric thermosetting reaction that occurs during mixed waste microencapsulation is one of crosslinking these polyester chains. Commercially available resins are generally medium viscosity liquids that contain unsaturated polyesters dissolved in a polymerizable monomer, usually styrene. Once the uniform stable dispersion of the waste in the resin is accomplished, the gelling and curing of the continuous resin phase is achieved to form a hard polymer by initiating the polymerization of the styrene monomer with a suitable peroxide catalyst system. Because the catalyst takes part in the crosslinking reaction, it is termed an initiator.

Free radicals, formed by breaking the O-O bond of the initiator with a promoter, open up the double bonds of the monomer and of the unsaturated polyester, and crosslink them into a closed cell network structure that encapsulates the mixed waste. A common initiator that can yield free radicals when heated is methyl ethyl ketone peroxide. To initiate polymerization at room temperature, a promoter, which is a reducing agent that is readily oxidized by the peroxide catalyst or initiator, is used. The combined role of the promoter and catalyst is termed “redox” initiation. The prime advantage of redox initiation is that free radical production occurs at reasonable rates at a moderate room temperature, thus enabling rapid cure times lasting only a few minutes. The use of a compatible initiator-promoter combination is critical in ensuring a reasonable working time before the polyester-waste mixture sets. Typical promoters are cobalt naphthenate or dimethyl aniline.

The crosslinking reactions provide microencapsulation of the waste, resistance to chemical and organic solutions, and superior structural strength of the waste form. Unlike condensation polymerization, crosslinking of the polyester with styrene is achieved via a reaction referred to as free radical polymerization because it involves the breaking of double bonds and the formation of oxidized and reactive carbon species. These species react in a chain-like manner to form single bonds that connect the various polyester chains to the styrene chains, which in turn link to different polyester chains.

The resin can be purchased prepromoted or, for formulation flexibility, the user can add the promoter separately to the resin. For prepromoted resins, the quantity of initiator/catalyst added and the initial temperature of the ingredients used are the main variables in determining gel time. Sample preparation temperature, which affects curing rate, is kept ambient throughout the tests and resin gel times are adjusted by varying initiator amounts. To avoid any unwanted crosslinking of the polyester in shipment or storage (before initiator/catalyst addition and waste encapsulation), the resins are shipped with an inhibitor. A typical inhibitor employed is hydroquinone, which acts as a free-radical scavenger during transportation.

Vinyl ester resins, although broadly classified as polyesters, are typically diesters that contain repeating ester linkages. Vinyl ester resins have carbon-to-carbon double bonds only at the ends of the molecular chain, giving a more chemically resistant structure than other polyester resins. Because the entire chain is not restricted, it can elongate under stress thereby making vinyl ester resins more suitable for absorbing mechanical or thermal shocks. Vinyl ester resins are less polar than polyester resins and on curing are less prone to hydrolysis. These resins also exhibit excellent resistance to acids, alkalies, and many solvents. Vinyl ester resins, having a lower ester content, may be more resistant to hydrolysis by water than polyester resins. However, with greater unsaturation in the polyester backbone, the polystyrene linkages in cured polyester resins hold together the wire-mesh-like grid structure more effectively.

Commercial polyester resins that have been used to treat wastes include Altek 78-50 ERM, Ashland WEP-662 (Franz et al., 1987), Ortho Polymal 820, and Hetron 922 (a vinyl ester) (Chan et al., 1999b). Resins used by researchers at Washington State University (WSU) (Subramanian and Mahalingam, 1979) included Aropol™ WEP-661P from the Ashland Chemical Co. During this research, the initiator peroxides included Lupersol Delta (MEK in dimethyl phthalate, a water-soluble substance from Pennwalt), Superox 38 (MEK as a water-dispersible solution from Reichold Chemicals), and Aposet (ketone peroxide, an organic phase-soluble substance from M&T Chemicals).

Laboratory Methods

Field applications of S/S technologies are, by necessity, preceded by laboratory studies. Past S/S technology deployers were not driven by regulatory factors such as the banning of liquids in landfills. However, future S/S processes for mixed waste will be required to meet much more stringent performance criteria because S/S technology is recognized as a Resource Conservation and Recovery Act (RCRA) Best Demonstrated Available Technology for treating hazardous wastes.

The laboratory evaluations of polyester-based S/S methods were simple and straightforward. In fact, the laboratory methods used in the pioneering development (Subramanian and Mahalingam, 1979) of the polyester waste solidification process are still applicable. The solidification procedure depends on the form of the waste. In the case of liquids and slurries, the waste is dispersed within the promoted resin to form a stable waste-in-resin emulsion. When the waste is a dry particulate, it is dispersed in a preformed water-in-resin emulsion or directly into the neat polyester resin. The subsequent solidification is then achieved by the addition of the initiator.

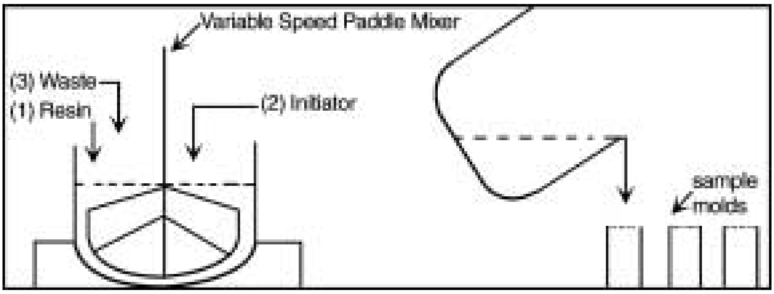

TABLE 6.4.1 Particulate waste treatment.

As depicted in Figure 6.4.1, the basic flowsheet needed to fabricate polyester mixed waste forms from a particulate waste consists of a simple mixer, as well as containers for waste specimen curing.

The common method for dry mixed waste consists of adding predetermined amounts of the initiator to one of three of the polyester-styrene blends (i.e., orthophthalic, isophthalic, or vinyl ester) that have been previously batched to the mixing bowl. Free-flowing solid powder waste is then added in amounts to achieve the desired waste loading, while intimate mixing is initiated.

For aqueous wastes (Figure 6.4.2), the waste is added as a steady stream into a prebatched amount of WEP resin already in the mixing vessel. Mixing continues until the desired ratio of waste to resin is reached and a homogeneous emulsion is formed (5 to 10 min). A predetermined amount of initiator is then added and mixing is continued for another 2 to 5 min to thoroughly disperse the initiator into the emulsion. The emulsion is then transferred to molds where it hardens to a final waste form.

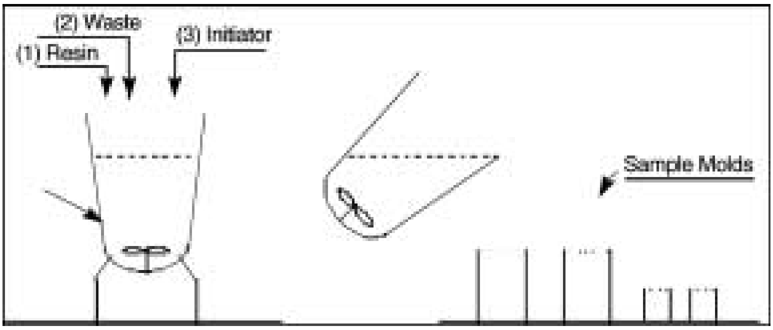

FIGURE 6.4.2 Aqueous waste treatment.

For testing purposes (DOE, 1999), the filled molds are placed in an insulated chamber. Use of the adiabatic chamber simulates conditions in large-scale operations, where the dissipation rate of heat from the polymerization reaction is considerably less than that of the smaller test specimen forms. This procedure was necessary to determine the maximum temperature rise that could be expected from the exothermic polymerization and crosslinking reactions occurring in large waste forms. Mahalingam et al., (1981a) have carried out a computer simulation of solidification temperature profiles for peak exotherms applicable to monoliths of different sizes. These simulations were then verified experimentally for 1-gal size monoliths.

Waste form samples used for the Toxicity Characteristic Leaching Procedure (TCLP) must be less than 1 cm in their narrowest dimension. The rigidity of the solidified waste forms produced as described above made it very difficult to achieve this size reduction, even by sawing the waste form. Additionally, sawing generated considerable dust. To resolve this problem, researchers (Kalb, 1998; DOE, 1999) were obliged to use a specialized mold with cavities to prepare sample pellets that meet the TCLP sample-size criteria. This simplified the sample preparation because the <1 cm diameter pellets were sized for direct use in the TCLP test.

Solidified Matrix Evaluations

Researchers at WSU performed extensive S/S testing with polyester resins and both actual and hazardous and nuclear wastes, as well as simulants (Subramanian and Mahalingam, 1979). The wastes used were either synthesized in the laboratory or obtained directly from various industries. The wastes consisted of typical low-level waste (LLW), such as contaminated aqueous solutions of sodium sulfate and boric acid, as well as several other types and forms of hazardous wastes. Example waste constituents studied included PCBs, organic solvents, arsenic, hexavalent Cr, mercury, organic chlorides, cyanides, and pigment sludges. The polyester treatment and subsequent disposal of decontamination chemicals used in the nuclear industry is described by Bailey and Mahalingam (1981).

Throughout the DOE complex, large quantities of nitrate salt waste have been produced in various nuclear fuel cycle operations. Treatment for DOE's high-level waste is expected to generate even more LLW and mixed nitrate salt-containing waste. Brookhaven National Laboratory (BNL) evaluated the use of polyester (including WEP) resins in treating a simulated particulate waste containing sodium nitrate (Franz et al., 1987). High waste loadings of 70 wt% were achieved with nitrate leach rates lower than regulatory limit by an order of magnitude. This performance is very similar to that of polyethylene waste forms with comparable waste loadings. In addition to the particulate nitrate wastes, an aqueous slurry of sodium nitrate with 30 wt.% salt was also tested at BNL using the WEP resin. The resulting leach rates of the slurried waste form were similar to the waste form with dry particulate at the same salt loading. Additionally, the compressive strength of the polyester waste form in the BNL study exceeded the NRC recommended minimum value by at least an order of magnitude.

A point about the BNL study needs clarification. The salt loading in waste forms containing slurried wastes is limited because of the water content of the waste. In general, aqueous wastes containing ~25 wt% total dissolved solids can be typically loaded at 50 to 70 wt%. This results in an actual salt loading of about 12 to 18 wt%. When the BNL study pushed this salts content in aqueous wastes beyond 30 wt%, the results were not surprising; WEP waste forms made with 50 to 70 wt% salt swelled and cracked during the water immersion test.

The polyester microencapsulation technology relies primarily on a physical barrier to retain the waste. The minimum amount of resin needed to form this adequate shield must be determined by careful optimization achieved through laboratory tests. Waste forms (e.g., cement or bitumen) of highly soluble salts, when immersed in water, have been known to degrade prematurely due to swelling. The waste forms may crack. When stretched beyond the safe loading levels, polyester waste forms are no exception.

Many of the waste form performance criteria evaluations are based on established EPA (RCRA) and NRC tests required for the land disposal of both LLW and mixed wastes. Use of standardized performance testing allows users to compare and select among alternative stabilization and microencapsulation methods.

The polyester microencapsulation process was evaluated (DOE, 1999) in a comparative study using both surrogate and actual salt-containing, mixed waste streams. One of the surrogate waste streams tested contained a high quantity of nitrate salts (~60 wt%) and represented a waste stream that had previously been unsuccessfully stabilized with simple Portland cement. Such waste streams are not uncommon in the DOE complex. Another surrogate waste stream contained salts of chloride (~10 wt%) and sulfate (~5wt.%) at levels representative of a dried, spent incinerator off-gas scrub solution (i.e., blowdown).

The two particulate wastes had no free moisture, contained oxide forms of RCRA heavy metals (~0.1 wt%), and trichloroethylene as a trace organic contaminant. These surrogates were employed in evaluating the waste loading and performance of vinyl ester, orthophthalic, and isophthalic polyester resins. Initial experiments with the two particulate surrogates were aimed at determining the upper limit of waste loading into the resin. At 60 wt%, it was observed that the resin waste mixture became very viscous and difficult to mix. Therefore, it was conservatively estimated that 50 wt% loading would be the feasible upper limit in full-scale processing. The preliminary tests also enabled determination of suitable initiator ratios for curing each resin waste mixture.

A factorial study of variables was performed at 40 and 50 wt% waste loading and spanned a 3 × 2 × 2 experimental design to explore the three primary factors: resin type, waste type, and waste loading. The performance of the WEP resin was evaluated with a third surrogate waste that represented an actual mixed waste stream from the Effluent Treatment Facility (ETF) at the DOE Hanford complex. Surrogate waste testing with the WEP resin involved the preparation of waste forms at 60 and 70 wt% loading. All waste form preparations were initiated at ambient conditions. Table 6.4.2 presents bulk costs and physical property data of the four resins tested and gives results (i.e., highest temperature reached during encapsulation, time to peak temperature, and compressive strength).

TABLE 6.4.2 Physical Data and Run Averages by Resin Type

	Vinyl Ester	Orthophthalic	Isophthalic	WEP
Resin I.D.	Hetron 922L-25	S2293-T15	Aropol 7334-T30	WEP-662
Cost (\$/lb)	1.62	0.72	1.07	1.42
Resin viscosity (cp)	275	425	450	130
Resin specific gravity	1.03	1.07	1.09	1.03
Wt% styrene in resin	48	45	46	60
Avg. T_{max} (°C)	112.5	112.0	127.0	80.6
Avg. Time to Peak Temp (hr)	2.3	2.2	2.4	1.78
Avg. compressive strength, MPa (psi)	42.2 (6120)	33.7 (4893)	36.0 (5217)	16.8 (2441)
Wt% initiator	2.5; 3[a]	1.0; 1.25[a]	1.75; 2.25[a]	1.25

[a] For nitrate and chloride surrogate waste, respectively

For the actual mixed waste encapsulation, only the WEP resin was used. The waste chosen for this treatability study consisted of the aqueous salt concentrates from the treatment of Hanford contaminated groundwater in the ETF complex. The ETF is a centralized wastewater treatment complex (consisting of filters, ion-exchange columns, organic oxidation units, evaporators, and a dryer) for conditioning a variety of Hanford's current and projected mixed wastewaters. Presently, the residues are nonhazardous and are usually dried to a concentrated salt before disposal as a LLW. However, future operations will generate mixed waste residues that will require further treatment before land disposal, and a process to encapsulate these wet residues may eliminate use of the dryer.

The salt slurry residues chosen for the treatability study contained sodium nitrate and calcium sulfate at a total salt concentration of ~25 wt%. The waste was spiked further with solutions of RCRA heavy metals and radionuclides to test contaminant retention in the waste form and improve the detectability of any contaminants during leach testing. Based on the ETF surrogate waste study and other trial runs, the treatability study was carried out by preparing a stable WEP emulsion at a pH of 9 and a waste loading of 62 wt%. An MEK peroxide initiator amount of 1.25 wt%, measured as a percent of the resin mass, was used.

Leachability of the RCRA hazardous heavy metals in the polyester surrogate waste forms was determined using the EPA TCLP. Because this single test can facilitate land disposal of RCRA hazardous waste, it is usually of greatest interest to waste managers. All existing hazardous waste disposal sites in the United States require that waste forms demonstrate leach levels below the established TCLP limits prior to land disposal.

All leachate specimens from the surrogate testing were below the allowable limits for all of the RCRA metals, except cadmium. The failure of cadmium was attributed to how the TCLP specimen sample was prepared from the waste form. The TCLP requires that the specimen be sized to less than a 9-mm fraction. The attrition and cutting used to achieve this size from the larger waste specimens destroyed the polyester coating on the surface of the waste form; consequently, the hazardous metal contaminants became exposed to leaching. To counter this effect and eliminate the need for size reduction, pellets of polyester waste forms of less than 9-mm diameter were specifically prepared for TCLP testing. A TCLP sample, when thus prepared, passed the leachability limit for all tested metals, including cadmium. With the outer resin layer intact in the specimen, true contaminant leaching characteristics were evaluated.

Therefore, the method chosen to reduce waste form size could have a pronounced effect on the TCLP leachate contaminant concentration. Thus, this variation in sample preparation could result in an inequitable assessment of the TCLP results.

Leaching as a function of time was also evaluated using a modified version of the ANSI/ANS 16.1 test. This leach test is not required by the RCRA for land disposal, but is recommended by the NRC. The test does not require grinding or crushing of the specimen; it determines a leachability index (LI) for any chemical or radiochemical anion or cation in the waste form, and is an excellent indication of the waste form's ability to stay intact during its disposal life. The LI is proportional to the logarithm of the inverse of the effective diffusivity of the contaminant under study. Thus, a higher value is considered better. Values of 6 or more are needed to meet the NRC's Branch Technical Position (BTP) requirement (NRC, 1991). The LI was evaluated for different species (including metals [Hg, Cd, Cr, Pb], salt anions [Cl, NO_3, SO_4] , and radionuclides [^{137}Cs, ^{60}Co, ^{99}Tc]. For the surrogate waste forms, the LI ranged from 6.1 to 12.6 (Biyani, 1998a); whereas for the treatability test specimen, the LI ranged from 7.5 to 10.8 (Biyani, 1998b).

Results of both the ANSI/ANS 16.1 and RCRA required TCLP leach tests indicate that for most cases there will be acceptable performance for land disposal of the polyester mixed waste form. The adequate TCLP leach performance can be partly attributed to the TCLP sample preparation method, where 8-mm pellets were prepared, as opposed to cutting or grinding from a larger waste form. Recently, the leach limits of RCRA hazardous metals allowable for land disposal have been lowered to more stringent Universal Treatment Standards (UTS). These levels would, however, cause failures unless waste loadings are reduced in the test specimens.

Waste loading, sometimes described by waste volume reduction, is an important parameter because it directly affects disposal costs. In the DOE study, the bulk density of the surrogate chloride and nitrate waste used was quite low, approximately 0.42 and 0.68 g/mL, respectively. Consequently, there was waste volume reduction (average of 25%) after polyester resin immobilization. In an attempt to make surrogate waste mixtures homogeneous, various blending methods can be used. Variation in mixing/blending methods (e.g., use of a planetary mill for homogenizing the waste, as opposed to manual mixing) could change waste particle size distribution and bulk density, and may result in variations in the test results (e.g., waste loading) obtained by different researchers.

The concept of volume reduction and waste loading needs careful evaluation. For particulate waste of high bulk, a reduction in volume is possible as the resin fills up the void spaces and facilitates settling and compaction of the waste particles. A lower bulk density provides opportunity for a high volume reduction but it also lowers the waste loading because a larger waste surface area requires wetting. Although the practical limit of salt waste loading using the DOE surrogate salt waste was determined to be 50 wt%, loading of reagent grade salts up to 70 wt% has been demonstrated (DOE, 1999). The physical makeup of the waste stream is as important as its chemical composition in determining a feasible waste loading with proper encapsulation.

Additionally, it is important to note that, based on a scanning electron microscope (SEM) observation of the polyester cell matrix (Subramanian and Mahalingam, 1979) and from theories on close-packed spheres, the limit of incorporation of any aqueous mixed waste into the polyester matrix is ~74 vol%. Higher volume fractions could be achieved by generating a distribution of sizes for the spheres and by distorting the particle shapes. Fracturing the waste form and examining it under the SEM shows a closed cell matrix (Figure 6.4.3). In this matrix, the individual waste droplets/particles are encapsulated by the resin with cell sizes ranging from 2 to 10 μm.

A comparative evaluation of three different S/S agents, including polyester, has recently been completed by the EPA. The waste streams consisted of five contaminants spiked into four separate soil and sludge wastes. The contaminants Cs and Sr served as surrogates for radionuclides, and hazardous metals Pb, As, and Cr (VI) were also added. A report on these test results has recently been published (EPA, 2000).

An evaluation of waste form properties of toxic metal/asbestos waste solidified with polyester resins has recently been completed (Chan et al., 1999b). This particulate waste was generated during the production of automobile brake lining. About 16 wt% of the raw material input is generated as brake lining waste, mainly dust containing asbestos as the main constituent.

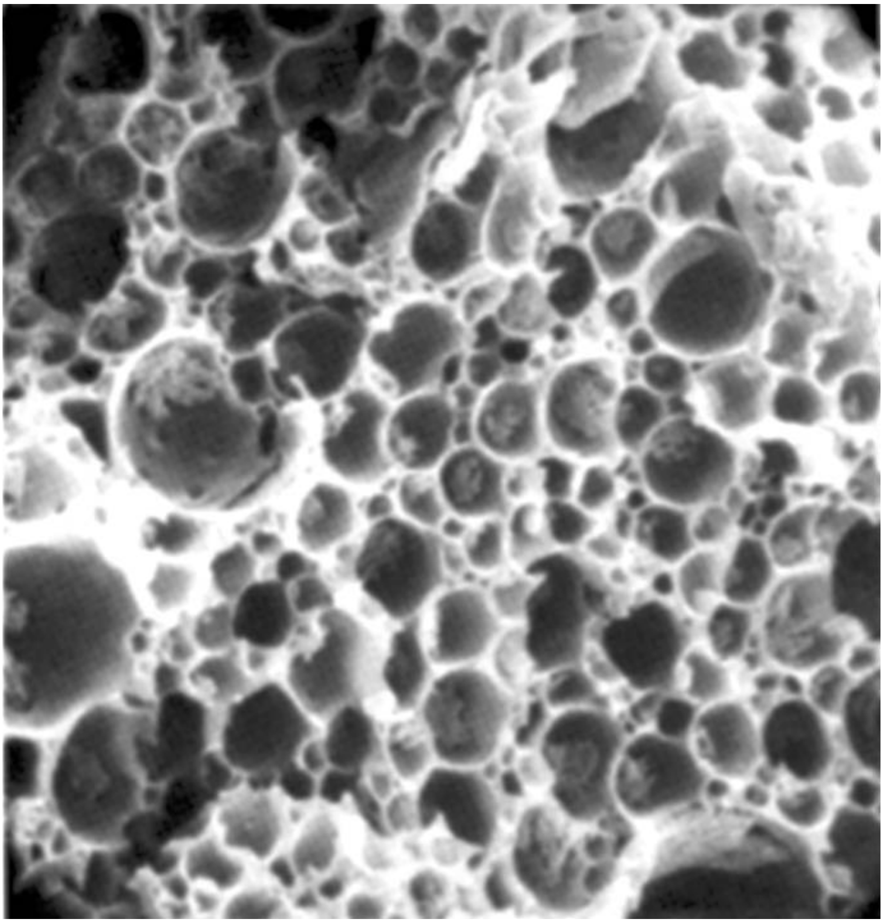

FIGURE 6.4.3 Scanning electron micrograph of solidified waste.

Although asbestos consumption in the United States has dropped drastically since 1973, it has grown significantly in developing countries. Health implications of asbestos are well documented in the literature and the EPA regulates all materials with more than 1% asbestos. The two types of resins used for the polymeric encapsulation of the brake lining waste were Ortho Polymal 820 produced by Takeda Chemicals Industries and Hetron 922 vinyl ester manufactured by the Ashland Chemical Co. (Columbus, Ohio). The resins were prepromoted to facilitate room-temperature curing and methyl ethyl ketone (MEK) peroxide was used as the solidification initiator.

Based on preliminary curing experiments, two initiator amounts of 3 and 5 wt% of the resin mass, and waste loading of 40 to 55 wt% were evaluated. Above 60 wt% waste loading, the added lining dust agglomerated and complete wetting was difficult. To prepare test specimens, the laboratory method for particulate wastes (Figure 6.4.1) was followed. The time to harden with the MEK initiator ranged from 1.5 to 12 hr. This time increased with the waste loading, possibly due to the presence of organic compounds (phenol and formaldehyde) and heavy metals.

The waste forms exhibited high compressive strength (53 to 68 MPa) and increases in the waste load decreased this strength. Untreated dust would not pass the regulatory limits for Zn, Pb, and Cr as stipulated in the Malaysia Environment Quality Act 1979 (Standard B). Data obtained from the TCLP test indicated that S/S by both resins allowed leachate concentrations to drop below those limits. The leachable fraction for each element is defined as the percentage of a particular heavy metal extracted from the waste form relative to the amount extracted from untreated dust. Polymal reduced the leachable fraction of all metals (Ba, Pb, Zn, Fe, Cr, Cu) originally present in the fines to less than 15%; in the case of Hetron, these were reduced to well below 18%.

The LI of heavy metals in both resins treated, as established by a modified ANSI/ANS 16.1 procedure, ranged between 9 and 10, and retention capability declined as the waste loading increased. The LIs obtained were thus much larger than the guidance value of 6.

The NRC BTP (NRC, 1991) requires that Class B and C low-level wastes (10 CFR 61) have structural stability. In addition to compressive strength testing of as-cured specimens, the waste forms must withstand thermal cycling, exposure to a minimum of 10E+8 rads, and biodegradation. Limited testing with polyester resin waste forms has been performed and the results documented (IAEA, 1988). These IAEA referenced data supplement the results from recent evaluations and are given below.

The compressive strength:

- Measured after thermal cycling for 80 days yielded no noticeable change (IAEA, 1988)
- Improved by 30 to 50% after irradiation up to 10E+9 rads (Subramanian and Mahalingam, 1979; IAEA, 1988)
- Did not change after various tests for microbial resistance (IAEA, 1988).

The flammability of polyester waste forms, as determined by burn tests conducted at 800°C, demonstrated a self-extinguishing tendency (IAEA, 1988). Flame tests at 537°C, in accordance with contemporary International Atomic Energy Agency (IAEA) and U.S. Department of Transportation (DOT) requirements, also showed compliance (Filter and Roberson, 1977).

There is a valid concern over the flammability of polyester waste forms containing nitrate wastes, a strong oxidizer. Researchers at the BNL (Upton, New York) have evaluated the self-ignition temperatures of waste forms made with 50 wt% sodium nitrate and polyester resin (Franz et al., 1987). The compatibility of polyester resins and nitrate salt waste at temperatures up to 400°C was confirmed using differential scanning calorimetric techniques.

Pilot Plant Polyester-Waste S/S Experience

Pilot plant studies on a variety of simulated wastes have been performed to evaluate process parameters for the scale-up to commercial units, to optimize equipment, and to simulate and solve potential process upsets that could occur in full-scale commercial operations. Two types of pilot plants have been built and evaluated: a pilot plant for semicontinuous operations, and another for continuous operations.

The semicontinuous unit had the capacity to treat 15 gal/hr of liquid waste (Subramanian and Mahalingam, 1979). In this unit, a batch of a waste-in-resin emulsion is initially formed. The resin and waste are then continuously added in a predetermined ratio to the preformed emulsion while a stream of the emulsified waste is withdrawn and transferred to the disposal container. Alternatives to impeller mixing for waste dispersion have also been evaluated (Mahalingam et al., 1981b). Finally, the initiator is mixed into the waste in the disposal container to achieve solidification.

The variation made for continuous operation is that the emulsification and the initiation of curing are carried out in a single, continuous-length static mixer filled with a calculated number of mixing elements (Powell and Mahalingam, 1992a). The waste stream and the resin are continuously pumped into the feed end of the static mixer where they emulsify during flow through the mixer. At a point downstream, where a stable waste-in-resin emulsion has formed, the peroxide catalyst is injected to initiate curing of the resin layer. Residence time in the mixer was set to preclude premature gelling within the static mixer/reactor system. The stream at the exit end of the static mixer is directed into the disposal container for completion of the curing reaction and waste form solidification. Leach rates for the solid waste matrices, evaluated using a modified ANSI/ANS 16.1 protocol, were dependent on the emulsion droplet size and the waste loading (Powell and Mahalingam, 1992b). These results were extrapolated to be substantially lower than those reported for grout and urea formaldehyde waste forms.

Field Applications

Factors important in the selection, design, implementation, and performance of polyester waste form processes include: waste characteristics (chemical and physical), processing requirements, the S/S product management objective, regulatory requirements, and economics. Other site-specific factors include: location, condition, climate, and hydrology. The chemical effects of some compounds in the waste can reduce the strength of the binder/waste mix, while some compounds can accelerate or retard the S/S curing rate. Temperature can also retard or accelerate curing. Size and shape of the waste particles can affect the viscosity of the mix, overmixing or undermixing can affect final product strength.

A 55-gal capacity planetary type mixer is usually the preferred method for full-scale systems, but any vessel containing a variable speed impeller-type mixer will suffice. Industrial-scale systems currently in use for the polyester microencapsulation of nuclear power industry wastes vary. Some consist of blend tanks, feed hoppers, premixers, and drum conveyor components. In these systems, the waste polymer blend is transported from the mixer to the disposal drum before hardening. In other arrangements, the drum serves as both the mixing vessel and the final disposal container.

An industrial-scale plant for the S/S of spent organic ion-exchange resins was recently commissioned at the Narora Atomic Power Station (NAPS) in India (Misra et al., 1997). A polyester resin with styrene monomer was chosen as the S/S media after evaluating different binders. The spent ion-exchange resins are hydraulically transferred to specially designed disposal drums and then dewatered by vacuum. The ion exchange resins are then mixed with the polyester resin and additives, and then cured in the drum. Free moisture on the surface of the ion exchange beads was incorporated into the matrix and was not detrimental to the final waste form quality. Process parameters were established via several radioactive and nonradioactive trial runs that resulted in full-scale waste forms. Approximately 100 drums of polymerized waste form have been produced.

Spent ion-exchange resins containing borate were slow in curing. This curing time was shortened by pretreating the ion-exchange resins with calcium hydroxide prior to mixing in the binder. Alternatively, a small increase in the initiator/promoter quantities also improved the curing time. Two initiator/promoter systems — benzoyl peroxide (BPO)/dimethyl aniline (DMA) and MEKP/cobalt naphthanate — were evaluated in the NAPS plant. Both systems yielded satisfactory curing. However, the waste forms made with BPO/DMA exhibited fewer surface cracks and a lower curing exotherm than those made with MEKP/cobalt naphthanate. Successful trial runs were also made with the initiator and promoter premixed into the polyester resin. This modification simplified plant operations and improved product uniformity.

Spent ion-exchange resin beads and borated evaporator concentrates from Electricité de France pressurized water reactors (PWRs) have been embedded in a polyester matrix using a mobile unit called "PRECED." This unit has been in operation in Europe since 1985 and was designed and manufactured by PECSIE and Technicatome of France. The technology used in PRECED" is based on the "Dow" process and this unit is operated by Société des Techniques en Milieux Ionisants (Figure 6.4.4). The matrix enables the incorporation of up to about 50% of waste that may contain water.

The spent ion-exchange resins are hydraulically transferred from a storage tank to an intermediate metering hopper where they are drained through a strainer. The supernatant is then removed using a pump. Once drained, the resins are transferred from the metering hopper to the encapsulation container via a twin-screw conveyer. The filling rate in the container is monitored with a camera and controlled by weighing. The polyester resin and its additives are stored in drums and transferred to the container by metering pumps.

Batch mixing of the resins with the binding agents is performed in the container with a disposable paddle. Mechanical agitation is used to obtain an emulsion with the aqueous phase and disperse the solid particles within the polyester resin. The mixture hardens in about 30 min after addition of the promoter and the benzoyl peroxide initiator. Hardening is gauged by monitoring the rise in temperature with time. Approximately 1.5 m^3 of spent ion-exchange resin can be processed in an 8-hr shift of the PRECED unit. Since 1985, approximately 2000 containers of solidified ion exchange resins, ranging from 230 to 430 L, have been produced. This unit has also been operated at the Belgium Tihange PWR site.

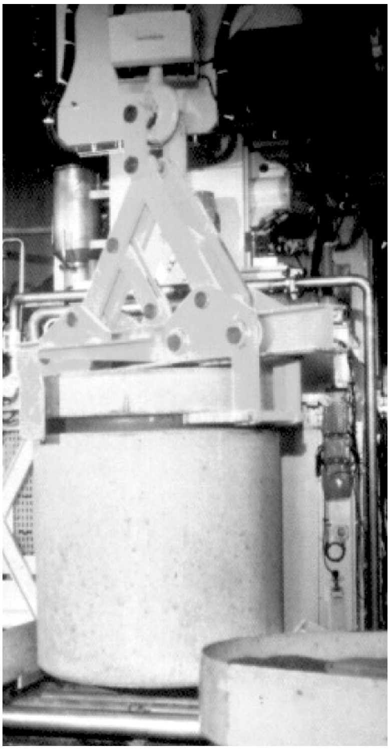

Figure 6.4.4 PRECED mobile unit for the S/S of IX resins.

Technology Economics

Cost estimates on established systems for cementitious stabilization were used to estimate the cost for an industrial-scale system involving the polyester microencapsulation of mixed wastes. Available cost documentation for existing or planned stabilization systems at both Argonne National Laboratory-East (ANL-E) and Idaho National Engineering and Environmental Laboratory (INEEL) indicate that capital costs, including equipment design and development, amount to a total of ~$2000K. This cost is valid for either cement systems or nonextruder microencapsulation methods based on polymers. The capital cost estimate assumes a 55-gal drum batch system and that infrastructure and facility housing to support the system are available.

The cost-effectiveness of the polyester microencapsulation waste treatment process is best determined by comparing it to the traditional baseline process of Portland cement stabilization. For a given waste form throughput, it is assumed that the processing times, batch capacities, and types of equipment are similar for both processes. The basis used is that labor cost and the number of drums of waste forms produced per day for the two processes are the same. A summary of the costs and associated data calculated for the two waste forms is provided in Table 6.4.3. All estimates are based on immobilizing a dry sodium nitrate salt-containing waste with a bulk specific gravity of 0.7.

A waste form production rate of nine drums a day corresponds to a waste throughput of ~1.87 m^3 per day, assuming an average waste-to-waste form volume expansion of ~0%. This mixed waste throughput is based on waste form performance data collected during recent evaluations of the polyester process (DOE, 1999). This data indicates that the polyester waste forms can consistently and reliably maintain a 50 wt% loading of dry mixed waste containing an appreciable salt component.

Labor costs are based on four full-time equivalents (FTEs) at the fully burdened rate of $70.00 per hour. The personnel required include two full-time operational technicians, as well as part-time management, engineering, safety, maintenance, health physics, documentation, and transportation

Table 6.4.3 Cost, Material, and Performance Evaluations

Item	Polyester Waste Form	Cement Waste Form
Waste form density (kg/m^3)	1400	2650
Waste form production rate		
Drums/day	9	9
Gal/day	495	495
m^3/day	1.87	1.87
kg/day	2623	4965
Waste:waste form vol expansion	0%	75%
Waste Treated		
(m^3/day)	1.87	1.07
(kg/day)	1312	749
Waste loading (wt%)	50%	15%
Binder use (kg/day)	1312	4220
Binder cost ($/lb)	1.21	0.05
Binder ($/day)	3499	465
Drums ($/day)	900	900
Labor ($/day)	6720	6720
Disposal		
($/ft^3 waste form)	60	60
($/m^3 of waste form)	2119	2119
($/day)	3969	3969
(1) Binder ($/kg waste)	2.67	0.62
(2) Drums ($/kg waste)	0.69	1.20
(3) Labor ($/kg waste)	5.12	8.97
(4) Disposal ($/kg waste)	3.03	5.30
Total Cost (1) – (4) ($/kg waste)	11.50	16.09

personnel. Polyester resin costs (initiator costs are considered negligible) are assumed at the supplier (for example, Ashland Chemical Company) bulk rate of $1.21/lb and are based on an average of the four costs provided in Table 6.4.2. New standard DOT 7A drums are estimated at $100.00 each, and the assumed operation consists of using the same drum for the mixing, curing, and final disposal of each 55-gal waste form batch.

Disposal fees and other associated costs vary widely, depending on which available LLW Subtitle D disposal site is used. At the INEEL Radioactive Waste Management Complex (RWMC), a relatively low disposal cost of $7.08/ft^3 waste form is available, whereas at the Barnwell Site in South Carolina, the cost can run as high as $1500/ft^3 waste form. For this analysis, a value of $60/ft^3 waste form was chosen because it is an intermediate number that has been previously used in cost and systems-engineering studies on mixed waste management in the DOE complex.

The analysis in Table 6.4.3, yields the various cost components as $/kg waste treated and enables a direct comparison between processes. Assuming that the waste volume expansion in a cementitious waste form is 75%, the waste form volume generated using a polyester matrix is ~57% of the volume of the cement waste form. In this example, the total cost of treating and disposing salt waste with cement is ~40% higher than polyester. There are many other factors that have bearing on the final process selection, but processes that can treat many forms of wastes and are less sensitive to waste composition variations will be favored.

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For Further Information

Information on the VERI™ process developed by Diversified Technologies can be found in the following:

NRC, 1992. Technical Evaluation Report related to Topical Report DT-VERI-100-NP/P, VERI™ (Vinyl Ester Resin *In Situ*) Solidification Process for Low-Level Radioactive Waste. Diversified Technologies Docket No. WM-105. Low-level Waste Management Branch, Division of Low-Level Waste Management and Decommissioning. United States Nuclear Regulatory Commission, Office of Nuclear Material Safety and Safeguards, Washington, D.C.

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Other references of interest are:

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6.5

Polyethylene Encapsulation

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Introduction

Polyethylene microencapsulation physically homogenizes and incorporates mixed waste particles within a molten polymer matrix, forming a solidified final waste form upon cooling. Each individual particle of waste is embedded within the polymer block and is surrounded by a durable, leach-resistant coating. The process has been successfully applied for the treatment of a broad range of mixed wastes, including evaporator concentrate salts, soil, sludges, incinerator ash, off-gas blowdown solutions, decontamination solutions, molten salt oxidation process residuals, ion exchange resins, granular activated carbon, shredded dry active waste, spill clean-up residuals, depleted uranium powders, and failed grout waste forms. For waste streams containing high concentrations of soluble toxic metal contaminants, additives can be used to further reduce leachability, thus improving waste loadings while meeting or exceeding regulatory disposal criteria. In this configuration, contaminants are both chemically stabilized and physically solidified, making the process a true stabilization/solidification (S/S) technology.

Unlike conventional hydraulic cement grouts or thermosetting polymers, thermoplastic polymers such as polyethylene require no chemical reaction for solidification. Thus, a stable, solid, final waste form product is assured on cooling. Variations in waste chemistry over time do not affect processing parameters and do not require reformulation of the recipe. Incorporation of waste particles within the polymer matrix serves as an aggregate and improves the mechanical strength and integrity of the waste form. The compressive strength of polyethylene microencapsulated waste forms varies based on the type and quantity of waste encapsulated, but is typically between 7 and 17.2 MPa (1000 and 2500 psi), well above the minimum strength of 0.4 MPa (60 psi) recommended by the U.S. Nuclear Regulatory Commission (NRC) for low-level radioactive waste forms in support of 10 CFR 61 (NRC, 1991; 1983) Because polyethylene is a relatively new material, it is difficult to predict its long-term durability. However, prior to scale-up of the microencapsulation process, a study was conducted to evaluate potential degradation mechanisms. The study examined potential effects on mechanical integrity from exposure to chemicals and solvents, thermal cycling, saturated environments, microbial attack, and high gamma-radiation fields (Kalb et al., 1991). At ambient temperatures, polyethylene is relatively inert to most chemicals, including organic solvents, acids, and alkaline solutions. Exposure to changes in temperature or saturated soil conditions have been shown to degrade the mechanical integrity of some waste forms, but had little or no measurable impact on polyethylene waste forms. Low-density polyethylene is not susceptible to growth of microbial organisms, a fact that is evidenced by the lack of plastics decomposition in municipal waste landfills. When exposed to gamma-radiation at total doses of up to 10^8 rad, additional cross-linking of the polymer occurs, resulting in increased strength and lower leachability.

Polyethylene microencapsulation was initially proposed for the treatment of low-level radioactive waste by Brookhaven National Laboratory (BNL) in 1983 (Kalb and Colombo, 1983; 1984; Colombo et al., 1983).

Since then, under support from the U.S. Department of Energy (DOE), the technology has progressed steadily from proof-of-principle testing and laboratory-scale development, through pilot- and production-scale demonstration, and finally on to commercial deployment. In addition to the development activities conducted at BNL, the DOE has supported several years of process testing at Rocky Flats Environmental Technology Site (RFETS) (Faucette et al., 1994) As the need for treatment of mixed wastes emerged in the late 1980s, application of the technology for hazardous wastes was also established. Following numerous bench-scale processing studies, final waste form product performance testing (Fuhrmann and Kalb, 1996; Lageraaen et al., 1995; Kalb, 1983) and studies investigating long-term durability (Kalb et al., 1991; 1993) a full-scale demonstration was conducted in 1994 (Kalb et al., 1996). Using a production-scale extruder capable of processing 2000 lb/hr, the demonstration successfully confirmed all aspects needed for a fully integrated processing system, including pretreatment of aqueous wastes, precise feed metering, extrusion processing, online quality control monitoring, and computerized process control. Figure 6.5.1 is a photograph of the full-scale polyethylene encapsulation extrusion process installed at BNL. Following successful development of the extrusion-based microencapsulation process, an alternative processing method using a kinetic mixer was developed and demonstrated (Lageraaen et al., 1997). A pilot-scale kinetic mixing process for polyethylene microencapsulation is shown in Figure 6.5.2. Each method has advantages for specific waste types and properties. BNL currently holds three patents for the polyethylene microencapsulation process, with several others pending (Kalb and Colombo, 1997; 1998; 1999). In 1997, BNL issued a commercialization license to Envirocare of Utah, where polyethylene microencapsulation has been deployed to treat DOE and commercially generated mixed wastes using both kinetic mixing and extrusion processing. Various polyethylene microencapsulation processing options, selection of optimal polymer feedstock, pretreatment requirements and options, critical process parameters and formulations, and typical final waste form performance results are discussed in this chapter section.

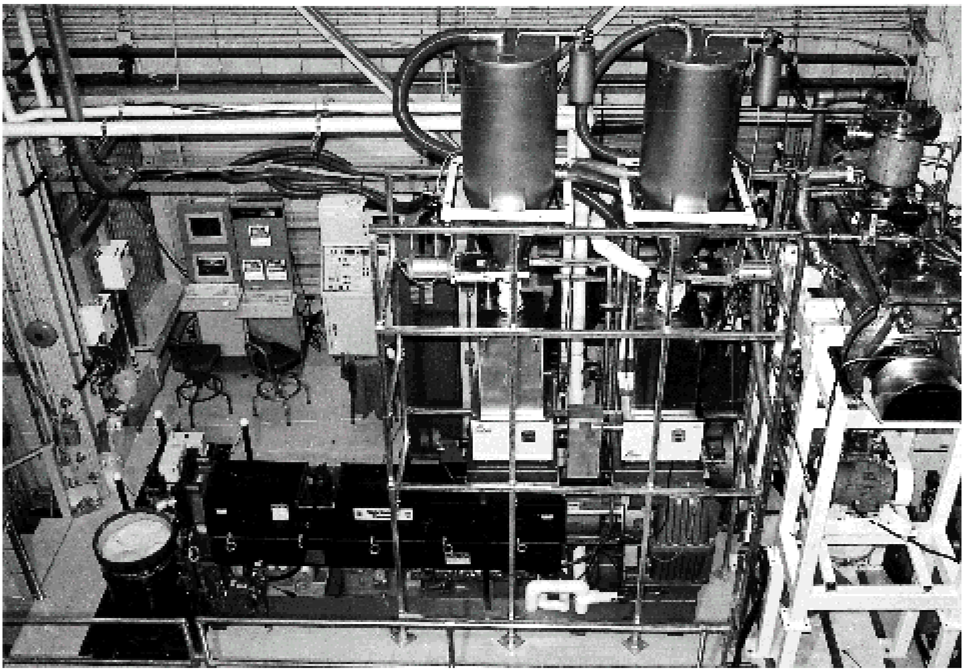


FIGURE 6.5.1 Full-scale polyethylene encapsulation extrusion process.

For waste streams that contain large particles not conducive to microencapsulation processing (e.g., pieces of lead, large debris with a particle size >60 mm), a related technology known as polyethylene macroencapsulation was developed (Kalb et al., 1995). For macroencapsulation, the waste is consolidated or

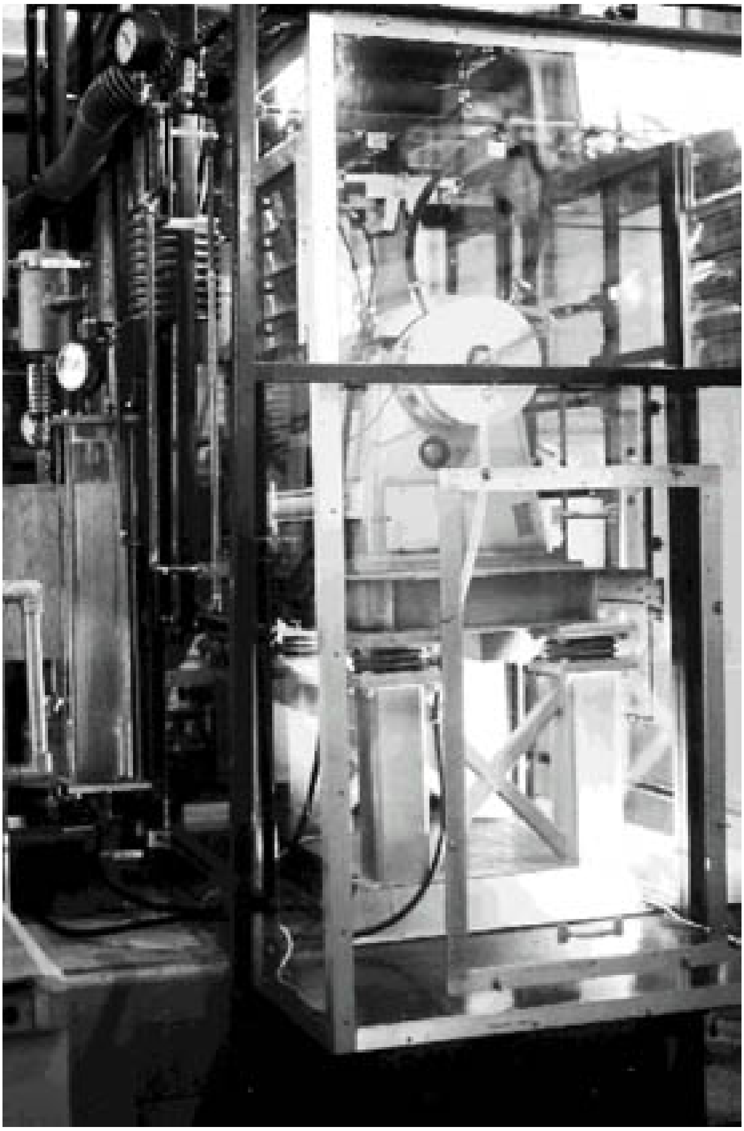


FIGURE 6.5.2 A pilot-scale kinetic mixing process for polyethylene microencapsulation.

compacted and a clean layer of molten polymer is extruded around it to form a thick, durable, leach-resistant barrier around the entire waste package. The U.S. Environmental Protection Agency (EPA) has established macroencapsulation as the Best Demonstrated Available Technology (BDAT) for these types of wastes. Thus, for these waste streams, the treatment vendor is not required to demonstrate compliance with specific performance criteria for treated macroencapsulated waste form packages. With DOE supported technology transfer assistance provided by BNL, Envirocare has also implemented polyethylene macroencapsulation and has successfully treated over a million pounds of mixed waste lead and debris to date. Macroencapsulation treatment techniques and applications are also discussed in detail in this chapter section.

Equipment Selection

Several types of processing techniques have been explored for polyethylene encapsulation (Patel et al., 1995). Selection of the optimal system must consider the type, properties, and volume of waste to be treated; equipment, operation, and maintenance costs; ease of operation; and performance requirements. Versatility is also an important consideration when selecting polyethylene encapsulation process equipment. For example, extruders can be used for both microencapsulation or macroencapsulation, and kinetic mixers can, in some cases, eliminate the need for pretreatment. Each type of equipment has advantages and limitations. When operated for microencapsulation, extrusion processing is limited by the amount of moisture or other volatiles present in the waste. As the mixture of plastic and waste is heated in an extruder, gases generated through vaporization of moisture or organics may become trapped within the viscous molten polymer and create an undesirable foamy product. Some extruders are equipped with a venting zone between the transition and metering zones, which can remove trapped air and volatile gases. Kinetic mixers do not trap vapors as readily as extruders, but operate in batch mode rather than continuous processing achieved by extrusion.

Single-Screw Extruders

The first successful application of polyethylene microencapsulation of waste was conducted using a single-screw extruder, the most commonly used technique in the plastics industry. In fact, extrusion has been routinely used for plastics processing for more than 60 years, confirming its reliability and ease of operation. Extrusion is accomplished in a heated cylindrical barrel in which an augered screw conveys and mixes the material. Figure 6.5.3 is a schematic view of a typical plastics extruder. The process consists of three basic steps: feed, transition, and metering. In the feed zone, polyethylene pellets or powder are gravity-fed to the feed throat. Fillers, including waste and additives, can be introduced with the polymer or added upstream through a mechanical "crammer" feeder. Figure 6.5.4 is a photograph of a typical extruder screw. As the unmelted materials are moved forward by the rotating auger, pressure builds due to decreasing volume of the screw channels. In the transition zone, heat to melt the plastic is gradually introduced by a series of external band heaters and, to a lesser degree, by frictional heat generated by the polymer. Thermocouples in the barrel monitor temperatures in each zone, which are precisely controlled by solid-state proportional-integral-derivative (PID) controllers. Excess heat created by frictional energy is removed by cooling fans or by circulating liquid coolant. Mixing occurs as the materials are further compressed by the decreasing channel volume and the shearing forces generated by the rotating screw. Several types of screw designs, shown in Figure 6.5.5, are available to enhance mixing in single-screw extruders, although adequate mixing for microencapsulation has been established with basic metering screws. Some extruders are equipped with a venting zone between the transition and metering zones that removes trapped air or volatile gases generated during processing. A sudden increase in the channel volume reduces pressure, allowing vacuum to be applied through a vent in the barrel. A vented

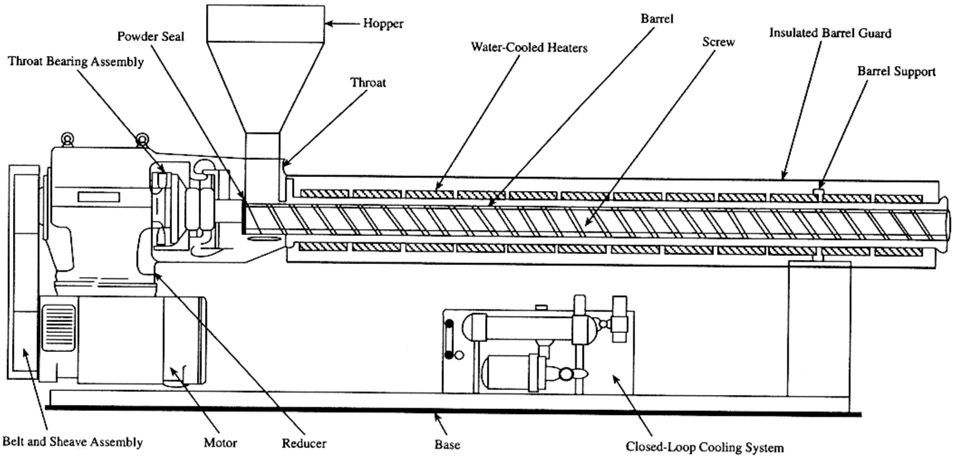


FIGURE 6.5.3 Schematic of typical plastics extruder.

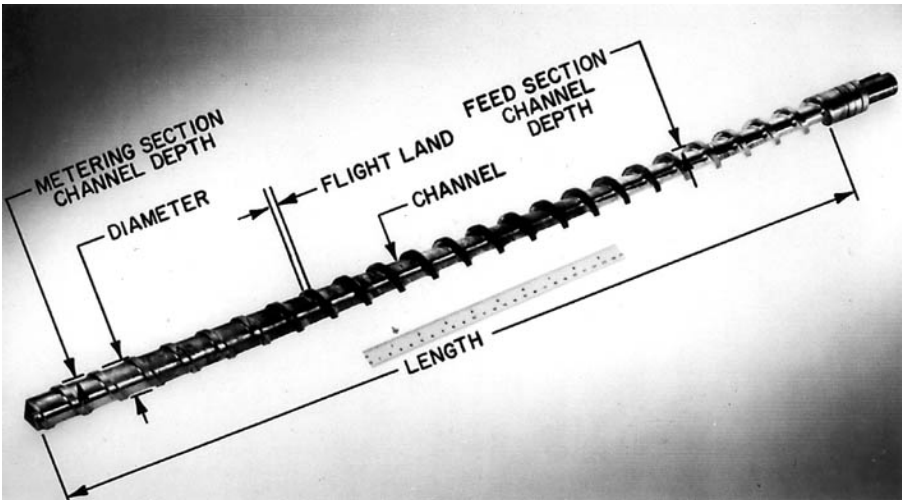


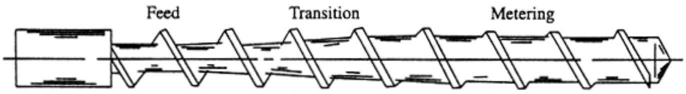
FIGURE 6.5.4 A typical extruder screw.

screw design is highly recommended for microencapsulation applications because wastes typically contain some residual moisture or other volatile gases that, if not removed, get trapped within the plastic yielding an undesirable foamy product. Finally, pressure is increased as the materials are further compressed in the metering zone in preparation for discharge through an output die.

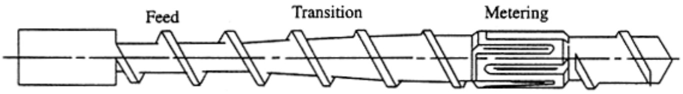
Twin-Screw Extruders

Twin-screw extruders, equipped with two side-by-side screws, have been used in the plastics industry for difficult compounding applications, such as the addition of glass fibers or other bulky fillers. They were initially applied for waste encapsulation in the mid-1970s using bitumen as the binder matrix (Werner and Pfleiderer Co., 1976). A production-scale twin-screw bitumen processing system was installed at the Palisades Nuclear Power Station in Michigan to treat aqueous borated salts. Twin-screw processing was successfully applied for polyethylene microencapsulation at RFETS (Faucette et al., 1994). Various configurations are available, including co- and counter-rotating, and intermeshing and non-intermeshing screws, as shown in Figure 6.5.6. The action of the two screws can provide increased shear and improved pumping for those materials that are difficult to feed. Each design has unique mixing and flow characteristics that must be balanced, depending on the specific engineering requirements. For example, counter-rotating, intermeshing screws provide improved mixing control, increased shear, and conveying properties. Non-intermeshing, counter-rotating designs sacrifice the degree of shear, but can deliver higher throughputs. Due to improved dispersive mixing, twin-screw extruders may be able to more readily process fine particles compared with single-screw extruders. Larger particles, however, may be more problematic for twin-screws due to tight clearances between screw flights. While twin-screw extruders have been successfully demonstrated at bench scale for polyethylene microencapsulation (Faucette et al., 1994), there are no data indicating improved processing or performance of final waste forms compared with those produced by single-screw processing.

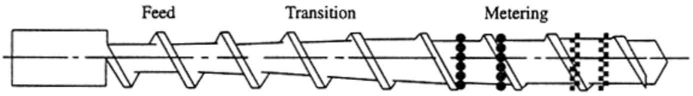
Vented twin-screw extruders are also available. The twin-screw extruder used at Palisades Nuclear Power Station was equipped with multiple vacuum ports at several stages along the barrel to remove excess volatiles. This enabled gradual feeding of aqueous wastes, which were evaporated within the heated barrel. Water vapor was collected and condensed before being trapped within the thermoplastic polymer. However, this design was limited by the ability of the extruder to drive off and collect the moisture, and as a result, the overall process rates were prohibitively slow. Thus, for either single- or twin-screw microencapsulation applications, pretreatment of aqueous wastes using process equipment specifically designed for moisture removal (e.g., vacuum dryers) is recommended.



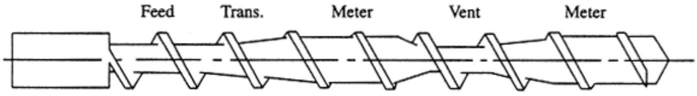
Basic Metering Screw



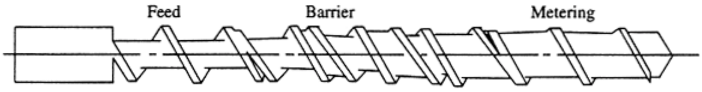
Maddock Mixing Screw



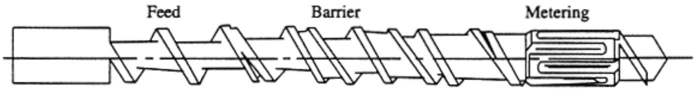
Pin Mixing Screw



Two-Stage Venting Screw



Barrier Screw



Barrier-Maddock Mixing Screw

FIGURE 6.5.5 Various screw types available for single-screw extruders.

Thermokinetic Mixers

Unlike extruders, thermokinetic mixers (also known as kinetic mixers) do not rely on external thermal energy to melt the plastic. Instead, polymer melting occurs due to the frictional (kinetic) energy that results from high-speed, high-shear mixing. They also differ from extruders in that they operate in batch, rather than continuous mode. This allows for a greater degree of mixing than can be achieved with extrusion techniques. The high-shear mixing occurs through the action of a rapidly rotating rotor with offset blades (blade tip speeds are typically up to 45 m/s) in a relatively small mixing chamber. Materials are loaded through a gravity-fed hopper controlled by a slide or pinch gate, and are then transferred to the mixing chamber by an auger mounted on the rotor. Melting or fluxing of the polymer occurs rapidly, typically in 15 to 30 s and can be monitored by infrared temperature probe, predetermined batch time, or the change in vibration and sound that occurs as the molten plastic mass is formed. The pitch of the mixing blades moves the material toward the pneumatically controlled discharge gate, which allows the molten material to exit the mixer.

Because of the rapid increase in temperature and the design of the batch-mixing chamber, volatile gases can be removed before being trapped within the viscous polymer. This method allows the successful processing of wastes with higher moisture or volatile organic constituent (VOC) concentrations (up to about 35 wt%) without pretreatment. Current kinetic mixer processing vessels are not designed to hold

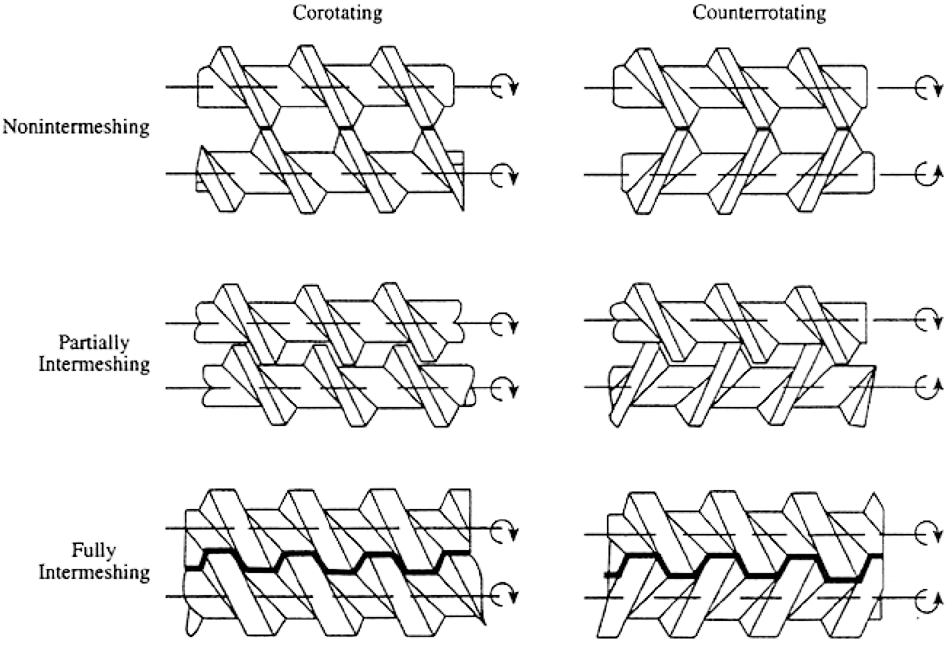


FIGURE 6.5.6 Types of screw configurations for twin-screw extruders.

"free liquids." As a consequence, higher moisture contents or wastes containing freestanding (unsorbed) liquids are difficult to process because the liquids tend to leak before being volatilized. The robust mixing action of kinetic mixers can also provide effective size reduction for wastes with larger particle sizes (e.g., >2 mm) that cannot be microencapsulated by extrusion. For example, pieces of failed cement grout waste forms (up to 19 mm in diameter) have been reprocessed by polyethylene microencapsulation using a kinetic mixer. The larger chunks of grout are broken down by the action of the high-shear rotor and frictional force of the polymer beads. The homogeneously mixed molten product is then discharged, allowed to cool, forming a leach-resistant waste form. Finally, the design of the kinetic mixer permits varying polymer type with only minor operational changes. Therefore, different recycled plastics can be easily substituted and comingled with little or no impact on the ability to process (Lageraaen and Kalb, 1997).

Ancillary Process Equipment

As with any S/S process, ancillary equipment is required to pretreat the waste if necessary, deliver the waste to the processing equipment (materials handling), meter the waste and binder materials to the process vessel, collect and treat any secondary off-gases that are generated, and monitor and control critical parameters. These components, as well as the types of processing devices described above, are generally "off-the-shelf" equipment and need only be properly sized and specified before being assembled to form an integrated processing system. Waste and binder materials can be accurately metered by means of volumetric feeders, or more precisely by loss-in-weight feeders. Computer-controlled loss-in-weight systems can be set to operate at a predetermined mixture ratio, with accuracies of ±0.5%. Process controls and monitoring can be integrated and controlled remotely by computer. For example, BNL's production-scale microencapsulation process monitored output rate through a solid-state scale and then maintained feed rates at optimal levels through computerized process control feedback. A transient infrared spectroscopy (TIRS) online monitoring system was developed by Ames Laboratory to provide real-time information on the actual waste loadings being processed, thus improving overall quality assurance (Wright et al., 1994).

Polymer Selection

Polyethylene is a relatively new engineering material. It was originally developed in 1933, with the first production-scale process capability emerging in 1939. Initial demand for the material was for cable insulation during World War II. Since then, continuous product improvements, coupled with expanding industrial applications, have made polyethylene the most widely used of all plastics today. Current production capacity in the United States alone is about 7 billion pounds annually (McGraw Hill, 1989).

As discussed in Chapter 6.1, low-density (0.914 to 0.925 g/cm^3) polyethylenes (LDPE) have lower melting and processing temperatures (typically 120°C and 150°C, respectively) than high-density polyethylenes (typically 180°C and 200°C, respectively). Polyethylenes are also available in a wide range of molecular weights, which are inversely proportional to their melt viscosity, or ability to flow while molten. The measure of melt viscosity is known as melt index, which describes how well the material flows (in units of g/10 min) under conditions specified by the American Society of Testing and Materials (ASTM) (ASTM D-1238, 1990). Thus, high-melt index plastics exhibit low-melt viscosities. LDPE is commercially available with melt indices ranging from 0.2 to 60 g/10 min. Mechanical properties (e.g., strength and durability) are generally better for high-molecular-weight (low melt index) polymers. Thus, selection of the optimal melt index plastic for microencapsulation is a balance between ease of processing while incorporating high waste solids loadings, and final product performance (Kalb and Colombo, 1984).

One distinct advantage for polyethylene microencapsulation compared with other S/S alternatives is that many modern plastics, including polyethylene, are routinely recycled both at industrial and post-consumer levels. Because it is difficult to maintain aesthetic properties (e.g., color) for recycled plastics, the commercial market for these materials is currently underdeveloped. However, recycled polyethylenes have potential for use as a microencapsulation waste binder because aesthetics is not a concern. A study conducted to evaluate issues of processibility and impact on final waste form performance found little effect due to use of recycled polyethylene as opposed to virgin materials (Lageraaen et al., 1997). However, supplies of well-characterized, homogeneous, recycled polyethylene are limited because commingling of different types of plastics during post-consumer collection is a common practice. Due to their varying properties, commingled plastics are more difficult to process. In such cases, mixing of virgin and recycled polyethylene resulted in superior processing performance.

Pretreatment Requirements

Because polymer microencapsulation does not rely on a chemical reaction for solidification, it is not susceptible to chemical interactions with the waste that can adversely impact other S/S alternatives. However, physical properties of the waste, such as particle size and distribution, density, and moisture or other volatiles can affect processing, sometimes requiring pretreatment steps to ensure success.

Plastics extruders can generally handle waste particles in the 50- to 2000-μm size range. Smaller, low-density particles tend to "float" on the viscous polymer and resist homogeneous mixing. Larger particles are restricted due to clearances between the screw and barrel. These difficulties can sometimes be overcome through use of higher melt index (lower melt viscosity) polymers, pretreating fine particles by agglomeration, and grinding or size-reducing large particles.

Wastes with moisture or VOC contents >2 wt% can be pretreated by the use of indirectly heated vacuum dryers, spray dryers, wiped film evaporators, or other suitable technique. The final product from any pretreatment process must not only meet process specifications for maximum volatiles content, but particle size requirements as well. Spray dryers tend to produce a particle size distribution skewed to the low end (ð50 μm), whereas vacuum dryers may produce a product containing large agglomerated clumps that require size reduction. Kinetic mixers can also be used to pretreat wastes with excessive volatiles by discharging the waste-polymer mixture prior to complete fluxing (Kalb et al., 1997). This mixture of polymer and dried waste is then fed to an extruder for final processing. With proper coordination, this approach converts the process from a batch method to a continuous one.

Hydrated ion exchange resins containing 40 to 60 wt% moisture require drying prior to microencapsulation. This causes the beads to shrink. Upon exposure to saturated conditions, the re-swelling of ion exchange resin beads within a microencapsulated waste form can cause the waste form to expand and even crack. This condition can be ameliorated by reducing the resin waste loading to 30 wt% or less or by thermal pretreatment of the beads to eliminate their ability to swell.

Macroencapsulation

Polyethylene macroencapsulation provides a suitable alternative for treatment of mixed waste lead or debris (particle sizes >60 mm). Such wastes include lead shielding contaminated equipment, drums, metal scraps and shavings, dismantlement and decommissioning residuals, laboratory or process trash, previously treated waste, or failed waste form products. These wastes are compacted or consolidated and then placed in a larger mold, drum, or container that is subsequently surrounded by a layer of clean molten plastic. Once the molten plastic cools, it forms a durable physical barrier that contains the waste and helps isolates contaminants from the environment. The thickness of the polymer layer can vary, but is typically 1 to 2 in. Single-screw extrusion is ideally suited for macroencapsulation because it can readily deliver a steady flow of molten polymer. With technology transfer assistance from the DOE and BNL, Envirocare of Utah, Inc., has successfully commercialized polyethylene macroencapsulation processing.

Formulation Optimization

As with other S/S technologies, optimization of waste matrix formulations is a balance between economic efficiency (i.e., optimal waste loading per unit volume) and final waste form performance (i.e., meeting regulatory and disposal site performance criteria). For polyethylene microencapsulation, waste chemistry is not a limiting factor, but the mixed waste's physical properties do limit the amount of waste that can be effectively mixed in the viscous polymer. When maximum waste loading is exceeded during extrusion, the melt pressure, amperage load, and mechanical wear increase. In the extreme, the extruder screw can become jammed if insufficient polymer is available for processing. If this occurs, feeding of pure polyethylene or a polymer purging compound usually corrects the problem. When maximum waste loading is exceeded during kinetic mixing, insufficient frictional energy is available to melt the polymer, thus significantly increasing process time and resulting in discharge of unencapsulated waste. Regardless of which processing technique is used, contaminants are more readily mobile through leaching or dispersion if the waste is not adequately encapsulated. For soluble wastes, leaching is usually directly proportional to the waste loading, until a break point is reached in which the individual waste particles are inadequately coated and a dramatic increase in leachability can be observed. For most dry solid wastes (e.g., dried evaporator salts, incinerator ash, soil) loadings between 50 and 70 dry wt% waste can be achieved by polyethylene microencapsulation while still meeting the minimum leaching criteria established by both the NRC and EPA. By comparison, maximum equivalent loadings in hydraulic cement are typically 10 to 30 dry wt%.

Final Waste Form Performance

Performance criteria for final waste forms depend on the generator (commercial vs. Department of Energy); type of waste (radioactive, hazardous, or mixed waste); and the disposal sites' waste acceptance criteria (WAC) and performance criteria. As mandated by the NRC in 10 CFR 61, all commercial low-level radioactive or mixed waste characterized as greater than Class A (based on isotope-specific activity levels) must be either solidified or packaged in a licensed high- integrity container (HIC) for disposal (U.S. NRC, 1991). Specific testing protocol and performance criteria for solidified final waste forms are identified by NRC or disposal sites to establish long-term stability and immobilization of contaminants. These include leachability, mechanical integrity, resistance to biodegradation, radiation damage, freeze-thaw, and saturated soil conditions. As discussed, the performance of polyethylene microencapsulated waste forms has been shown to exceed these minimum performance standards.

Leachability

Assuming long-term durability is established, leaching is the most important final waste form performance metric because it quantifies the ability of the waste form to isolate contaminants from the environment. Depending on the type of waste, several leach tests are commonly used to evaluate waste form leachability. The NRC recommends testing using ANS 16.1 protocol developed by the American Nuclear Society (ANS), which is designed to evaluate releases of contaminants in demineralized water under controlled conditions (ANS 16.1, 1986). This test provides a relative measure of leachability expressed as the leaching index, which is inversely proportional to the log of effective diffusivity. Thus, an incremental increase in the leaching index is equivalent to an order of magnitude reduction in leaching. Table 6.5.1 presents leach data results for sodium nitrate waste microencapsulated in polyethylene. For polyethylene microencapsulated waste forms, leachability is generally diffusion controlled and inversely proportional to the waste loading. Leach indices range from slightly more than 11 (30 wt% loading) to just under 8 (70 wt% loading). For comparison, these results are between almost 2 and more than 5 orders of magnitude better than the minimum leach index of 6.0 recommended by the NRC for final waste forms containing low-level wastes. These data reflect the relatively low leachability of polyethylene waste forms and clearly show the direct relationship of waste loading and leach rate for soluble salt wastes encapsulated in polyethylene.

TABLE 6.5.1 ANS 16.1 Leach Test Data for Sodium Nitrate Waste Microencapsulated in Polyethylene

$NaNO_3$ Waste Loading, (wt%)	Cumulative Fraction Leached of Na	Diffusion Coefficient (cm^2/s)	Leach Index
30	0.9	8.4×10^{-10}	11.1
50	6.3	6.0×10^{-9}	9.7
60	15.0	1.1×10^{-8}	9.0
70	73.4	1.5×10^{-7}	7.8

The Accelerated Leach Test (ALT), an alternative method recently approved by the American Society of Testing and Materials (ASTM C-1308), is, like ANS 16.1, a semi-dynamic test in distilled water with leachate replacement at regular intervals (ASTM C-1308, 1996). Several improvements (e.g., accelerated testing at elevated temperatures, computer analysis/modeling of data) have enabled the determination of leaching mechanisms and prediction of long-term leaching behavior. Actual leach data is compared with predicted diffusion-controlled releases and a goodness-of-fit is established. If the actual data fits the predicted model results, then the diffusion equation can be used to extrapolate the leaching of actual final waste forms over time. Accelerated Leach Testing of sodium nitrate waste microencapsulated in polyethylene confirmed that diffusion is the predominant leaching mechanism. Predicted releases as a function of waste loading are shown in Table 6.5.2. Projected cumulative fractional contaminant releases after 300 years from a full-sized waste form (2 m in diameter by 2 m in height), under worst-case fully saturated conditions, range from 3.7 to 9.5%.

Wastes containing hazardous components defined by the EPA under the Resource Conservation and Recovery Act (RCRA), or a combination of hazardous and radioactive components (i.e., mixed wastes), must meet leaching criteria established in 40 CFR 61 (known at the Toxicity Characteristic Leaching Procedure, or TCLP). This is a very short-term (18 hr) test designed to mimic conditions at a typical landfill to try and determine contaminant concentrations if the waste was not segregated and was disposed of at a conventional Subtitle C landfill. For example, the leachant is an acetic acid that is typically produced at landfills from the degradation of organic materials. TCLP was originally designed assuming treatment by a chemical stabilization method or by conventional grout S/S that would eventually lose mechanical integrity and disintegrate. In other words, no credit is allowed for physical microencapsulation of the waste. The procedure requires passing the testing material through a 9.5-mm sieve. If the material is a

TABLE 6.5.2 Projected Releases from a Production-Scale Polyethylene Microencapsulated Waste Form Following 300 years Leaching under Fully Saturated Conditions

$NaNO_3$ Waste Loading, (wt%)	Diffusion Coefficient, (cm^2/s)	Projected Cumulative Fraction Leached, (%)
50	3.05×10^{-9}	3.7
60	8.6×10^{-9}	5.0
70	5.58×10^{-8}	9.5

monolithic solid, it is size-reduced so that pieces of the monolith that fit through the sieve are tested. Because polyethylene microencapsulation is a durable final waste form that is not expected to degrade under disposal conditions, a modified preparation procedure was developed to meet TCLP size requirements, without sacrificing the integrity of the encapsulation. Pellets that fit through the 9.5-mm sieve, representing miniature waste forms, are cast and tested. This modified procedure is described in the operational permit for polyethylene microencapsulation, approved by the State of Utah Department of Environmental Conservation, Division of Hazardous Waste. The TCLP test is also biased toward alkaline pH-based systems because the leachant is slightly acidic and can be easily neutralized by highly alkaline additives. And because the solubility of most toxic metals is limited under high pH conditions, these systems resist leaching under the short-term test conditions but are not evaluated over long-term conditions. The EPA is currently examining alternatives to TCLP; but until another test is specified, all treated wastes must still meet these criteria. Results from TCLP leaching of polyethylene microencapsulated waste forms is summarized in Table 6.5.3.

Summary

Polyethylene encapsulation is a physical process to treat radioactive, hazardous, and mixed wastes that provides good, long-term stability and low leaching. Microencapsulation combines waste particles with the molten polymer to form a homogeneous mixture that results in a solid final waste form on cooling. Macroencapsulation, used for contaminated lead or other debris (particles >60 mm), surrounds the waste in a layer of clean plastic that provides mechanical integrity, reduces potential for intrusion, and lowers leachability. Because no chemical reaction is required for this process, it is compatible with a wide range of wastes, is insensitive to waste chemistry, and results in final waste forms with relatively high waste loadings (e.g., 50 to 70 wt% of dry waste). Recycled polyethylene can be successfully used in place of virgin plastics, providing a market for this valuable resource and reducing the overall process costs. The technology has been deployed at production scale and is currently commercially available for treatment of mixed wastes.

Defining Terms

Microencapsulation: Thorough and homogeneous mixing of small waste particles (i.e., <60 mm) with a liquid binder that then solidifies to form a solid, monolithic final waste form. Individual waste particles are coated and surrounded by the solidified binder to provide mechanical integrity and act as a barrier against leaching of contaminants.

Macroencapsulation: Packaging large pieces of waste (i.e., >60 mm) not suitable for processing by microencapsulation and surrounding the package with a layer of clean binder material. The binder forms a protective layer around the waste that provides structural support, prevents dispersion, and helps reduce migration of contaminants.

Thermosetting polymers: Polymers that require a chemical polymerization reaction (through the interaction of monomer, catalyst, and promoter) to form a hardened, monolithic, solid product.

TABLE 6.5.3 Toxicity Characteristic Leaching Procedure Data for Polyethylene Microencapsulated Waste Forms

		Toxic Metal Source Term Conc.[a] (Microencapsulated Waste Form TCLP Concentration) (ppm)					
Waste Stream	Waste Loading (wt%)	Pb	Cr	Cd	Hg	Se	As
DOE mixed salts	60	3000 (0.07)	3000 (0.10)	3000 (0.37)			
DOE incinerator ash	60	5000 (0.01)	5000 (0.01)	5000 (0.01)			
SRS CIF blowdown	40	2250 (<0.05)	500 (0.07)	125 (<0.05)	250 (<0.04)		
INEEL carbonate salt	50	120 (<0.14)					
INEEL ion exchange resin	40	1200 (1.6)					
INEEL sodium bearing waste	40	218 (<0.14)	351 (2.4)	246 (0.34)	242 (<0.0002)		
Commercial incinerator ash	50					15 (< 0.15)	
Molten salt oxidation residuals	50		2400 (1.6)				
Fernald Silo 1sludge	50	(0.712)					
Fernald Silo 3 sludge	60	(0.058)	(0.029)	(0.002)		(0.088)	(0.245)
Maximum allowable concentration, TCLP		5.0	5.0	1.0	0.2	1.0	5.0
Maximum allowable concentration, UTS[b]		0.75	0.85	0.2	0.025	5.7	5.0

[a] Toxic metal concentration in the waste, i.e., source term.

[b] EPA is phasing in new Universal Treatment Standards (UTS) with lower allowable concentrations for toxic metals.

Thermoplastic polymers: Polymers with a linear molecular structure that repeatedly melt to a flowable state when heated and then harden to a solid when cooled.

Melt index: A measure of the relative flowability of plastic resins while molten. The value is quantified by application of a standard test method (ASTM D-1238) that specifies the temperature and flow conditions using a plastics rheometer. The units are given in g/10 min.

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For Further Information

Two volumes of the Innovative Site Remediation Technology series, published by the American Academy of Environmental Engineers, contain useful information about polymer stabilization/solidification technologies. Each of these books compares polymer technologies with conventional hydraulic cement S/S technologies, as well as other innovative processes such as vitrification. The first series, entitled "Stabilization/Solidification" (Colombo et al., 1994) presents a broad overview of the technologies, process descriptions, potential applications, process evaluations, and limitations of the technologies. The second edition, entitled "Stabilization/Solidification Design and Application" (Kalb et al., 1997b) provides more specific information required for technology deployment, including application concepts (e.g., principles, applications, treatment trains), design development (e.g., design basis, equipment selection, pre- and post-treatment processes, instrumentation/controls, safety, permitting, performance measures), and implementation/operation (e.g., start-up, operational, and maintenance procedures).

6.6

Sulfur Polymer Encapsulation

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Introduction

Sulfur polymer cement (SPC) is a thermoplastic polymer consisting of 95 wt% elemental sulfur and 5 wt% organic modifiers to enhance long-term durability. SPC was originally developed by the U.S. Bureau of Mines as an alternative to hydraulic cement for construction applications. Previous attempts to use elemental sulfur as a construction material in the chemical industry failed due to premature degradation. These failures were caused by the internal stresses that result from changes in crystalline structure upon cooling of the material. By reacting elemental sulfur with organic polymers, the Bureau of Mines developed a product that successfully suppresses the solid phase transition and significantly improves the stability of the product. SPC, originally named modified sulfur cement, is produced from readily available, inexpensive waste sulfur derived from desulfurization of both flue gases and petroleum. The commercial production of SPC is licensed in the United States by Martin Resources (Odessa, Texas) and is marketed under the tradename Chement 2000. It is sold in granular form and is relatively inexpensive (~\$0.10 to 0.12/lb).

Application of SPC for the treatment of radioactive, hazardous, and mixed wastes was initially developed and patented by Brookhaven National Laboratory (BNL) in the mid-1980s (Kalb and Colombo, 1985; Colombo et al., 1997). The process was subsequently investigated by the Commission of the European Communities (Van Dalen and Rijpkema, 1989), Idaho National Engineering Laboratory (Darnell, 1991), and Oak Ridge National Laboratory (Mattus and Mattus, 1994). SPC has been used primarily in microencapsulation applications but can also be used for macroencapsulation of waste. SPC microencapsulation has been demonstrated to be an effective treatment for a wide variety of wastes, including incinerator hearth and fly ash; aqueous concentrates such as sulfates, borates, and chlorides; blowdown solutions; soils; and sludges. It is not recommended for treatment of wastes containing high concentrations of nitrates because of potentially dangerous reactions between sulfur, nitrate, and trace quantities of organics. Recently, the process has been adapted for the treatment of liquid elemental mercury and mercury contaminated soil and debris.

SPC is similar to polyethylene in that they are both thermoplastic binders; but because the melt viscosity is significantly lower (25 centipoise), it can be easily processed using a simple, heated, stirred mixing vessel. The melt temperature of SPC is 119°C and the acceptable process temperature range is 130 to 150°C. Unlike conventional hydraulic cement formulations, SPC final waste forms do not typically result in an increase in volume because the molten SPC can fill interstitial void spaces in the waste. SPC combined with an aggregate filler (such as waste) tends to develop relatively high compressive strength, typically 13.8 to 34.5 MPa (2000 to 5000 psi). SPC waste forms are comparatively brittle and fail by a shattering fracture when subjected to an axial compressive load. Thermal cycling and exposure to radiation doses of up to 10^8 rad have little measurable impact on mechanical integrity. Similar to hydraulic cement, expansion of some waste materials on becoming rehydrated through exposure to saturated conditions can cause swelling and/or cracking of the waste form, depending on the type and quantity of waste encapsulated. However, BNL has shown that addition of a small percentage of fiberglass fibers supplements the tensile strength of the binder and greatly improves resistance to swelling and cracking under these conditions (Colombo et al., 1997). Testing for microbial degradation using current test method protocols (ASTM G-21 and ASTM-G22, 1970), has not resulted in any negative impacts. However, these methods are not designed to examine the effects of specific thiobacillus microbes, which can potentially attack sulfur. Relatively long-term durability for SPC has been observed by examining sewer pipes fabricated from SPC concrete after numerous years in service and finding no significant deterioration.

Sulfur Polymer Stabilization/Solidification

Mercury is a particularly hazardous element because it is highly toxic and has a very high vapor pressure. In addition, it is a difficult constituent to treat effectively, especially if commingled with radioactive contaminants (i.e., mixed waste). Conventional techniques for treating elemental mercury, commonly referred to as amalgamation, reduce the leachability of the toxic mercury, but result in a highly dispersible powder and do not effectively immobilize the radioactive contaminants. A new technique developed at BNL (patent pending) known as Sulfur Polymer Stabilization/Solidification (SPSS) was specifically developed for the treatment of liquid elemental mercury and mercury-contaminated soil and debris. SPSS treatment is conducted in two stages. SPC binder and proprietary additives are first reacted with the waste to chemically stabilize the mercury. Then the mixture is heated, melted, and cooled, forming a solid final waste form in which the stabilized waste is physically encapsulated. Mercuric sulfide formed by the stabilization reaction has a low solubility under normal and low pH conditions (hence leaches at a low rate) and a much lower vapor pressure than elemental mercury (greatly reducing volatilization). Tests have shown that the process effectively captures 99.7% of the mercury in the stabilized waste form while very little of the mercury (0.3%) is volatilized during processing where it is captured in the off-gas system.

Equipment Selection

Batch Processing Vessels

Because of its low melting point and low melt viscosity, SPC can be successfully processed by a variety of simple, heated mixing vessels. Bench- and pilot-scale development work was conducted using several types of heated batch mixers, including low- and high-shear blade mixers and double planetary orbital mixers (Kalb and Colombo, 1985). The latter provides a highly efficient mixing pattern at relatively low mixing speeds, thereby diminishing air and gas entrainment within the molten mixture. Heating can be provided by thermocouple-controlled electric resistance band heaters, steam generators, or hot oil circulation heaters (Kalb et al., 1991; Kalb et al., 1999). A pilot-scale cone mixer (Ross Mixers, Happauge, New York) equipped with a helical auger that rotates on its own axis and around the circumference of the vessel, is shown schematically in Figure 6.6.1. This vessel was used to demonstrate the SPSS process and treat several drums of mercury contaminated soil and more than 90 kg of liquid elemental mercury. The system is heated by a circulating hot oil system and volatiles are condensed by a chiller. Figure 6.6.2 is a photograph of the integrated pilot-scale processing system.

Other processing techniques have also been examined. Two types of production-scale mixers — the Holo-Flite mixer (Denver Equipment Co.) and Porcupine Processor — have been evaluated by Idaho National Engineering and Environmental Laboratory (Darnell, 1993). Each uses hot oil media to heat the vessel and the hollow mixing shafts. The Holo-Flite, depicted in Figure 6.6.3, has dual shafts with auger-type flights and is discharged by raising the height of the vessel to allow gravity feed through a weir pipe. The Porcupine Processor, shown in Figure 6.6.4, has a single shaft with hollow, flat-shaped paddles that are separated by breaker bars protruding from the vessel walls to provide better scraping and mixing action. GTS Duratek (Oak Ridge, Tennessee) has successfully microencapsulated incinerator fly ash in SPC using a steam-heated, high-shear mixer in batches of approximately 1360 kg (1.5 tons). Mixers that allow processing under negative pressure are preferred as they reduce the required process temperature and facilitate capture of off-gases.

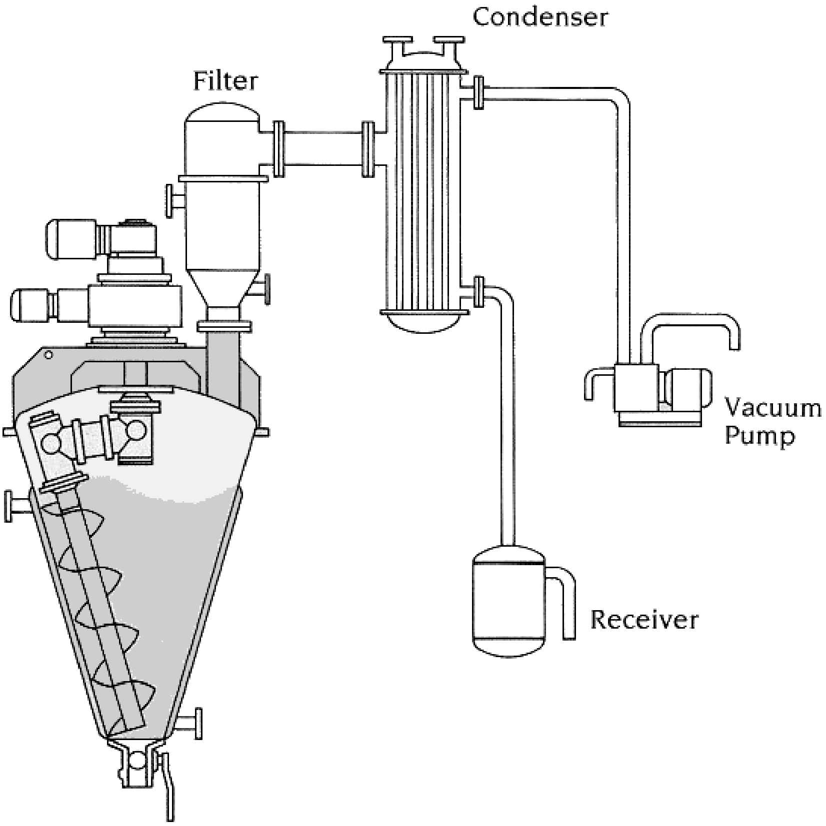

FIGURE 6.6.1 Schematic diagram of a double planetary cone mixer manufactured by Ross Mixer, Inc.

Ancillary Process Equipment

Unlike polyethylene, SPC microencapsulation is usually conducted in batch mode, in which proper feed ratios of waste and binder are more easily achieved because segregation of materials is not as critical. Volumetric, loss-in-weight, or belt feeders can all be used. Because the process temperature for SPC microencapsulation is 130 to 150°C, moisture and VOCs may be volatilized during processing, thus requiring installation of an appropriate off-gas collection system. A typical system includes a condenser and/or other means of trapping vapors (e.g., cryogenic trap, impinger), carbon filter to collect VOCs and mercury vapor, and a HEPA filter for radioactive particulates. Figure 6.6.5 is a schematic diagram of the SPSS off-gas collection system used for treatment of mixed waste mercury. Process results at BNL indicated that 99.7% of the mercury treated remained in the final waste form, 0.3% was captured in the off-gas treatment train, and no mercury was detected in the gas vented to the environment.

Pretreatment Requirements

Volatile constituents that are vaporized are not readily trapped in the molten mixture and can be removed in the off-gas system because the relatively low viscosity of the molten SPC mixture does not tend to entrain the vapors. Likewise, batch processing allows sufficient time for vapor removal. Nevertheless, for wastes that contain high concentrations of moisture or other volatiles, it is usually more efficient to pretreat the waste using equipment described elsewhere. Compared with polyethylene, its lower-melt viscosity makes SPC microencapsulation able to tolerate a broader range of particle sizes. Only those particles that exceed the size specifications of the process vessel require pretreatment prior to processing.

FIGURE 6.6.2 The integrated pilot-scale SPSS process installed at BNL.

Formulation Optimization

Successful optimization of SPC final waste form composition requires consideration of both processing parameters and final waste form performance. Sufficient workability of the mixture must be ensured to allow homogeneous mixing and operation of equipment within mechanical limits. The range of successful waste loading for SPC microencapsulation varies, depending on the physical properties of the waste stream and the concentration of the contaminants of concern. Typically, waste loadings for SPC microencapsulated waste forms range from 40 to 70 wt%, depending on the chemical and physical properties of the waste. This compares with typical waste loadings of 10 to 30 wt% for hydraulic cement waste forms.

If maximum waste loadings are exceeded, the molten mixture can become excessively dry and thick, preventing adequate distribution of the materials. In extreme cases, excessive load on the equipment can cause mechanical failures in mixing blades, shafts, motors, and gears. Operating mixing equipment with overly dry, abrasive mixtures can also create premature wear on vessel surfaces. Successful workability and processing do not guarantee that the final waste form product will meet the desired performance criteria. If waste loadings exceed the point at which the SPC binder can effectively microencapsulate individual waste particles, the ability of the waste form to immobilize contaminants will be diminished.

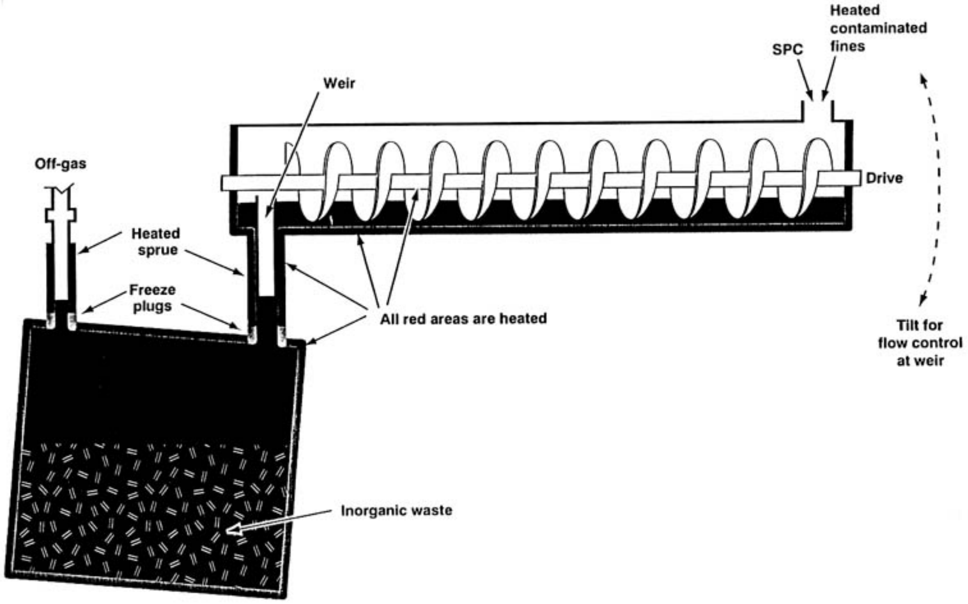

FIGURE 6.6.3 Holo-Flite mixer.

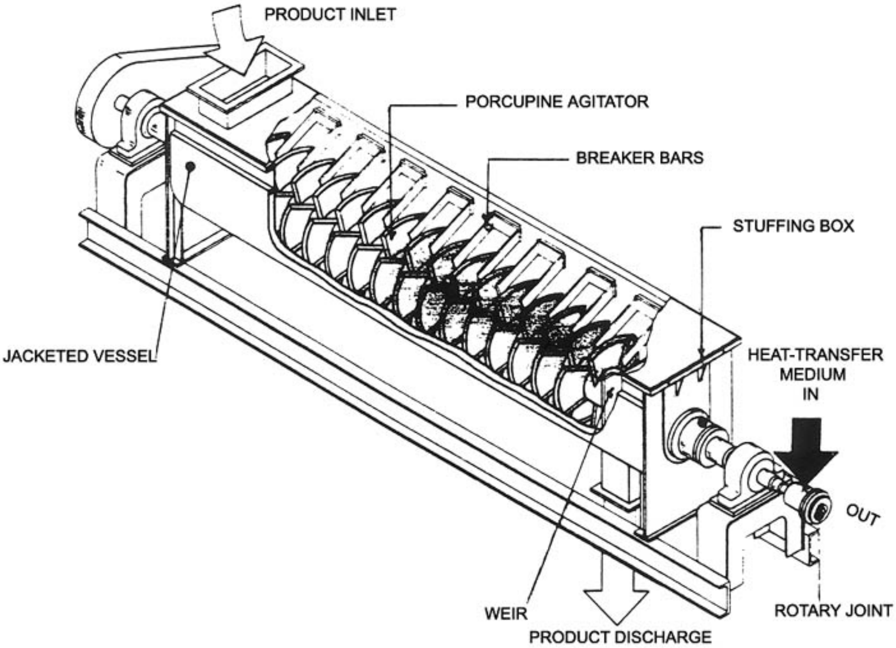

FIGURE 6.6.4 Porcupine processor.

Final Waste Form Performance

As discussed previously, SPC waste forms are relatively durable and have been demonstrated to meet minimum durability criteria established by the NRC for low-level radioactive waste forms (e.g., compressive strength, thermal, microbial, and radiation stability).

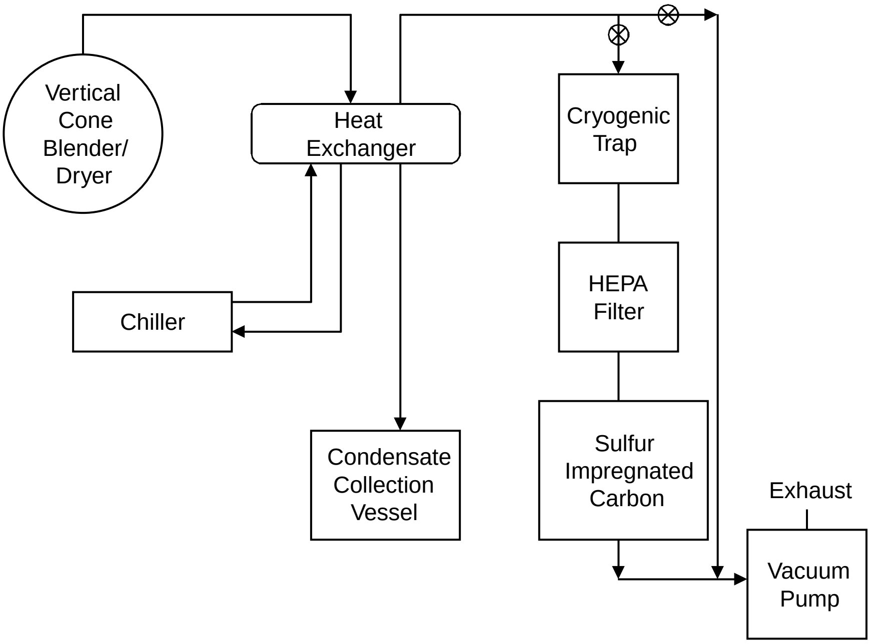

FIGURE 6.6.5 Schematic diagram of the SPSS off-gas collection system.

Leachability

As with other microencapsulation technologies, leachability of wastes treated by SPC microencapsulation varies as a function of the waste characteristics (e.g., solubility), waste loading, and contaminant concentration. Leachability for SPC waste forms is typically four to eight orders of magnitude better than the minimum requirements established by the NRC. Leach index data for SPC waste forms is shown in Table 6.6.1 and ranges from 9.7 to 14.6.

TABLE 6.6.1 Leach Indices for Sulfur Polymer Microencapsulated Waste Forms

		Leach Index	
Waste Type	Waste Loading (wt%)	^{60}Co	^{137}Cs
Na_2SO_4	25	12.5	10.6
	40	10.7	9.7
Incinerator ash	20	14.0	11.2
	40	14.6	11.1

Because the SPSS process combines both chemical stabilization and microencapsulation, leachability is reduced even lower. Long-term leachability of mercury was measured from SPSS final waste forms by means of the Accelerated Leach Test (ASTM C-1308). Similar to ANS 16.1, this method is a dynamic leach test in which the leachant is replaced on a periodic basis. Data is evaluated using a related computer program that calculates incremental and cumulative contaminant fractions released, identifies predominant leaching mechanisms and effective diffusion coefficients, and enables prediction of long-term leachability if diffusion is the controlling mechanism. Leach data closely matched that predicted by the diffusion model, thus indicating that diffusion predominates. Following 11 days of leaching, a total of only 5.8×10^{-4} percent of the mercury leached from the waste form. The effective diffusion coefficient was measured to be 4.15×10^{-18}.

Leachability of toxic metals from SPC microencapsulated waste forms is generally low and can be enhanced by the use of stabilization additives. Toxicity Characteristic Leaching Procedure (TCLP) data for incinerator ash containing extremely high concentrations of lead and cadmium before and following SPC microencapsulation is presented in Table 6.6.2. Leachability of these metals can be further reduced by optimization of the stabilization additive formulation and/or by means of the chemical stabilization step employed in SPSS. Leachability of toxic mercury from SPSS waste forms, given in Table 6.6.3, is well below current TCLP concentration limits for both of the drums treated. In addition, leach results were well below the more stringent Universal Treatment Standard criteria when the formulation was optimized by adding 0.5% additive.

TABLE 6.6.2 Toxicity Characteristic Leaching Procedure (TCLP) Data for Incinerator Fly Ash Treated by SPC Microencapsulation

Formulation	TCLP Conc. (mg/L)	
	Cd	Pb
Untreated fly ash	85	46
55% ash; 45% SPC	27.5	17.6
40% ash; 60% SPC	13.6	12
40% ash; 53% SPC; 7% additive	0.1	1
43% ash; 50% SPC; 7% additive	0.2	1.5
TCLP limit	1.0	5.0
UTS limit	0.2	0.75

TABLE 6.6.3 Toxicity Characteristic Leaching Procedure (TCLP) Data for Mixed Waste Mercury Contaminated Soils Treated by SPSS

Formulation	TCLP Conc. Hg, (μg/L)	Total Hg, (μg/L)
Untreated soil, Drum E	208	4190
60 wt% Drum E soil, 40 wt% SPSS	147	NM[a]
Untreated soil, Drum A	914	5570
60 wt% Drum A soil; 39.5% SPSS; 0.5% additive	0.5	NM[a]
TCLP limit	200	NA[b]
UTS limit	25	NA[b]

[a] NM = not measured.

[b] NA = not applicable.

Summary

SPC is a low-temperature thermoplastic material that can be used for both microencapsulation and macroencapsulation of wastes. SPC can be produced from abundant waste sulfur, and thus cost of the binder is relatively inexpensive. The low-melt viscosity of SPC allows for easy processing using simple heated mixing equipment. High-waste loading and low leachability have been established for a wide range of radioactive, hazardous, and mixed wastes. SPC has been demonstrated at bench, pilot, and production scales. Sulfur Polymer Stabilization/Solidification is a newly developed process specifically designed to treat mercury and mercury-contaminated soil and debris. The mercury is chemically stabilized to lower vapor pressure and leachability, and the chemically stabilized residual is then physically encapsulated, further lowering leachability and dispersion hazards. SPSS is currently under commercial development.

Defining Terms

Microencapsulation: Thorough and homogeneous mixing of small waste particles (i.e., <60 mm) with a liquid binder which then solidifies to form a solid, monolithic final waste form. Individual waste particles are coated and surrounded by the solidified binder to provide mechanical integrity and act as a barrier against leaching of contaminants.

Macroencapsulation: Packaging large pieces of waste (i.e., >60 mm) not suitable for processing by microencapsulation and surrounding the package with a layer of clean binder material. The binder forms a protective layer around the waste that provides structural support, prevents dispersion, and helps reduce migration of contaminants.

Thermoplastic polymers: Polymers with a linear molecular structure that repeatedly melt to a flowable state when heated and then harden to a solid when cooled.

Hydraulic cement: Class of cementitious materials that require addition of water and solidify as a result of various hydration reactions that occur.

Amalgamation: Process by which materials are reacted with various metals such as copper, gold, silver, etc. to form an alloy with different properties. In the case of mercury amalgams, the products have reduced volatility and solubility. Reacting mercury with elemental sulfur also results in products with lowered volatility and solubility and thus is typically referred to as an amalgamation process. Because these reaction products are actually new compounds, however, the reaction is not actually an amalgamation process.

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For Further Information

The references cited in Section 6.6 provide additional useful information on sulfur polymer microencapsulation as well as other alternative S/S technologies.

6.7

In Situ Buried Waste Stabilization Using Jet Grouting

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Introduction

A series of *in situ* technologies have been developed for stabilizing mixed waste buried in landfills and contaminated soil sites. The technologies involve nonreplacement jet grouting to create a solid monolith from buried waste such that subsidence abatement is achieved while eliminating contamination migration. The monolith is created by jet grouting in a relatively tight pattern directly into the soil/waste matrix. The process has also been applied to buried waste as a pretreatment for eventual waste retrieval. The grout agglomerates fine geological media containing contaminants such that contamination control during normally dusty retrieval operations is performed relatively dust-free. Full-scale field demonstrations have been performed in numerous simulated mixed waste sites. In addition, the technology has been applied to a contaminated mixed waste site. This subsection presents details of the testing and an engineering cost estimate for applying the technology.

Most subsurface containment strategies involve creating a vertical barrier wall and horizontal barrier under the waste to create a "bathtub" around the contaminated zone. However, the jet-grouting technology creates a simultaneous horizontal and vertical barrier by forming a solid monolith of the buried waste. As an example of a site for possible application, the Idaho National Engineering and Environmental Laboratory (INEEL) has more than 2 million cubic feet (56,000 cubic meters) of transuranic contaminated mixed waste commingled with 6 to 8 million cubic feet (169,000 to 224,000 cubic meters) of soil in shallow land burial. Improving the confinement for *in situ* disposal is one of the options being considered for this material. Another option is to retrieve the waste and process it for final disposal separately. The technology of jet grouting to create a monolith supports both of these potential decisions. For the disposal option, the resultant monolith is immune from subsidence, which can compromise any capping actions. In addition, the monolith lowers the water permeability through the material, thus reducing contaminant transport. If certain grouting agents are used, some contaminants can also be chemically stabilized such that they are not soluble in water and thus not prone to leaching and migration.

Basically, the only grouting agents considered are those that would tend to produce a solid matrix with a long-lived and natural geological analog. In addition, for the long-term disposal option, the grouting material is designed to be chemically and thermodynamically stable in the present burial environment. For the disposal option, it is assumed that as long as environmental effects do not change the chemical and thermodynamic equilibrium, then the monolith can be considered stable for geological times (thousands to millions of years). This concept is important for transuranic waste with materials that have radiological half-lives on the order of 24,000 years in that modeling for these timeframes appears difficult.

For the retrieval option, the monolith produced by jet grouting has a property such that the contaminants and fine soils are agglomerated into larger, less aerosolizable particles, which improves the chances of controlling the spread of contaminants during retrieval and handling, especially for the plutonium-239/americium-241 particles. The first studies (Loomis and Thompson, 1995) involved only the grout/retrieval concept; however, it was realized that the monolith concept was also applicable to the disposal option, and later studies involved a variety of grouting materials and grouting strategies (Loomis, Thompson, and Heiser, 1995; Loomis, Zdinak, and Bishop, 1997). Most recently, the technology was extended to the creation of monoliths in contaminated soil zones (Loomis et al., 1999). What follows is a detailed description of how the technology is applied, followed by results of various full-scale studies performed on simulated mixed waste sites called pits.

Description of the Technology

The grouting apparatus consists of a CASA GRANDE JET-5 class high-pressure positive displacement pump, low-pressure feed pump with hopper assembly, CASA GRANDE C-6 class track-mounted drilling/grouting rig, and associated high-pressure hoses. A 9-cm diameter drill stem is driven into the soil waste matrix using rotopercussion. Most insertions into buried debris are accomplished within 1 to 2 minutes of drill time. While drilling, a low volume flow of grout is injected at the bit end of the nozzle to reduce friction.

The technology involves driving a drill stem into the waste and injecting grout at 400 bar (6000psi) through the rotating drill stem while withdrawing the drill stem in precise increments. Repeated applications on a nominal 50-cm triangular pitch matrix form a series of interconnected columns that eventually turn the soil/waste seam into a solid monolith. Contamination spread during drilling and grouting is reduced using a specially designed “thrust block” and shroud/catch cup assembly. This equipment contains any grout returns due to the high-pressure grouting process shown in Figure 6.7.1.

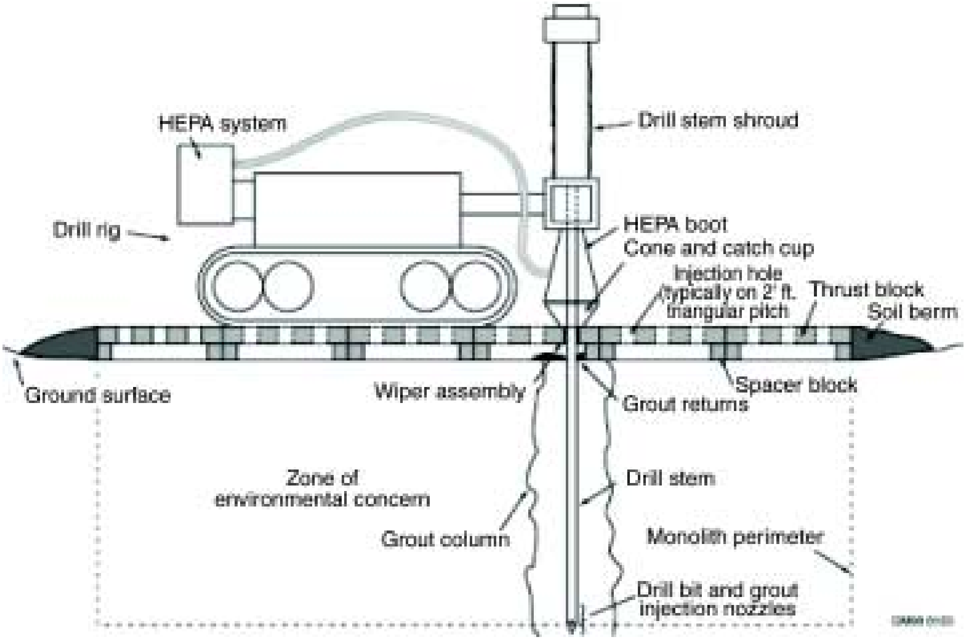

FIGURE 6.7.1 General schematic of grouting operation.

By using a shroud around the drill stem, the rotating contaminated drill stem does not spread contaminants during withdrawal. In addition, at the bottom of the drill rig, a catch cup assembly was developed to prevent grout used for lubrication during insertion from flowing onto the surrounding work area. Besides providing a volume to collect grout returns during grouting, the thrust block offers a clean area for worker protection and adds a degree of shielding in the case of radioactive waste. In addition, the preformed holes through the thrust block have a neoprene wiper material to clean the drill stem of contaminated material during withdrawal. During field studies, a variety of grout materials were injected, including both single and dual materials as well as molten waxes. What follows is a description of test results.

Grouting with Single-Material Injection for *In Situ* Disposal

A series of materials have been jet grouted while successfully minimizing return of material to the surface. The jet-grouting action mixes the grout with the waste and interstitial soils to create monoliths in the buried wastes (Loomis and Thompson, 1995; Loomis, Thompson, and Heiser, 1995; Loomis, Zdinak, and Bishop, 1997), thus providing for final *in situ* disposal. The pits were typically constructed of containerized simulated waste material.

For these studies, the transuranic pits and trenches at the INEEL were used as a model. For these pits, typical waste consists of paper, cloth, wood, metal debris, concrete, asphalt, and various sludges delivered to the INEEL from the Department of Energy's (DOE) Rocky Flats Plant. The wastes were originally containerized in metal drums and plywood boxes. Some of the waste has been buried in shallow pits for up to 40 years, such that the containers have been destroyed. For testing purposes in the simulated pits, cardboard boxes and drums are used to simulate long-term aging of the containers in an actual pit.

For the single-component materials, grout is forced through two nozzles located 180° apart on the bottom of the drill stem. The nozzles are offset 5 cm. At the bottom of the drill stem is usually a conical drive point to facilitate driving the rotating drill stem into the waste. A typical set of parameters for grouting a variety of single-phase materials includes two revolutions of the drill stem per discrete step (a step is nominally 5 cm), with the step time usually between 2 and 6 seconds, depending on grout returns. It was found that 400 bar pressure created the best penetration and filling of voids within the waste.

Single-component materials that have been successfully grouted include simple Type I Portland cement (Loomis and Thompson, 1995; Loomis, Thompson, and Heiser, 1995; Loomis, Zdinak, and Bishop, 1997); Type H Portland cement (Loomis, Zdinak, and Bishop, 1997); TECT, a proprietary iron oxide cementitious grout from Carter Technologies of Houston, Texas (Loomis, Zdinak, and Bishop, 1997); and WAXFIX, a molten hydrocarbon product also from Carter Technologies (Loomis, Zdinak, and Bishop, 1997). Table 6.7.1 shows grout injection data for these single-phase materials. In general, for pits containing debris, the average amount of injected grout per 30 cm (1 ft) that supported minimal grout returns was 42.4 L (11.2 gal). However, when injecting grout directly into soil, the amount of grout is reduced to nominally 26.49 L/30 cm (7 gal/ft), primarily due to fewer voids in the soil than in debris to absorb the injected grout. However, all of these waste materials were successfully grouted to form cohesive *in situ* monoliths.

The molten WAXFIX material was found to be easy to grout, although approximately 40% of what was injected came to the surface as grout returns. This mandates a required large plenum volume under the thrust block or some other berming technique to contain the returning material. While the cementitious pits would cure (hydrate) in the 24- to 36-hr timeframe, the pit injected with WAXFIX took up to 1 week to cool to a solidified mass.

Once cured, the monoliths were both cored and destructively examined. In general, through examination of the cores and the excavated monolith, it was observed that the jet-grouting process created a monolith free of voids. It was also found that the cementitious grout such as Portland cement and TECT could not penetrate the tightly bound paper products but filled all interstitial voids in the waste containers, thus completely encapsulating these difficult-to-penetrate materials. The jet-grouting action created a

TABLE 6.7.1 Single-Component Grout Injection Data[a]

Grout Type/Pit Type	No. Holes	Injected Grout (L/gal)	Total Grout Returns (L/gal)	Injected Grout per 30 cm or 1 ft (L/gal)	Comments	Ref.[a]
Type H cement/debris pit	27	11435/3021	427/113	47/12.5	Grout mixed 1:1 by volume = 18 sacks/m^3	1
TECT™ Carter Technologies/debris pit	11	4417/1167	189/50	66/17.6	—	
Type H cement/debris pit	19	5435/1436	79/21	47/12.5	Grout mixed 1:1 by mass (= 14 sacks/m^3)	1
WAXFIX™ Carter Technologies/debris pit	15	4644/1227	1483/392	51/13.5	Molten wax @ 60°C (140°F)	1
Type I Portland/debris pit	36	18347/4847	760/201	51/13.5	Mixed 1:1 by mass; created a monolith for retrieval studies	2
Type I Portland/debris pit	52	18347/4847	435/115	39/10.3	Grout mixed 1:1 by mass; created a wall barrier for retrieval studies	3
TECH-HG™ Carter Technologies/soil only	52	12472/3295	2759/729	26/7.0	Acid pit stabilization in soil only	4

Note: Nominal injection pressure, 400 bar. See first four references for other injection parameters such as drill rotation speed, withdrawal rate, step size, and time on a step.

[a] 1 = Loomis, Zdinak, and Bishop, 1997; 2 = Loomis and Thompson, 1995; 3 = Loomis, Thompson, and Heiser, 1995; 4 = Loomis, Zdinak, Ewanic, and Jessmore, 1999.

"soilcrete" material from mixing the grout and surrounding soil. The soilcrete appears to be a mixture of neat grout, grout intimately mixed with soil, and small inclusions of ungrouted soil.

For the pit grouted with the hydrocarbon WAXFIX, all waste materials showed a complete penetration by the molten WAXFIX — as if the grout had soaked into the material prior to curing (solidifying). For the WAXFIX case study, the soil inclusions commonly observed in the soilcrete were completely soaked in the molten hydrocarbon-based grout in contrast to the inclusions found in the soilcrete for the cementitious pits. In addition, waste material such as paper and wood likewise showed penetration by the WAXFIX hydrocarbon. Even metallic objects showed a "coating" of hydrocarbon on outer surfaces. This is attributed to the relatively long time for the molten hydrocarbon pit to transfer heat to the surrounding soils. The permeation of the molten material into the waste material and soil continued long after a cementitious grout would cure.

For the INEEL soil conditions used in these studies, the general soil hydraulic conductivity is relatively low (1e-5 to 1e-6 cm/s); therefore, most of the injected molten hydrocarbon remained in the pit and did not tend to leak out to the surrounding soils. In pits where the surrounding soils are more porous, molten material may tend to disperse to the surrounding soils, thus leaving voids in the soil/waste zone. In addition, the destructive examination of the pits filled with cementitious grouts tended to be extremely difficult to remove. The best analogy is destroying a concrete building reinforced with rebar. However, the waste pit injected with molten hydrocarbon is an exception, in that the contents of the pit are removed with simple digging.

Grouting with Dual Materials for *In Situ* Disposal

Three separate two-component materials were jet grouted in simulated waste pits with varying results (Loomis, Thompson, and Heiser, 1995; Loomis, Zdinak, and Bishop, 1997). The materials included (1) an acrylic polymer from Minnesota Mining and Manufacturing Company (3M) known as Hard 5750 and Soft 5751, (2) a DOE-developed natural analog grout called hematite, and (3) a Carter Technologies-supplied water-based two-part epoxy.

TABLE 6.7.2 Two-Component Grout Injection Data

Total Holes	Total Grout Returns (L/gal)	Total A Part (L/gal)	Total B Part (L/gal)
Hard Polymer Pit (3M 5750)			
18	476/126	2157/570	2187/578
Soft Polymer Pit (3M 5751)			
15	113/30	1934/511	1934/511

Grouting parameters: 3 cm/step; 3 s/step
2 revolutions/step for both pits

Note: Acrylic polymer from 3M hard (5750) and soft (5751).

The 3M acrylic polymer was found to be fully field implementable; however, the hematite and epoxy products could not be jet grouted. Grouting parameters for the 3M acrylic polymer are given in Table 6.7.2. The hard material (3M-5750) was developed to form a hard durable monolith suitable for *in situ* disposal. The soft material (3M-5751) was created to allow ease in the retrieval process, with the added benefit that contaminants would be agglomerated to a nonaerosolizable size, which would eliminate contaminant spread. Grouting was performed using the CASA GRANDE system as discussed above. However, a separate positive displacement pump was added for the second component; and the drill stem, nozzle, and swivel (coupling between the delivery hose and rotating drill stem) were modified as shown in Figure 6.7.2.

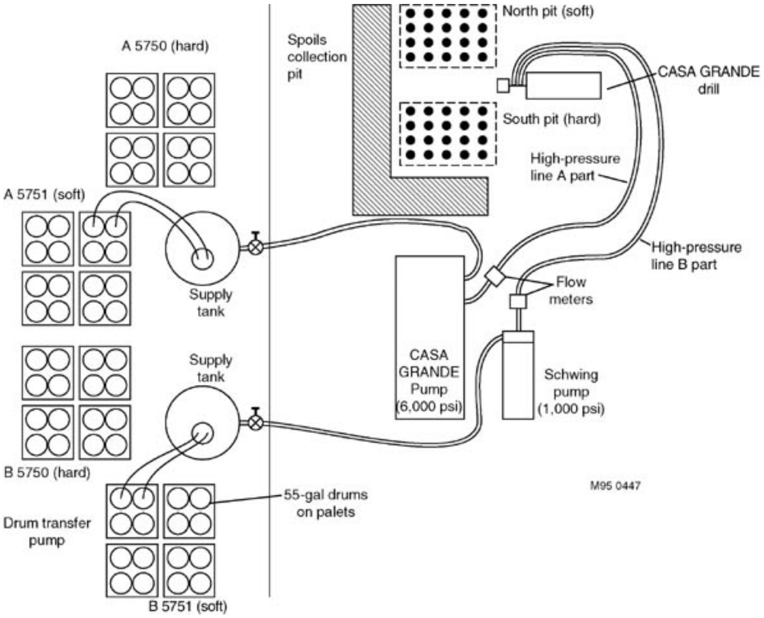

FIGURE 6.7.2 Schematic of two-phase injection process.

The drill stem was a dual concentric annulus arrangement such that the two components were delivered into the waste through a dual concentric nozzle at the bottom of the drill stem (see Figure 6.7.3).

Mixing of the two components occurred in the waste as the two streams of grout encountered the soil and waste.

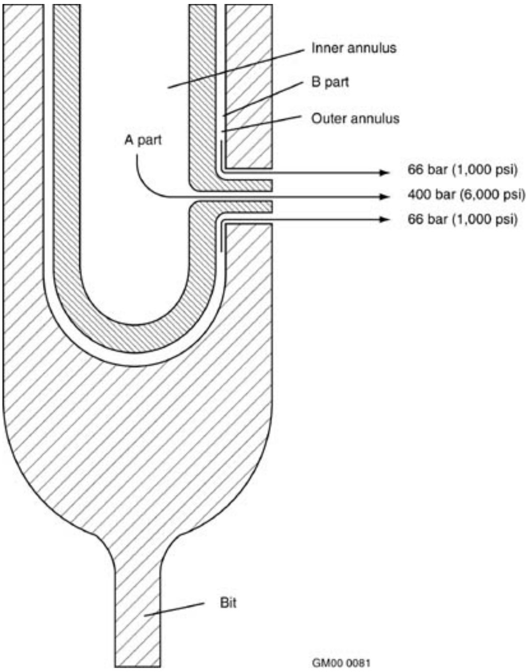

FIGURE 6.7.3 Dual concentric annulus drill stem and nozzle.

The 3M polymers consisted of two co-monomers with select benzoyl peroxide and amine additives to start the polymerization process. When mixed with soil, the polymer formed a high-molecular-weight waste form that had excellent durability results. Laboratory testing on samples of polymer and soil (33% polymer and 67% soil by mass) included hydraulic conductivity measurements; resistance to immersion in water, trichloroethylene, and alkali; and resistance to wet-dry cycling. The laboratory hydraulic conductivity of the soil/polymer mixture was 2.8e-12 cm/s. This is several orders of magnitude lower than the hydraulic conductivity of concretes. Ninety-day immersion testing and the wet-dry cycling testing indicated negligible change in compressive strength. Following grouting and curing, the pit was cored and then excavated. Cores showed that the polymer had indeed cured, suggesting that the process sufficiently mixed the two components downhole. The cores also exhibited little void space, indicating good waste penetration.

When the pit was excavated, the resultant monolith was freestanding. In fact, it could be moved as a complete unit (approximately 1.8 × 1.8 × 1.8 m [6 × 6 × 6 ft]). Examination of the debris within the monolith showed similar results to those found in the pit injected with WAXFIX in that there was considerable soaking of paper, cloth, etc. with the fluid prior to the polymerization process. One drawback to the process is that polymerization is exothermic. Temperatures approaching 140°C were encountered, with visible smoke emanating from the grout holes. In addition, although not hazardous, the acrylic polymers emit an obnoxious odor. To mitigate both the high exotherm and the obnoxious odor would require reformulation of the 3M product.

Grouting of the hematite and the Carter Technologies epoxy as formulated were not field deployable. For the hematite (a two-part mixture of simple slaked lime slurry and an aqueous solution of ferrous sulfate fertilizer), an attempt was made to inject the mixture into a simulated pit. In geological media near the INEEL's Radioactive Waste Management Complex, it was noted that iron oxide-rich deposits tended to be stable in nature and not prone to the natural aging process; therefore, injection of a slurry that cured to a hard form in the interstitial voids within the waste should promote the natural making of hematite out of the soil/waste matrix in geological times. Unfortunately, the slaked lime slurry caused filter caking, which is where particulate in the lime phase tended to separate out in the process of delivery from the high-pressure pump to the drill stem nozzle. This led to system plugging at points where the slurry was at low velocity. Field attempts to alter the viscosity of the lime slurry by adding water failed to eliminate the filter caking, and additional jet grouting using this material was abandoned. The iron sulfate slurry, however, was found to be jet groutable. As a minimum, to make the hematite grout material jet groutable, a new formulation for the lime slurry is required. Another possible solution is to reformulate the mixture and inject it as a single-phase mixture with a retarded cure.

For the Carter Technologies epoxy, there were two components: an A part and a B part. The B part was simply too viscous to be pumpable, and the entire load was abandoned. The lesson learned from this unsuccessful experience is that strict quality control of the various parts of the material must be maintained when converting from laboratory formulations to thousands of liters of material. However, it is possible through more rigorous quality control that the A and B parts could both be jet groutable, because the A part was shown to be pumpable in the CASA GRANDE class system. The epoxy had the desirable property when mixed with soil that there was not an excessive exotherm nor an obnoxious odor.

Using Grouting as a Pretreatment Prior to Retrieval

Grouting followed by retrieval was performed using three different grouting materials including Type I Portland cement, acrylic polymer, and the WAXFIX product discussed previously.

Retrieval of a Monolith Grouted with Portland Cement

The original jet-grouting operations to form monoliths in simulated buried waste were performed as a pretreatment to the retrieval of buried transuranic waste (Loomis and Thompson, 1995). It was thought that by grouting the waste, the fine soil particles would be agglomerated and the ultrafine plutonium particulate would be bound in larger pieces of debris and not easily aerosolized during removal operations. If bound sufficiently, it was speculated that retrieval operations could be easily serviced by manned entry into retrieval arenas using bubble suits. Studies involving retrieval with common mining techniques (Thompson et al., 1993) such as misting with water and surfactants on the waste showed that, at best, during digging and dumping operations the contamination control only achieved a 70% reduction in dust spread (this assumes that the plutonium and dust move together, which has been suggested [Loomis et al., 1994]).

It was desired to achieve 90% or better reduction in dust spread to allow manned entry during retrieval operations to perform routine maintenance on remote retrieval equipment. The first effort involved creating a monolith in a full-scale 3 × 3 × 3-m (10 × 10 × 10-ft) pit filled with typical 208-L (55-gal) drums and 1.2 × 1.2 × 2.4-m (4 × 4 × 8-ft) boxes containing simulated waste such as cloth, paper, metal, sludge, concrete, and asphalt. The simulated waste was randomly dumped into the pit and backfilled with soil in a manner similar to the actual burial practices in past INEEL disposal operations.

During grouting, the pit was jet grouted with Type-I Portland cement mixed 1:1 by mass. Once a hole was grouted, 5-cm (2-in.) diameter thin-walled metal tubes were inserted into each of the just-grouted holes. These tubes were access holes to insert expandable grout to help break up the monolith and generally facilitate retrieval. Once cured (in approximately 2 weeks), the expandable demolition grout (BRISTAR) was inserted. However, very little demolition of the monolith occurred. It was determined that the BRISTAR material correctly operates in a fairly narrow temperature band. Due to the heat of hydration of the monolith when curing, temperatures as high as 60°C (140°F) were measured.

In the 2 weeks of curing, the bottom contact temperature of each of the 5-cm (2-in.) tubes in the monolith was measured daily; and after 2 weeks, the temperatures equilibrated at about 21°C (70°F). From the data, it was assumed that the entire monolith was at this temperature. This assumption proved false, which led to an improper application of the expandable grout. When applying the BRISTAR, the bottom contact temperature of the holes was used; and although the holes showed a relatively even temperature, it was not in hindsight indicative of the temperature throughout the monolith. To correctly apply the BRISTAR would require waiting until internal temperatures in the monolith were uniform (perhaps months).

Approximately 200 g dysprosium oxide tracer material simulating plutonium was placed in each container. The spread of this tracer material was assessed for the grouting and retrieval phases of the innovative grout/retrieval operation. No tracer spread was measured in high-volume air samplers above background for the entire grouting operation. Once the pit was cured and the attempt was made to apply the BRISTAR, the pit was excavated with a standard backhoe using a thumb-lifting attachment.

Retrieving the monolith was extremely difficult and involved dropping the backhoe bucket onto the monolith. The resulting monolith resembled a reinforced concrete building demolition project. Especially difficult were the regions of the grouted 1.2 × 1.2 × 2.4-m (4 × 4 × 8-ft) boxed waste material. An evaluation of filters in air samplers showed that during the retrieval process, as much as a 90% reduction in dust spread over a base case of simply digging in surrounding soils was achieved as long as the clean overburden was removed first. If the overburden was not removed first, the top relatively dry material sloughed off into the pit and caused aerosolization of the soil, which was picked up on the high-volume samplers. The tracer material (dysprosium oxide powder) was measured on the high-volume air sampler filters at 1.35 times background for the retrieval activity.

Retrieval of a Monolith Grouted with Acrylic Polymer

Grouting of a two-part polymer was previously discussed. Two versions of this acrylic polymer were grouted, including a "soft-retrievable" version and a "hard-durable" version for disposal. The soft version of acrylic polymer was jet grouted into a simulated pit, allowed to cure, and then retrieved while taking air samples. For the pit grouted with the acrylic polymer, the simulated waste material had as a tracer dysprosium oxide powder at 200 g per container to act as a stand-in for plutonium in an actual transuranic pit or trench. Using lanthanide oxides as stand-ins for transuranic materials has been discussed (Loomis et al., 1994).

During retrieval, evaluation of the air samplers showed a 91% reduction in dust spread. However, the tracer measurement on the air filters showed a two-order-of-magnitude increase over background levels. This was attributed to the fact that an ungrouted portion of the pit was inadvertently retrieved along with the grouted region, thus invalidating the data. The grouted portion of the pit was very easy to retrieve, and no voids were present in the monolith. The acrylic polymer permeated items such as cloth, wood, and paper prior to curing, such that it would be difficult for contaminants to become aerosolized during retrieval operations.

Retrieval of a Monolith Grouted with WAXFIX

The monolith created by grouting with WAXFIX showed very desirable properties for retrieval of buried waste. The molten material successfully penetrated all positions in the waste pit and agglomerated all fines into essentially nonaerosolizable particles. The retrieval was easily performed with a standard backhoe, and no visible dust was observed. No tracer material was used in the simulated waste containers, nor was dust data taken; however, on a qualitative basis, this material has the potential to greatly reduce dust spread — perhaps as much as 98%.

Along with the large reduction in dust spread is expected to be a corresponding reduction in contaminant spread. Future treatability studies at the INEEL will evaluate the retrieval properties and contamination spread by incorporating tracers in the simulated waste. Dust measurements will also be made.

Stabilization of the Acid Pit Using Jet Grouting

The technology was extended to a mixed waste contaminated soil site called the Acid Pit located at the INEEL. This pit contained both mercury at a maximum concentration of 5200 ppm and minor amounts of fission products and pCi/g quantities of transuranics. Grouting this soil pit was extremely difficult to accomplish without excessive grout returns. While the debris pits could accommodate up to 66 L/30 cm (17.6 gal/ft) without excessive returns, the Acid Pit grouting averaged 26 L/30 cm (7 gal/ft). The operation was successfully completed in that the process was accomplished inside a radiation-controlled zone without the spread of either hazardous or radioactive materials (Loomis et al., 1999). It was estimated that the grouting process filled voids with grout equal to about 25% of the volume of the pit, which is consistent with the void volume in the soil. Based on experience during grouting, it was recommended that, when grouting contaminated soil zones, more grout volume per foot be delivered and more grout collection space under the thrust block be allowed.

Contamination Control During Grouting

For most grouting demonstrations, contamination control was assessed by evaluation of smears and high-volume air sampling for tracer materials. In all cases, tracer materials were placed in each debris container and generally were the "flour" form of a lanthanide oxide (tracers used included oxides of dysprosium, praseodymium, and cerium). Smears were obtained on the top of the thrust block and on the drill stem, and grab samples were collected under the thrust block. For the smears obtained on the drill stem (under the shroud) and for the grab samples, tracer materials were found to be above background values. However, the smears on the thrust block showed no spread of tracer. In previous studies (Loomis and Thompson, 1995; Loomis, Thompson, and Heiser, 1995; Loomis, Zdinak, and Bishop, 1997; Loomis et al., 1999) encompassing grouting with and without use of the thrust block, the high-volume air samplers showed no tracer above background. This was attributed to the simple fact that any contaminant brought to the surface was locked up in a slurry of grout and soil or actually in neat grout returns, and this slurry eliminated airborne release of contaminants.

Jet Grouting Cost Evaluation

Preliminary cost estimates have been prepared for a specific grout application of this technology to buried transuranic waste pits or trenches at the INEEL. The cost estimate includes grouting an acre-sized pit in a 2-year period with a waste seam 2.4 m (8 ft) deep. The cost evaluation assumed that 47 L/30 cm (12.5 gal/ft) of grout is emplaced, resulting in 379 L/2.4 m (100 gal/8 ft) of waste. A 50-cm triangular pitch matrix is assumed, with 18,640 holes per 0.4 ha (1 acre) for the single-phase injected materials and up to 24,000 holes using a 45-cm (18-in.) triangular pitch matrix for the two-phase material.

The following costs are the grouting expenses exclusive of the project management and permitting costs associated with Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) paperwork. The costs do, however, include expenses for secondary waste management. The cost for grouting TECT is $16.8 million per acre ($1049 per cubic meter of waste). The grouting cost for WAXFIX is $16.8 million per acre ($1049 per cubic meter of waste). The grouting cost for Type H cement is $8.5 million ($531 per cubic meter of waste). The grouting cost of applying the two-phase material such as acrylic polymer is $61 million per acre, or $3828 per cubic yard of waste. For grouting followed by retrieval options, the cost for the WAXFIX material for a 1-acre retrieval after the grouting operation is approximately $20 million; for using the acrylic polymer, it is $66 million. It is noted that these cost estimates could easily be doubled when factoring in high-profile CERCLA operations such as project management and related paperwork.

Conclusions

Applying jet grouting to form monoliths in buried mixed waste sites is currently deployable, having been demonstrated for *in situ* disposal and for agglomerating fine contaminants so that contamination control is achieved during retrieval. Resulting monoliths are freestanding and free of voids, and thus not prone to future subsidence. A variety of materials have been shown to be jet groutable while forming adequate monoliths for *in situ* disposal or enhanced retrieval. The monolith formation can be accomplished without spread of contaminants to the worker or surrounding environment. Use of the thrust-block concept shows that any contaminated grout returns remain under the thrust block and do not spread to surrounding regions. Most importantly, costs associated with applying this technology are favorable compared with other options for remediating buried mixed wastes.

The technology is ready for advancement to further hot (mixed waste) applications. Ideal candidate sites include buried transuranic waste pits at the INEEL's Subsurface Disposal Area. This technology can also be applied to contaminated soil regions.

Defining Terms

Columns: Roughly cylindrical masses of grouted soil/waste formed by rotating the drill stem during its withdrawal.

Grout returns: A mixture of grout and soil/waste that emanates up the outside of the drill stem during grouting. This material can also emerge from adjacent holes recently grouted.

Jet grouting: An *in situ* waste stabilization process in which grout exits through small (millimeter-sized) nozzles under high (400 bar [6000 psi]) pressure.

Monolith: A series of interconnected columns joined together to form a single solidified mass.

Nonreplacement jet grouting: Subsurface jet grouting without returns of material to the surface.

Rotopercussion: Simultaneously pounding and rotating the drill stem during drilling.

Soilcrete: A mixture of neat grout, soil fines, and soil inclusions.

Step: The distance the drill stem is raised incrementally during grouting.

Step time: Time spent on a step.

Thrust block: A reinforced concrete block used to support the drill rig and collect grout returns in recesses in the bottom of the block.

Acknowledgments

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Chapter Seven

7

Off-Gas Control for Mixed Waste Thermal Treatment Systems

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Introduction

Mixed waste treatment is often required to meet treatment objectives that include (1) destruction of hazardous organics in the waste, (2) volume reduction, and (3) stabilization of hazardous metals and radionuclides in less leachable and more durable final waste forms such as vitreous, ceramic, or cement-stabilized products. Thermal treatment to destroy and ultimately oxidize hazardous organics and reduce the mass and volume of mixed wastes, together with stabilization of the inorganic components, has been used at many facilities worldwide (IAEA, 1989). For example, in the United States, incineration (or treatment that is demonstrated to be equivalent to incineration) of Department of Energy (DOE) combustible mixed wastes is generally required to meet Resource Conservation and Recovery Act (RCRA) Land Disposal Restriction (LDR) treatment standards and requirements, Site Treatment Plan commitments, and "Path To Closure" commitments. Other waste streams, such as radioactive liquid wastes currently stored in liquid storage tanks at the Idaho National Engineering and Environmental Laboratory (INEEL) Idaho Nuclear Engineering and Technology Center (INTEC), at the Hanford Site in Washington state, and at the Savannah River Site in South Carolina may also require treatment to reduce waste volume, destroy hazardous organic compounds, and separate or stabilize the radionuclides and hazardous metals in a better waste form for final disposal.

Thermally treating mixed wastes can produce off-gas that contains pollutants, including particulate matter (PM), radionuclides, toxic metals, organic products of incomplete combustion (PICs), polychorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (D/Fs), and acid gases. Increasingly strict regulatory standards and increasing public concerns are forcing operators of mixed waste treatment facilities to control air emissions to unprecedented low levels, and to provide more assurance through monitoring that emissions controls are effective. 40 CFR 61, National Emission Standards for Hazardous Air Pollutants (NESHAPS): Subpart EEE, Final Standards for Hazardous Air Pollutants for Hazardous Waste Combustors (EPA, 1999a), requires more stringent emissions control and more extensive monitoring for mixed waste treatment facilities. These standards are also known as the Hazardous Waste Combustor (HWC) Maximum Achievable Control Technology (MACT) standards (or MACT Rule), because the standards are based on MACT. Even if some mixed waste treatment facilities ultimately are not regulated under the MACT Rule, emissions from these facilities will likely be regulated with similar emission limits and monitoring requirements for at least some pollutants in order to obtain public acceptance and to be considered adequately protective of human health and the environment.

Public and regulator concern about hazardous air emissions from mixed waste treatment processes affects the ability to permit and operate mixed waste treatment processes. Public unease or even outcry and lawsuits against either the permitting or continued operation of treatment processes have occurred at several mixed waste treatment facilities, including the Toxic Substances Control Act Incinerator (TSCAI) at the East Tennessee Technology Park in Oak Ridge, Tennessee, and the privatized Advanced Mixed Waste Treatment Facility (AMWTF) at the INEEL.

Public concern about air emissions from mixed waste treatment has resulted in part from:

- An increased awareness of potential risks of exposure to various hazards
- Distrust in the ability of off-gas control systems to control air emissions to within safe limits
- A perception that there is no limit below which emissions of hazardous air pollutants, including radionuclides, is safe

Public concerns are often exacerbated by perceptions of incineration and off-gas control from decades ago when there was less emissions control because hazards were less understood, monitoring and control technologies were less advanced, and regulations were less strict.

Treatment facility operators and workers, and even regulators, often consider potential risks to be minimal and acceptable when all applicable regulatory requirements, including risk assessments, are satisfied. In fact, treating most mixed wastes before final disposal is regulatorily required, and not treating mixed wastes can result in higher potential risks to the public and the environment than risks posed by treating the wastes. However, even with regulatorily acceptable mixed waste treatment facility design, permitting, and operation, public concerns need to be addressed and resolved by cooperation and communication between treatment system operators, regulators, and the public.

Thermal and Non-Thermal Treatment Technologies

In response to public concerns about air emissions from waste incineration, “non-thermal” technologies have been evaluated in recent years as possible alternatives to thermal treatment technologies such as incineration (Biagi et al., 1997; DOE 2000; Schwinkendorf et al., 1997). Non-thermal technologies have been classified for simplicity as those that perform hazardous organic compound destruction at temperatures below 350°C. Based on this definition, many treatment technologies, including plasma arc melters and steam reforming processes, that are alternatives to classic incineration are thermal processes, operating at temperatures that exceed 350°C. Technologies such as electrochemical oxidation, wet oxidation, non-equilibrium plasma oxidation, and photocatalytic oxidation can operate at temperatures below 350°C.

Demonstrations to date have shown that some non-thermal technologies, especially those that use oxidizers other than air, can result in smaller volumes of off-gas emissions. At lower operating temperatures, volatilization of most hazardous metals and radionuclides can also be reduced. Non-thermal technologies therefore can result in lower total off-gas emissions and lower emissions of hazardous metals and radionuclides that would need to be controlled in an off-gas system. However, these technologies also usually have applications in only certain niches of mixed waste treatment (Schwinkendorf et al., 1997). Some non-thermal technologies are only applicable to aqueous wastes, which account for only about 3.2% of the DOE’s mixed wastes that require treatment to destroy hazardous organic compounds.

The most recent DOE evaluation of technologies for mixed waste treatment (DOE 2000) recommended several thermal treatment technologies as most promising. None of the currently available non-thermal treatment technologies alone have the versatility and capability that thermal treatment has to treat a wide variety of heterogeneous organic and organic-contaminated mixed wastes. Most non-thermal treatment technology evaluations have recommended that DOE should (1) not depend solely on non-thermal technologies for treating the majority of the DOE’s mixed wastes; (2) continue to improve both air emissions control for all treatment systems, and also work to improve public acceptance of thermal treatment technologies; and (3) develop, on a limited basis, some non-thermal technologies that may be candidates for treating selected or unique niche waste streams.

Emission controls and risk assessments for non-thermal treatment technologies should be at least as protective of the public and the environment as those for incineration and other thermal treatment technologies. Most non-thermal treatment technologies will ultimately have emission limits and performance requirements that are similar to those for thermal treatment systems.

Because thermal treatment technologies continue to provide the best technical solutions for meeting treatment objectives for the majority of the DOE's mixed wastes, and because off-gas control technologies for thermal treatment systems will generally encompass off-gas control requirements for non-thermal treatment technologies, this section to be consistent focuses on off-gas control technologies and systems for thermal treatment technologies. Off-gas control systems for non-thermal treatment technologies may vary according to the design and operation of the particular treatment technology and the kinds of waste materials that the technology is designed to treat.

State-of-the-Art Air Emissions Control Capabilities

With increasingly strict regulations and higher levels of public concern, the ability to control air emissions from existing and new mixed waste treatment facilities can determine the fate of the facility. Air pollution control system (APCS) configurations that previously provided adequate control might not provide the emissions control necessary to meet stricter current or emerging emission limits without severely restricting potential pollutants or their precursors in the waste feed. Facility operators must design and use high-performance off-gas systems capable of meeting stricter emission limits during normal and non-normal operating conditions to better address public concerns.

Such high-performance off-gas systems are commercially available and may be the key to regulatory and public acceptance for mixed waste treatment facilities. Their use may also allow less rigorous feed characterization and control, resulting in lower overall treatment costs. Rigorous feed characterization and control for most mixed wastes can be very expensive and difficult because of the physical and chemical heterogeneity of the wastes. For example, without efficient mercury emissions control in the off-gas system of a hypothetical mixed waste treatment system, the Hg feed limit (and therefore analytical detection limit in the waste feed) may need to be 1 ppmw or lower to demonstrate regulatory compliance. With 90 to 99% mercury emissions control in the off-gas system, the facility can be permitted to operate with a more achievable and less costly analytical feed/analytical limit for Hg of 10 to 100 ppmw.

Waste treatment facility systems studies have estimated the life-cycle cost of the APCS for a mixed waste treatment system to be 5% or less of the total estimated life-cycle cost (Feizollahi and Quapp, 1996; Biagi et al., 1997). Estimated costs for upfront waste handling and characterization can range up to 30% of the total costs. If, by doubling the off-gas control system costs, the upfront waste handling and characterization costs could be halved (by making feed limits and resulting feed analytical limits less stringent), then the total life-cycle costs may be lowered by 10%. This savings could amount to $100 million for a treatment facility that has a total life-cycle cost of $1 billion.

Contents of this Section

Many books, reports, and other references have been published over the past decade on off-gas control for hazardous and mixed waste treatment. These are listed in the "References" and "For Further Information" subsections at the end of this section. The intent of this section on off-gas control is not to repeat information provided in these other references, but to update, focus, and apply this information and provide new information to aid in state-of-the-art off-gas control system design and operation for mixed waste treatment.

Following this introduction, the main components of this section include:

- *Design and performance objectives for off-gas control systems*: identifies regulatory, operator, and stakeholder objectives that off-gas systems for mixed waste treatment should satisfy.
- *Input off-gas flowrates and compositions*: provides estimated ranges for off-gas flowrates and compositions that an off-gas system for mixed waste treatment may be required to handle.

- *Examples of existing off-gas systems for mixed waste treatment*: summarizes the off-gas systems for several different existing or prior mixed waste treatment facilities, and provides a perspective and comparison for existing off-gas systems for mixed waste treatment.
- *APCS designs for reliable and efficient off-gas control*: describes designs that meet current objectives, because many existing and prior off-gas systems may not meet all new performance objectives, especially for emissions control based on new regulations.
- *Mercury emissions control technologies for mixed waste treatment*: Under the MACT Rule, mixed waste treatment may require more extensive mercury control than has been required in the past, or will be required at most hazardous waste combustion facilities. For this reason, mercury control for mixed waste thermal treatment has been specifically evaluated. Extra attention to mercury control is given in this section compared to control of other pollutants because of this unique need for mixed waste treatment.
- *Off-gas system design, mass and energy balances, and capital cost estimates*: summarizes some results of process simulations, including design and performance information, mass and energy balances, and installed capital cost estimates. Operating costs and life-cycle costs are not included.

Design and Performance Objectives for Off-Gas Control Systems

Off-gas systems for mixed waste treatment must be designed to reliably control off-gas emissions within regulatory requirements, protect workers from unnecessary exposure to radiological and other safety hazards, and provide an ample margin of safety to ensure that emissions are adequately controlled during both normal and upset operating conditions. The most important and fundamental design objectives are listed in Table 7.1.

Regulatory Requirements

Above all, the off-gas system must control off-gas emissions within regulatory limits. Concurrent with increasing information on the hazards to the environment and human health presented by air pollutant emissions, emission regulations for mixed waste thermal treatment are becoming more stringent. Regulatory compliance for mixed waste treatment is discussed in Chapter 1. Regulations that may apply either directly or indirectly to off-gas control for mixed waste treatment in the United States include:

1. 40 CFR 61, National Emission Standards for Hazardous Air Pollutants (NESHAPS): Subpart EEE, Final Standards for Hazardous Air Pollutants for Hazardous Waste Combustors (EPA, 1999a), also known as the Hazardous Waste Combustor (HWC) Maximum Achievable Control Technology (MACT) standards or MACT Rule for hazardous waste combustion. For simplicity, the terms "MACT standards" and "MACT Rule" are used in this section, although there are also other MACT regulations and standards for other industries and sources.
2. National Emission Standards for Hazardous Air Pollutants (40 CFR 61). Some large, mixed waste streams contain sludges produced from industrial wastewater treatment, so 40 CFR 61.52 for mercury emissions may apply. Because radionuclides are present in mixed waste, 40 CFR 61.92 would apply for DOE waste treatment facilities.
3. Standards for hazardous waste incineration [40 CFR 264, Subpart O (264.340–351)].
4. Standards for Boilers and Industrial Furnaces [BIF rules, 40 CFR 266 Subpart H (266.100–112)].
5. Standards from the Toxic Substances Control Act (TSCA, 40 CFR 761). Section 761 regulates the incineration of wastes that contain PCBs in concentrations greater than or equal to 50 ppmw.
6. Human Health Risk Assessment Protocol (HHRAP) guidance (EPA, 1998a) and ecological risk assessment protocols requirements (EPA, 1999b) for site-specific risk assessments.

TABLE 7.1 Design/Performance Objectives for Mixed Waste Treatment Off-Gas Control Systems

Design/Performance Objective	Comments
Control emissions of gaseous organics, radionuclides, toxic metals, particulate, and acid gases to meet expected regulatory limits	Emission limits can be derived from applicable final or proposed regulations such as the MACT Rule, permit requirements, new source performance standards, state implementation plans, requirements for prevention of significant environmental deterioration, and site-specific risk assessments. An administrative limit, generally 10 to 50% of the regulatory limit, should be used to provide an adequate margin below the regulatory limit to avoid frequent noncompliant conditions. Feasibility studies reported in Feizollahi and Quapp (1996) assumed an administrative limit of 10% of the assumed regulatory limits, and Soelberg et al. (1999) assumed a target of 50% of the regulatory limits. Selection of the appropriate margin within applicable standards must consider feed and operational variabilities of the treatment facility.
Provide ongoing, continuous emissions monitoring	Continuous emissions monitoring must meet regulatory requirements for monitoring specified pollutants and for instrument performance. Additional continuous monitoring may be necessary in some cases to provide added public and regulator confidence in the ability of the treatment and off-gas system to protect public health and the environment.
Ensure that a nuclear criticality condition will be avoided	Design and operation must avoid holdup of fissile radionuclides in amounts, concentrations, and geometries that could cause criticality, especially in wet scrubbing systems where the presence of water can increase the criticality potential.
Accept any likely off-gas flowrate and composition variations from the primary treatment process without upsets or degradation of performance beyond acceptable limits	This allows the treatment system to process widely varying feed materials with less feed characterization and sorting, turndown (feedrate reduction below the design level), or feed additives.
Operate reliably with minimal downtime and upsets	The annual availability of a mixed waste treatment system for actual operation has been estimated at only 50% or less (4400 hr/yr or less) in several studies (Eddy et al., 1995; Feizollahi and Quapp, 1996). Operating costs are the largest single component of a mixed waste treatment facility's life cycle costs. Operating costs per unit of waste treated and time required to treat waste increase substantially when availability is decreased.
Comply with As Low As Reasonably Achievable (ALARA) objectives by minimizing the exposure of workers, the public, and the environment to radiological hazards	An ideal goal would be to operate remotely during normal, routine conditions, although some direct operator-performed maintenance should be expected during shutdowns or unusual conditions.
Minimize amounts of secondary streams and maximize ease of secondary stream final treatment and disposal	Handling and disposal of off-gas system secondary product streams (such as used filter media, scrubber solution, and bulk fly ash) can involve significant ALARA and waste form issues because of the potential for concentrated toxic metals and radioactive contamination in or on small particles, regardless of the treatment or off-gas system design. Regulatory requirements prohibit the generation of any waste, including off-gas system secondary wastes, for which there are no available final treatment and disposal options.
Minimize total treatment facility life-cycle cost	While some higher performance off-gas systems that include more comprehensive monitoring may be more costly to purchase or operate, they may enable lower overall facility life-cycle costs if less downtime is required or if less upfront feed characterization, sorting, or blending is required. Costs for decomissioning and disposal following the working life of a facility should be estimated and included in total life-cycle costs.
Minimize technology implementation risk	This is important for any components or technologies that are not well demonstrated, proven, or accepted for the application in which they are specified.
Simplify equipment operation and maintenance by design	Achieve reliable operation with minimal downtime and minimal total facility life-cycle cost.
Interface adequately with the treatment process and secondary waste form handling process	This is an important systems engineering design objective to ensure that the entire treatment facility operates as desired.

7. DOE Orders 435.1, Radioactive Waste Management; 5400.1, General Environmental Protection Program; and 5400.5, Radiation Protection of the Public and the Environment. These DOE Orders regulate air emissions of radionuclides and hazardous materials from DOE facilities by specifying compliance to the EPA's 40 CFR Part 61 National Emission Standards for Hazardous Air Pollutants (NESHAPs) and 40 CFR Part 264 RCRA regulations.
8. State regulations. In the United States, state regulations may also apply to off-gas emissions from mixed waste thermal treatment facilities. Facilities must comply with the stricter of the state and federal regulations. EER 1997 lists many of the different state regulations that may apply (EER, 1997).

Examples of emission limits that may apply to off-gas emissions from mixed waste thermal treatment facilities are shown in Table 7.2. These emission limits are based largely on the MACT Rule for hazardous waste combustors. Not all of these limits necessarily apply to treatment facilities not directly regulated under the MACT Rule, and in some cases other limits may also apply in addition to MACT standards. Even if certain regulatory limits and standards do not directly apply to a given treatment facility, the RCRA permitting authority may apply them via the "Omnibus" provision in Section 3005(c) of RCRA, if it is deemed appropriate and necessary to adequately protect human health and the environment. Similarly, site-specific limits derived from risk assessment evaluations for projected and measured emissions can be applied by RCRA permitting.

MACT Rule Applicability

The MACT Rule may not apply directly to facilities that use processes that do not include combustion or pyrolysis of organic waste materials, or combustion of fossil auxiliary fuels. Some treatment processes thermally treat inorganic wastes using indirect or electric heating. In these cases, the off-gas from such processes consist largely of process air (on a dry basis), with negligible or unmeasureable products of organic combustion. The MACT Rule emission standards are based on concentrations of a given pollutant per volume of off-gas, corrected to 7% O_2, in combustion off-gas. The correction is used to eliminate any variations in concentrations for different facilities due to varying degrees of dilution of the off-gas with added combustion or other process air, placing concentration measurements on the same basis for comparison to the regulatory standards.

The mathematical correction to 7% O_2 is based on the O_2 content of the air used for combustion, atomization, fluidization, etc, and the O_2 content of the combustion off-gas*:

$$\text{Correction factor} = 14/(E - Y)$$

Where E = Average O_2 content of all input air, inerting gas, air inleakage, etc.
Y = Measured O_2 concentration in the off-gas on a dry basis

When only air is used in the process, without any input of other gases such as inerting N_2 or pure O_2, then E = 21%, which is the level of O_2 in ambient air rounded to two significant figures. Then the correction factor equation is simplified to**:

$$\text{Correction factor} = 14/(21 - Y)$$

When there is little or no combustion of organic matter, either in the waste or in auxiliary fuels, then the off-gas on a dry basis is primarily air or inert gas such as nitrogen, with unmeasureable amounts of combustion or pyrolysis products. The O_2 content of the off-gas on a dry basis approaches either E (in the general case when gases other than air are used in the process) or 21% (when only air is used in the process), and the correction factor approaches infinity:

$$\text{Correction factor} = 14/(21 - 21) = 14/0 = \text{Infinity}$$

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*_Federal Register,_ 55(82), 17918, April 27, 1990.

**40 CFR 264.343.

TABLE 7.2 Air Emission Standards That May Apply to Mixed Waste Thermal Treatment Facilities

	MACT Emission Standard[b]		Applicable Other Standard	
Pollutant or Surrogate[a]	Existing Sources	New Sources	Value	Ref.
D/F	0.20 ng TEQ[c]/dscm; or 0.40 ng/dscm and temperature at inlet to the PM control device ð 400°F	0.20 ng TEQ/dscm	—	—
Hg	130 µg/dscm	45 µg/dscm	—	—
PM	34 mg/dscm (0.015 g/dscf)		—	—
SVM (Cd, Pb)[d]	240 µg/dscm	24 µg/dscm	—	—
LVM (As, Be, Cr)[d]	97 µg/dscm		—	—
HCl/Cl_2[e]	77 ppmv	21 ppmv	—	—
HC[f,g]	10 ppmv (or 100 ppmv CO)		—	—
DRE[h]	99.99% for each specific POHC[i] except 99.9999% for specific dioxin-listed wastes		—	—
Be	See LVM standard		10 g/24 hr	40 CFR 61.32
Total radionuclides	—	—	0.1-10 mRem/yr[j]	40 CFR 61.92
PCB DRE[k]	—	—	99.9999%	40 CFR 761.70
Other metals[l]	—	—	Risk-based	EPA (1998a; 1998b)
PICs[m]	—	—	Risk-based	EPA (1998a; 1998b)

[a] Some parameters are used as surrogates to indicate compliance with hazardous air pollutants. PM is used as a surrogate for non-enumerated metals Sb, Co, Mn, Ni, and Se. CO and HC are used as surrogates for organic hazardous air pollutants. DRE is used to indicate the control of organic hazardous air pollutants other than D/Fs, which are controlled by a specific standard.

[b] All emission levels are corrected to 7% O_2; and EPA (1999a).

[c] Toxicity equivalency quotient, the international method of relating the toxicity of different D/F congeners to the toxicity of 2,3,7,8-tetrachloro dibenzo-*p*-dioxin (2,3,7,8-TCDD).

[d] Total metals regardless of speciation.

[e] Total HCl and Cl_2 in HCl equivalents (Cl_2 in ppm is multiplied times 2 to get HCl equivalents).

[f] Hourly rolling average. HC is reported as propane.

[g] Facilities that choose to comply with the CO standard by continuously monitoring CO rather than HC emissions must also demonstrate compliance with the HC standard of 10 ppmv during the comprehensive performance test.

[h] DRE = destruction and removal effiency.

[i] POHC = principal organic hazardous constituent.

[j] Total radioactive emissions are limited to an effective dose equivalent received by any member of the public to exceed 10 mRem/yr. Pollutant dispersion after the emissions leave the stack, and prior to potential human exposure, is considered in addition to the actual amounts and kinds of radionuclides emitted. Several mixed waste facilities are limited to an effective dose equivalent as low as 0.1 mRem/yr to maintain the effective dose equivalent for the entire site, which may contain many radioactive facilities, below 10 mRem/hr.

[k] PCBs = polychlorinated biphenyls.

[l] Other metals specified for inclusion in risk assessments in addition to those metals listed in the MACT standards [Hg, SVM (Cd, Pb) and LVM (As, Be, Cr)] are Ag, Al, Ba, Co, Cu, Mn, Ni, Sb, Se, Tl, V, and Zn.

[m] PICs = products of incomplete combustion, referring to speciated organic hazardous air pollutants.

This correction cannot apply when there is little or no combustion of organic matter either in the waste or in auxiliary fuels, because the off-gas on a dry basis is primarily air or inert gas such as nitrogen, and the correction factor approaches infinity. For example, electrically or indirectly heated calcination of acidic, primarily inorganic liquid wastes stored at the INEEL INTEC and at the Hanford Site would be in this category if they did not use fossil-fired auxiliary fuels for heat or fossil-fired secondary combustion. Electric-arc melters and indirectly heated thermal desorbers that treat inorganic wastes would also be in this category. Emission limits for such processes would need to be based on other standards, which would need to be protective of human health and the environment. Such limits may ultimately be as restrictive or more restrictive than the MACT standards.

Input Off-Gas Flowrates and Compositions

The design and performance of any APCS depend on the flowrate and properties of the off-gas to be treated, which in turn depend on the properties and processing rate of the input waste as well as the design and operation of the primary treatment system. Mixed wastes that are thermally treated include primarily combustible solids and liquids, but other significant waste streams such as aqueous liquids and largely noncombustible solids are also thermally treated. These different combustible, noncombustible, solid, and liquid waste streams can have very different chemical compositions and thus can result in widely varying off-gas flowrates and compositions when thermally treated. Knowledge of — or at least an estimate of — waste feed properties and feedrates is necessary for designing and operating an APCS for a thermal treatment system.

The APCS must also be tailored for compatibility with the primary treatment system. Several different processes have been or can be used to treat mixed wastes to (1) destroy hazardous organic contaminants, (2) reduce the waste volume, or (3) transform the waste into more easily disposable or recyclable waste forms. Example waste treatment processes include incineration, melting/vitrification, calcination, lower-temperature oxidation, gasification, and thermal desorption. Each of these treatment processes encompass various unique technologies such as slagging or non-slagging rotary kiln incineration, fixed-hearth controlled air incineration, plasma torch arc melting, graphite electrode arc melting, joule-heated (resistance) vitrification, non-thermal plasma oxidation, catalytic oxidation, and supercritical oxidation. In addition to waste feedrates and properties, treatment process conditions including operating temperatures, reactor configurations, sources of heat input, and added reactants will also affect the amounts and properties of off-gas.

Off-gas flowrates and compositions entering an APCS are rarely measured. Such measurements are difficult because of typically high temperatures and high particulate loadings. APCS input gas measurements are even more challenging in mixed waste treatment because of potential worker exposures to radioactive fields or radioactive contamination that is normally present upstream of off-gas filtration. Typically, there are no regulatory requirements for APCS input measurements. Values for most APCS input gas properties are usually estimated or calculated using mass balances, input feed and fuel compositions, flowrates, and APCS outlet off-gas measurements.

Possible ranges of treatment system off-gas flowrates and other relevant properties upstream of the off-gas system ("uncontrolled off-gas conditions") are shown in Table 7.3. These are the order-of-magnituded ranges of off-gas compositions, flowrates, and conditions that offags systems for mixed waste treatment need to be designed to accept and treat prior to atmospheric discharge. These ranges were calculated using measured or estimated air emission rates, adjusted for control performance of the APCS; or calculated using mass balances, waste input feedrates and properties, and treatment system operating conditions.

Table 7.3 also shows estimated ranges of some metals and PM emissions that can enter the off-gas system in off-gas from mixed waste treatment systems. One of the most important off-gas system functions is to control PM within applicable emission limits. Because many hazardous and toxic metals, radionuclides, and trace organics are associated with PM, emission limits for these pollutants, rather than PM emission limits, usually determine the required PM removal performance for the off-gas system. For this reason, most off-gas systems for mixed waste treatment facilities include high-efficiency particulate-arresting (HEPA) filters for radionuclide control, although such efficient control is usually not necessary to meet just PM emission limits.

Examples of Existing Off-Gas Systems for Mixed Waste Treatment

Many variations of off-gas control systems have been designed, installed, and used worldwide in radioactive waste treatment processes. The IAEA (1989) summarizes radioactive and mixed waste treatment and off-gas systems used, or at least demonstrated, up until the late 1980s in 15 different countries. Understandably, some of these off-gas systems vary widely in design and performance according to

TABLE 7.3 Example Off-Gas Conditions at the Inlet of the APCS for Mixed Waste Thermal Treatment Systems

Parameter	Typical Range	Comments
Off-gas temperature (°F)	1,700–2,200	Typical SCC outlet temperature range.
Off-gas flowrate (scfm)	1,000-10,000	Most mixed waste treatment systems are fairly small, with design waste feed input rates ranging from 100–3,000 lb/hr.
Off-gas composition (by volume, wet basis)[a]		
O_2 (%)	3–21	O_2 levels above about 15% can occur in systems that do not include auxiliary fossil fuel combustion, or in systems that use O_2-enriched air for combustion.
CO_2 (%)	5–30	CO_2 levels above ~15% are normally only possible with O_2-enriched combustion.
CO (ppm)	10–100	
NO_x (ppm)	100–4,000[b]	NO_x is mostly NO, except in off-gas from systems that treat aqueous nitric acid wastes; then, NO_x can be much higher, and mostly NO_2.
Total HCl & Cl_2 (ppm)	500–25,000[b]	Depends on the Cl feedrate and the amounts of off-gas generated from combustion of organic waste material or auxiliary fuels. Limited Cl_2 measurements suggest that Cl_2 levels range around 3% of HCl levels (Soelberg et al., 1999).
H_2O (%)	10–50	The range depends on waste and fuel types, moisture contents, and O_2-enrichment.
N_2 (%)	Balance	Air-fired systems can have N_2 levels ranging between 50 and 80%; O_2-fired systems can have lower N_2 levels ranging from 1 to 10%; O_2-enriched combustion systems can have N_2 levels between 10 and 50%.
Particulate and metals concentrations at 7% excess O_2 (dry basis)		
PM (mg/dscm)	200–50,000	Estimated from feed material partitioning to the off-gas and to bottom ash products.
SVM [total Cd and Pb], (µg/dscm)	200–1,300,000[b]	Depends on Cd and Pb feedrate and treatment system conditions; the maximum value is based on maximum estimated SVM levels in mixed waste, assuming 100% of the SVM evolves to the off-gas system.
LVM [total As, Be, and Cr], (µg/dscm)	<70,000[b]	Depends on the As, Be, and Cr feedrates and treatment system conditions; up to 10% of feed As, Be, and Cr is assumed to be carried over to the off-gas system.
Hg (µg/dscm)	10–500,000[b]	Depends on the Hg feedrate, assuming that all Hg partitions to the off-gas system.
Organic concentrations at 7% excess O_2 (dry basis)		
Total hydrocarbons (HC) (ppm)	<10	Most off-gas systems are not required to provide trace organics control in addition to organics control provided by the treatment and secondary combustion processes. Measured trace organic concentrations at the outlet of the off-gas system are often assumed to be representative of trace organic concentrations at the inlet of the off-gas system, except for any changes in diluting air or moisture content. If carbon adsorption is included in the off-gas system, then the carbon may adsorb some of the trace organics, making this assumption invalid.

[a] These values are for typical oxidizing systems. Those that produce a reduced gas (synthesis gas) will have a different chemical composition and flowrate.

[b] Such high estimated levels typically result from using relatively conservative estimates, because of limited measurements of off-gas conditions at the inlet to an APCS. Some of the high levels can result from the use of specific waste treatment processes. For example, high-temperature melters that may be desired for producing a good waste form may result in a carry-over of certain hazardous metals that is higher than for typical hazardous waste, municipal waste, or hospital waste incinerators. Such atypically high assumed or known emission levels can drive certain features of APCSs for mixed waste thermal treatment.

From Soelberg et al., 1998, 1999.

different performance requirements determined by wastes being processed, different local and national regulations, funding, facility size, and engineering approaches to off-gas control. In recent years, off-gas control systems even at a single location have evolved through retrofits or new installations as waste material properties have changed, regulations have become universally more strict, and new or better technologies and systems have become available.

Off-Gas Control for the Forschungzentrum Karlsruhe Alpha Waste Incinerator

The evolution of the state-of-the-art for off-gas control for mixed waste treatment is exemplified by the operating experience of the Forschungzentrum Karlsruhe (Karlsruhe Research Center) located in Germany (Dirks et al., 1992; Dirks and Muller, 1995; Dirks, 1998; Steinhaus and Dirks, 1994). For several decades since 1972, incineration of combustible radioactive wastes has been conducted at this facility. Three different incinerators have been used during this time to treat solid beta-contaminated waste, solid alpha-contaminated waste, and liquid waste from many different sources, including nuclear research laboratories, nuclear reactors, and a reprocessing plant at the Forschungzentrum Karlsruhe, and from several universities, commercial nuclear stations, and fuel element fabrication plants.

These incineration facilities and associated off-gas systems have changed considerably as waste types and regulatory requirements have changed. These changes have included retrofits of two-stage wet scrubbers (1989–1990), installation of D/F control (1991), and closures of the beta- and liquid waste incinerators in favor of extensive upgrades of the alpha waste incinerator done in 1996/1997 to comply with the 17th Federal Emission Control Regulations (BImSchV) of November 1990. The new regulations required a significant reduction in D/F emissions to 0.1 ng TEQ/dcsm at 11% O_2 (0.14 ng TEQ/dcsm at 7% O_2) and zero liquid secondary wastes by December 1996.

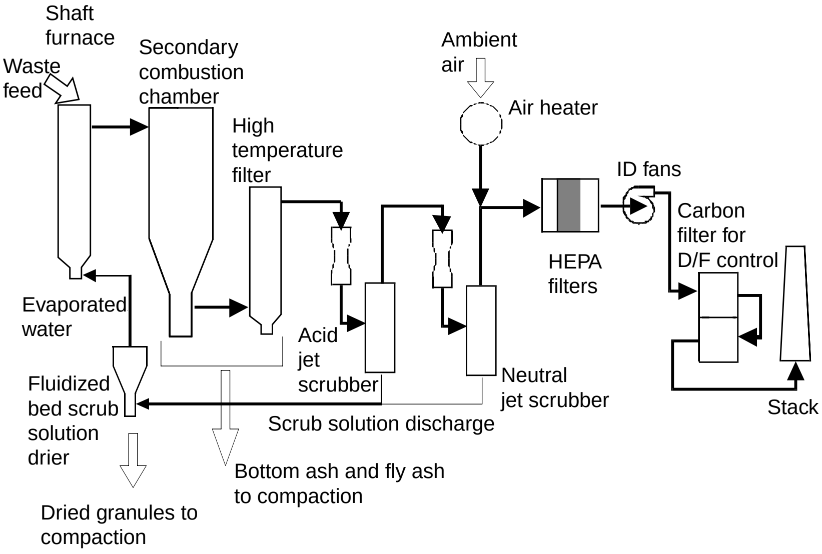

FIGURE 7.1 Process schematic of the alpha waste incinerator at Forschungzentrum Karlsruhe. (From Dirks, F., 1998, Radioactive waste incineration at the Forschungzentrum Karlsruhe, 1998 *Proc. Int. Conf. Incin. and Thermal Treatment Technol.*, Salt Lake City, UT, May. With permission.).

A schematic of the upgraded incinerator and off-gas system is shown in Figure 7.1. Retrofits to comply with the new regulations and to increase capacity included a larger afterburner, selective noncatalytic NO_x reduction (SNCR), activated charcoal and lignite coke D/F adsorber, off-gas temperature fast quench within the first scrubber step, fluidized-bed drying of the scrubber blowdown, and partial flue gas recycle.

Off-Gas Control for U.S. DOE Mixed Waste Incinerators

As of early 2000, the U.S. Department of Energy operated three low-level mixed waste incinerators. The DOE has been evaluating whether to continue operating any of these incinerators. Considerations in this evaluation have included (1) amounts, locations, and types of mixed wastes that could or should be incinerated; (2) past and expected operating costs; (3) costs and schedules for any facility modifications needed to needed to comply with the MACT Rule; and (4) potential alternative treatment and disposal options for wastes that would be "orphaned" should any of these incinerators be closed. These incinerators include the:

- Consolidated Incineration Facility (CIF) at the Savannah River Site (SRS) in South Carolina
- Toxic Substances Control Act Incinerator (TSCAI) at the East Tennessee Technology Park in Oak Ridge, Tennessee
- Waste Experimental Reduction Facility (WERF) incinerator at the Idaho National Engineering and Environmental Laboratory (INEEL) near Idaho Falls, Idaho

In 2000, the DOE determined to close the CIF and WERF incinerators, assuming that there are other adequate options for treating waste streams that were destined for treatment in these incinerators.

Major features for each of these DOE incinerators as of early 2000 are summarized in Table 7.4. All three incinerators have treated hazardous and mixed low-level waste; and the CIF and WERF incinerators have also treated low-level waste. The TSCAI was permitted to treat TSCA-regulated polychlorinated biphenyl (PCB) mixed wastes. The WERF incinerator could accept PCB-contaminated wastes that are not TSCA-regulated and contain less than 5 ppm PCBs. CIF and TSCAI are rotary kiln incinerators, while WERF is a fixed-hearth, controlled air incinerator.

The off-gas system for each of these three incinerators is uniquely designed to meet the requirements for that system. All three off-gas systems achieve highly efficient particulate matter and metals removal, typically below applicable PM and metals emission limits, because of the need to efficiently control radionuclide emissions. Each system employs multiple stages of PM removal. Off-gas systems for CIF and WERF use HEPA filters for final filtration, while the TSCAI off-gas system uses five stages of increasingly efficient PM removal.

As of 2000, these facilities were all permitted and were operated within permit requirements. An evaluation of how these facilities could comply with the recently promulgated MACT standards was reported in 1999 (Soelberg et al., 1999). The ability of these facilities to comply with the MACT standards finalized in September 1999 is summarized as follows:

1. None of these facilities presently has PM or HC CEMs. When the MACT Rule establishes the schedule for requiring PM CEMs, then PM CEMs would need to be added. If any of the facilities determine to use HC compliance monitoring instead of the CO compliance monitoring option, then those facilities will also need to add HC CEMs. While HC measurements have not yet been performed at any of the facilities, prior trial burn results for all three facilities suggest that the MACT HC standard can be met. Optional CEMs for Hg, metals, or total Cl would also need to be installed should the DOE opt to use them instead of, or in addition to, feed control.
2. The CIF can meet all MACT emission standards, although Hg feed control could be required to comply with the MACT Hg standard, assuming minimal or no removal efficiency for Hg in the off-gas system. If feed control for Hg is too restrictive, then the off-gas system will need to be modified to provide some level of Hg control that would allow a less restrictive Hg feed limit. While D/F emission measurements have in the past exceeded levels of the new standard, more recent D/F measurements have been within the standard. Other MACT emission standards can be readily met based on prior operating and trial burn experience.

TABLE 7.4 Overview of DOE Incinerators as of Year 2000[a-h]

	Consolidated Incineration Facility Incinerator (CIF), SRS	Toxic Substance Control Act (TSCA) Incinerator (TSCAI), East Tennessee Technical Park	Waste Experimental Reduction Facility Incinerator (WERF), INEEL
Treatment system	Rotary kiln with secondary combustion chamber (SCC)	Rotary kiln with SCC	Fixed hearth, controlled air primary combustion chamber (PCC) with SCC
Designed & permitted feed materials	Incinerable solid and liquid hazardous, LLW, and mixed waste from SRS. Solid waste is box-fed. Liquids are fired through a burner in the kiln or through a burner in the SCC.	Incinerable solid, sludge, and liquid hazardous, LLW, mixed, and PCB wastes. Solid and sludge wastes are box-fed to the kiln, and liquid wastes are injected through burners. Bulk-feeding of solids is not presently done.	Box-fed combustible LLW and mixed incinerable solid, sludge, and liquid waste from the INEEL and other DOE sites. Liquids are packaged in containers or with sorbent and placed in boxes. Liquid waste feed system was designed and partially installed in early 1990s, but is not operational.
Capacity (MMBtu/hr)	39.26 (permitted total)	30 max	5 (solid waste), 6.5 (total)
Waste feedrate (lb/hr)	2426 total for all waste	2500 max	400 (permit limit)
Treatment temperatures	PCC: >1500°F (>820°C) SCC: >1800°F (>980°C)	PCC: >1800°F (>1000°C) SCC: >2200°F (1200°C)	PCC: 1600–2200°F (870–1200°C) SCC: 1700–2200°F (930–1200°C)
SCC design residence time (s)	~2	>2 s-design ~4 s-actual	2
Off-gas flowrates (scfm)	Stack: ~16,800 (higher due to added water vapor used in evaporative cooling and scrub solution atomizing steam)	SCC outlet: ~10,000 Stack: ~20,000 (higher due to added water vapor used in evaporative cooling)	SCC outlet: ~1800 Stack: ~6600 (higher due to added cooling air)
APCS			
Off-gas cooling	Evaporative quench to a saturation temperature of ~180°F (stage 1 PM, radionuclide, and acid gas removal)	Water spray and scrub solution evaporation quench to a saturation temperature of ~180°F (stage 1 PM, radionuclide, and acid gas removal)	Air dilution to ~1250°F; gas/air heat exchanger to <625°F; air dilution to <395°F
PM and radionuclide control	Steam atomized scrubber removes PM and acid gases; cyclone separator provides liquid-gas separation of scrubbing mixture; mist eliminator removes entrained water droplets (Stages 2 and 3 PM, radionuclide, and acid gas removal)	Venturi scrubber removes PM 1 µm or greater and a portion of the HCl, followed by a demister to remove entrained water droplets (Stage 2 PM, radionuclide, and acid gas removal)	Baghouse with 27,000 dscm/hr (16,000 scfm) capacity; removes 99% of the dust; preceded by spark arrestors (Stage 1 PM and radionuclide removal)
Acid gas control		Cross-flow packed bed scrubber removes HCl, HF, and SO_2 (Stage 3 PM, radionuclide, and acid gas removal)	None by design, although the baghouse achieves some inherent dry scrubbing (19–34%). A spray dryer was designed and partially installed in the early 1990s, but not commissioned.
NO_x control	None	None	None
Final filtration	Prefilters and HEPAs (Stages 4 and 5 PM and radionuclide removal)	Two-stage ionizing wet scrubbers remove particulate less than 1 µm (Stages 4 and 5 PM, radionuclide, and acid gas removal)	Single-stage prefilters and single-stage HEPAs (Stages 2 and 3 PM, and radionuclide removal)

TABLE 7.4 (Continued) Overview of DOE Incinerators as of Year 2000[a-h]

	Consolidated Incineration Facility Incinerator (CIF), SRS	Toxic Substance Control Act (TSCA) Incinerator (TSCAI), East Tennessee Technical Park	Waste Experimental Reduction Facility Incinerator (WERF), INEEL
Off-gas CEM	Flowrate, O_2, CO, radioactivity, opacity	Flowrate, O_2, CO, CO_2, radioactivity and metals collected continuously on filters and in impingers, and analyzed offline	Flowrate, O_2, CO, HCl, and combustible gas, radioactivity
Measured emissions or control efficiencies:			
D/Fs	Worst-case 1997 trial burn D/F levels, 0.65–4.2 ng/dscm toxicity equivalent (TEQ) dry basis @ 7% O_2. More recent test results are lower at 0.043–0.253 ng/dscm TEQ.	<0.04 ng/dscm TEQ dry basis @ 7% O_2	Trial burn D/F levels averaged 6.2 ng/dscm TEQ (INEEL, 1998a)
Hg	19–45 µg/dscm dry basis @ 7% O_2 (Barber, 1999)	70–100µg/dscm dry basis @ 7% O_2 (0% SRE) (Lockheed Martin, 1995)	Not measured
PM	0.0013–0.0030 gr/dscf dry basis @ 7% O_2	0.0019–0.0049 gr/dscf dry basis @ 7% O_2 (94.5–99.986% SRE) (Lockheed Martin, 1995)	0.0015–0.0040 g/dscf (dry, 7% O_2) (INEEL, 1998a)
HCl/Cl_2	27–93 ppmv total HCl and Cl_2 concentration dry basis @ 7% O_2; HCl/Cl_2 removal efficiency of 99.97–99.99%	0.15–0.39 ppm dry basis @ 7% O_2 (99.82–99.909% SRE) (Lockheed Martin, 1995)	57–232 ppm HCl and <4 to 57 ppm Cl_2 (dry, 7% O_2) (INEEL, 1998a)
CO	5.2–17 ppm dry basis @ 7% O_2	1.8-3.0 ppm dry basis @ 7% O_2	0.0–5.1 ppm, dry basis @ 7% O_2 most recent trial burn results (INEEL, 1998a)
HC	Not measured	Not measured	Not measured
SVM (Cd, Pb)	Average removal efficiencies: 99.98% for Cd, 99.94% for Pb	Average Pb removal efficiency was 98.5%; Cd removal efficiency has not been measured but is assumed to be similar to that of Pb	Average Cd removal efficiency was >99.998% (INEEL, 1998a); Pb removal efficiency has not been measured but is assumed to be similar to that of Cd
LVM (Cr, As, Be)	Average removal efficiencies: 99.99% for Cr, 99.94% for As, 99.95% for Be	Average Be removal efficiency was 99.68%; As and Cr removal efficiencies have not been measured but are assumed to be similar to that of Be	Average Cr removal efficiency was >99.996% (INEEL, 1998a); As and Be removal efficiencies have not been measured but are assumed to be similar to that of Cr

[a] Soelberg, N.R., Knecht, M., and Haas, B., Air Pollution Control Status and Needs for Thermal Treatment Systems, presentation at the 1997 EPA/DOE National Technical Workgroup Annual Meeting, Newport Beach, CA., November 5–7, 1997.

[b] DOE, Summary of DOE Incineration Capabilities, DOE/ID-10651, July 1998, Revision 1.

[c] Soelberg, N. and Chambers, A., Screening Matrix of Modifications to Enable the WERF Incinerator to Meet the Proposed MACT Rule, internal draft INEEL report, January 1998.

[d] Idaho National Engineering and Environmental Laboratory, WERF High Temperature Trial Burn Plan, DOE/ID-10131(-98), May 1998.

[e] Knecht, M.A. and Priebe, S.J., Proposed MACT Rule for Hazardous Waste Incinerators and Potential Impacts on DOE MLLW Incinerators, presentation at INEEL on July 16, 1997.

[f] Radian International, Trial Burn Report, Consolidated Incinerator Facility, Savannah River Site, July 16, 1997.

[g] IT Corporation, RCRA Trial Burn Report for a Dual Purpose RCRA/TSCA Incinerator at the U.S. Department of Energy's K-25 Facility in Oak Ridge, Tennessee, August 31, 1989.

[h] Stack gas concentration limits are adjusted to 7% O_2.

3. The TSCAI can meet all MACT emission standards provided that the feedrates of sludges and solids are restricted to meet PM, SVM, and LVM standards, and provided the feedrate of Hg is limited to meet the Hg standard. Alternatively, the TSCAI can be retrofitted to include more efficient PM, SVM, LVM, and Hg removal. Cost estimates for such retrofits need to consider potentially extensive modifications to the existing facility to provide space needed to install additional equipment.
4. The WERF would require off-gas system modifications to comply with the MACT D/F standard. Modifications or very restrictive feedrate limits would also be required to comply with Hg and HCl/Cl_2 standards.
5. Other miscellaneous upgrades in areas such as feed control and characterization, continuous process monitoring, or automatic waste feed cutoffs may also be included for MACT compliance.

Brief descriptions and discussion for each of the three DOE incinerator facilities are provided below.

Consolidated Incineration Facility (CIF)

The CIF includes a rotary kiln incinerator which is designed to treat (1) solid and sludge wastes in the kiln, (2) liquid aqueous wastes fired through a burner in the kiln, (3) liquid blended radioactive wastes (BRW) fired through a burner in the kiln, and (4) liquid radioactive organic waste (ROW) fired through a separate burner into the secondary combustion chamber (SCC). The off-gas system (Figure 7.2) includes a wet quench, hydrosonic scrubber system (including free jet and agglomeration zones, a cyclone, and a demister), reheater, prefilters, and HEPA filters (Radian, 1997; DOE, 1998).

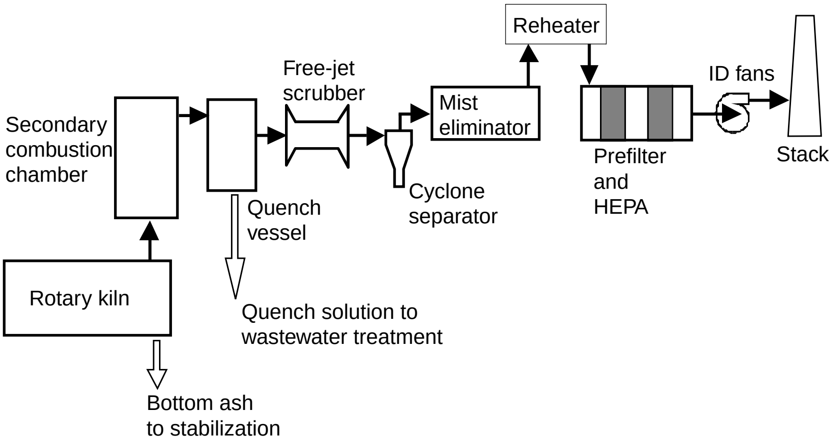

FIGURE 7.2 Process schematic for the CIF incinerator. (From DOE, 1998, Summary of DOE Incineration Capabilities, DOE/ID-10651, Revision 1, July.)

Off-gas leaving the SCC (at a nominal temperature range of at least 1800°F) is rapidly cooled adiabatically by sprays of scrubber liquid in the quench vessel. The quench vessel is Halar-lined carbon steel with acid-resistant refractory in the upper, higher temperature section. The off-gas is cooled to the saturation temperature of the blend of off-gas and some amount of evaporated scrub solution, normally 180 to 190°F. NaOH is added as needed to the quench solution for pH control and initial acid gas scrubbing. Particulate matter scrubbing also begins in the quench vessel, although downstream scrubbing provides much more efficient PM removal.

The quenched off-gas enters the steam-assisted, single-stage hydrosonic scrubber. Steam is used to atomize recirculated scrubber solution into the gas stream, induce the flow of off-gas from the quench vessel (minimizing induced-draft fan requirements), and provide free-jet mixing of the atomized scrub solution with the off-gas for very efficient acid gas and PM scrubbing. The three-phase mixture of off-gas, PM, steam, and atomized scrub solution flows through a section designed to provide residence time for agglomeration to form larger droplets of condensed steam, scrub solution, scrubbed acid gases, and wetted PM. The agglomerated droplets are removed in the downstream cyclone separator and higher efficiency mist eliminator.

The quenched, scrubbed, and demisted off-gas is then reheated from about 190°F to 240 or 250°F in an electrical resistance-heated reheater, to prevent moisture condensation in the prefilters and HEPA filters and induced-draft fans. The quenched, scrubbed, and filtered off-gas from the incinerator system is mingled with building ventilation air in the stack for discharge to the atmosphere.

The scrubber liquid is recirculated in the scrubber system, and a portion is also discharged to the quench system to make up for evaporation in the quench vessel. Clean makeup water is added to the scrubber system to replace scrub solution discharged to the quench system. Thus, the "dirtiest" water is contacted with the "dirtiest" gas, and the "cleanest" water is contacted with the "cleanest" gas. The quench water is recirculated until total dissolved solids (TDS) levels approach 10% and total suspended solids (TSS) levels approach 3% (both permitted limits). As these solids levels approach the permitted limits, the spent quench water is sent to one of two blowdown tanks for subsequent stabilization for disposal, or to the on-site Effluent Treatment Facility (ETF) for wastewater treatment. The scrubber liquid is subject to the same permitted TDS and TSS limits, but is maintained well below these limits with makeup water and by discharging scrubber liquid to the quench system.

The high efficiency of this off-gas system for controlling pollutant emissions is attributed to the multiple, increasingly efficient control devices. The wet quench is a relatively inefficient control device, but it can remove large-particle-size PM and some of the acid gases. The wet scrubber system (which includes the hydrosonic scrubber free jet and agglomeration zones, the cyclone, and the demister) provides highly efficient acid gas and PM removal in two stages. The prefilters and HEPA filters provide two additional stages of PM removal. Altogether, this off-gas system provides five stages of PM removal and three stages of acid gas removal.

Toxic Substances Control Act Incinerator (TSCAI)

The TSCAI includes a rotary kiln incinerator designed to treat solid, sludge, organic liquid, and aqueous liquid wastes fired in the kiln. High heating value organic liquid wastes can also be fired in the SCC. The off-gas system for controlling air emissions from this incinerator (Figure 7.3) includes a wet quench, venturi scrubber, demister, cross-flow packed bed scrubber, and two ionizing wet scrubbers in series (Lockheed Martin, 1995; DOE, 1998).

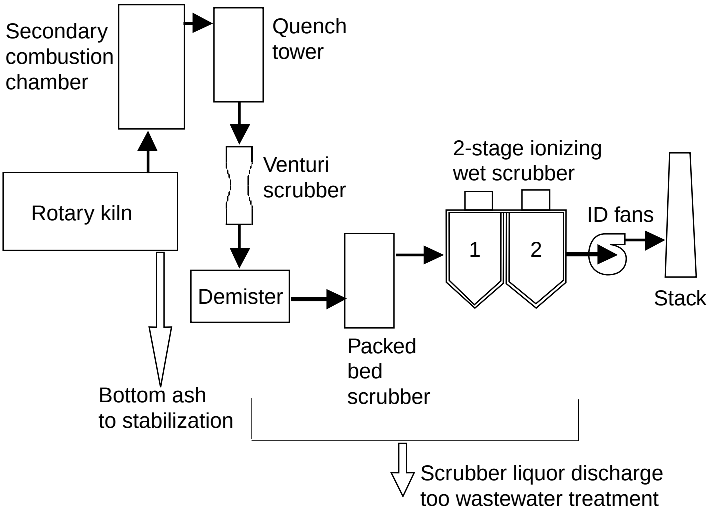

FIGURE 7.3 Process schematic for the TSCAI. (From DOE, 1998, Summary of DOE Incineration Capabilities, DOE/ID-10651, Revision 1, July.)

Off-gas exits the SCC at a nominal temperature of 2200°F, and is rapidly cooled adiabatically to around 180°F by contact with fresh water and recycled water. Excess quench water collects in the recycle tank at the base of the quench section. While the purpose of the quench section is to rapidly cool the off-gas, PM, radionuclide, and acid gas scrubbing is also initiated in the quench section.

The quenched off-gas enters the venturi scrubber, which provides the next scrubbing stage. The venturi scrubber is automatically controlled using an adjustable throat to provide a pressure drop of typically 9 to 12 in. water. Scrubber solution is injected into the gas stream just upstream of the throat, where the energy of the pressure drop provides efficient contacting of the scrubber solution with the off-gas. A demister downstream of the venturi scrubber separates the liquid droplets from the gas stream. The separated liquid is drained to the quench recycle tank.

Additional scrubbing is provided in the next three stages, which consist of a packed bed scrubber and two ionizing wet scrubbers (IWSs) in series. The primary function of the packed bed scrubber is acid gas removal, although it is also capable of removing some particulate. The IWSs remove submicron PM from the off-gas, and are also capable of removing some residual acid gases. The TSCAI off-gas system has four stages of PM and acid gas removal.

Waste Experimental Reduction Facility (WERF)

The WERF incinerator is a fixed hearth, controlled air incinerator, designed to treat solid, sludge, or liquid wastes that are packaged into solid waste boxes. The off-gas system (Figure 7.4) consists of a gas-to-air heat exchanger, controlled introduction of dilution air for further cooling, and a baghouse followed by HEPA filters (DOE, 1998). This off-gas system is a completely dry system. There is no wet quenching or wet scrubbing in this system, so that there are no wet aqueous secondary effluents.

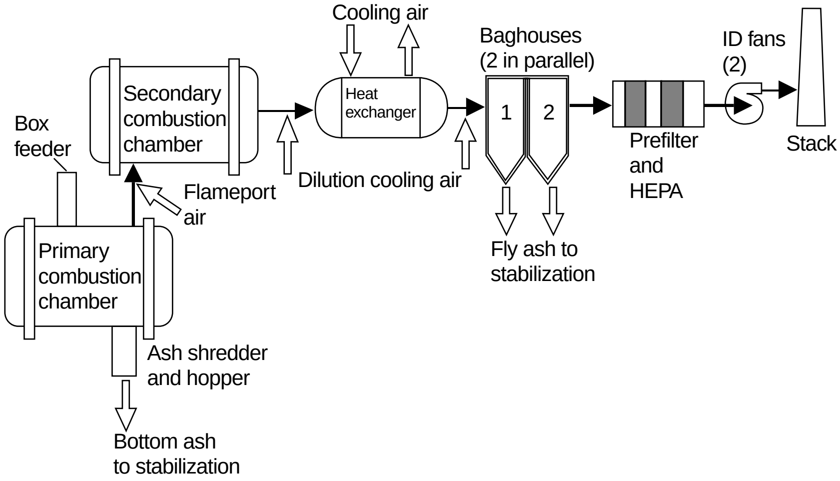

FIGURE 7.4 Process schematic for the WERF incinerator off-gas system. (From DOE, 1998, Summary of DOE Incineration Capabilities, DOE/ID-10651, Revision 1, July.)

Off-gas leaving the SCC (at a temperature of around 1800°F) is immediately cooled to around 1250°F by dilution with cool ambient air. The diluted, cooled off-gas passes through the tube side of a shell and tube heat exchanger, where the off-gas is cooled to around 625°F. The off-gas exiting the heat exchanger is further cooled to less than 395°F using additional air dilution. The cooled and diluted off-gas then enters the baghouse, followed by the prefilters and HEPA filters. This off-gas system has three stages of PM filtration, which also removes solid-phase metals and radionuclides. By design, the WERF off-gas system does not include acid gas control equipment, although tests have shown limited HCl scrubbing in the baghouse.

APCS Designs for Complying with New Regulations

Off-gas systems installed in the United States prior to 1996, such as those described in Chapter 7.4 for the DOE mixed waste incinerators, do not generally have all of the capabilities needed to provide compliance with the recently promulgated MACT Rule. In order to comply with the MACT standards or similarly restrictive regulations these facilities would need to either employ some feed restrictions (especially for Hg) or upgrade the off-gas system.

Incinerator off-gas systems designed or upgraded after 1996, when the EPA proposed the MACT standards for hazardous waste incineration (EPA, 1996), generally do have features needed to meet current performance requirements such as those described in a previous subsection ("Design and Performance Objectives for Off-Gas Control Systems") including compliance with the MACT standards. Various designs for reliable and efficient off-gas systems are described in Table 7.5. This table does not include all known existing or planned off-gas systems.

Dry, Dry-Wet, and Wet-Dry APC Systems

Off-gas systems included in Table 7.5 reflect the three general approaches for high-performance off-gas systems for mixed waste treatment:

1. Dry systems (partial cooling, dry particulate filtration, and dry acid gas scrubbing)
2. Dry-wet systems (partial cooling, dry particulate filtration, and then wet acid gas scrubbing)
3. Wet-dry systems (total quench and wet scrubbing for both particulate and acid gases, followed by dry final particulate filtration)

These high-performance off-gas systems were conceptually designed to better tolerate system upsets and to meet pollutant emission limits through the use of various combinations of traditional and innovative designs. Entirely wet systems (total quench and wet scrubbing for both particulate and acid gases) were excluded from the above categories. Although entirely wet systems are commonly used in many thermal processes, including hazardous waste incineration and some mixed waste incineration systems such as the TSCAI facility, they are not generally as efficient for radionuclide, PM, and metals removal as systems that include dry HEPA filtration. HEPA filtration is a standard for most radioactive and mixed waste handling and treatment processes, and also for ventilation systems for facilities that contain such processes.

Dry Off-Gas Systems

One example of a dry system was proposed for upgrading the WERF incinerator (INEEL, 1998b; Figure 7.5) to meet MACT standards. A primary objective of this design was to avoid any liquid secondary waste streams, and also takes advantage of operating experience with the existing dry baghouse at this facility. In this proposed design, off-gas that exits the SCC at a temperature of around 1,800°F is cooled to a temperature of around 300°F using automatically controlled evaporative cooling. The evaporative cooler uses air-atomized water sprayed directly into the off-gas stream. The operation of the evaporative cooler must be carefully monitored and controlled to avoid high-temperature upsets that could thermally damage the downstream baghouse, and also avoid low-temperature upsets that could allow incompletely evaporated water to wet and foul the downstream sorbent injection section and blind the baghouse bags. Multistage PM filtration is performed in the baghouse, the prefilters, and HEPA filters.

Acid gas scrubbing is accomplished by dry adsorption of acid gases onto hydrated lime sorbent that is injected upstream of the baghouse and collected in the baghouse. This dry scrubbing technique is common, commercially available, and demonstrated in operating facilities for many thermal processes including hazardous waste incineration. The dry secondary waste collected from the baghouse can contain largely spent and unspent hydrated lime, including all of the scrubbed adsorbed chlorides. With the added dry scrubbing sorbent, the mass flowrate of this secondary waste could be several times higher than for systems that do not use dry scrubbing. Hydrated lime and Cl in the secondary waste will affect

TABLE 7.5 Several Off-Gas System Designs that Meet the Chapter 7.2 Requirements

System	Functional Operations									Comments (Ref.)
	Gas Cooling	Particulate Control	Gas Cooling	Acid Gas Control	Gas Reheating	Hg Control	HEPA Filtration	NO_x Control	Continuous Monitoring	
Idaho Waste Processing Facility (IWPF) (wet-dry)	Water spray total quench	Free-jet scrubber/ mist eliminator	—	Free-jet scrubber, separator, packed tower, mist eliminator	Yes	S-impreg. carbon filters between prefilters and HEPAs	Prefilters and HEPAs	—	O_2, CO, THC, Hg, PM, beta/gamma, and alpha; Optional: SVMs, LVMs, HCl, and Cl_2	Conceptual design only (Eddy, 1995)
ITTS A-1, A-7, J-1 (dry-wet)	Water spray partial quench	Dry baghouse	Water spray total quench			2-stage activated C after baghouse	2-stage HEPAs after baghouse	NH_3-injected SCR	Not specified	Conceptual design only (Feizollahi and Quapp, 1996).
USBM arc melter (dry-wet-dry)	Water spray/air dilution	Dry baghouse	2-stage packed bed, cooler and condenser		Hot water reheater	Activated C filters	Yes	—	SCC outlet O_2	Installed and operated in demonstration facility (Soelberg et al., 1996)
Forschungzentrum Karlsruhe Alpha Waste Incinerator (dry-wet-dry)	Water cool to 700°C	Ceramic hot filters, max. 700°C	2-stage water quench	Acid pH ð1 jet scrubber, then pH ð7 jet scrubber	Hot air blend reheat dewpoint +25°C	Acid scrubber and activated C			Not specified	Installed and operating (Dirks, 1998)
R-1 (dry-wet)	Water spray cooler, partial	Dry baghouse	Water/scrub liquor total quench	Pressure-atomized free-jet scrubber, 2-stage demister	Electric-heated hot air reheater	S-impregnated C beds after prefilters	2-stage HEPAs	NH_3-injected SCR	O_2, CO_2, CO, THC, HCl, PM, beta/gamma, and alpha; SCR inlet & outlet NO_x outlet NH_3	Conceptual design only (Soelberg et al., 1998)

AMWTF system final design (wet-dry)	Scrub solution total quench	Venturi scrubber, packed tower w/pH 2–3, followed by packed tower w/pH 7–8, and condensing wet ESP, including gas sub-cooling to ~100°F using scrub solution heat exchanger			Electrical resistance heating	Wet scrubbing, S-impregnated carbon	Triple prefilters/ HEPAs	—	O_2, CO_2, CO, Hg, alpha radioactivity, more to be determined	Permit application (BNFL, 1999), 30% detailed design, March 2000
WERF upgrade design	Water spray partial quench	Fabric filter baghouse	—	Hydrated lime injection upstream of baghouse	—	S-impregnated C bed after HEPAs	Prefilter and HEPA filters	—	O_2, CO_2 CO, THC, HCl, PM, beta/gamma, alpha	Conceptual design only (INEEL, 1998b)
ATG GASVIT™ melter	Steam partial cool	High temperature filter	2 ejector scrubbers in series, with subcooling and high-efficiency mist eliminator		Finned steam reheater	?	Prefilter and HEPA in parallel	—	Not specified	Syngas conversion to fully oxidized products is done after scrubbing and filtration

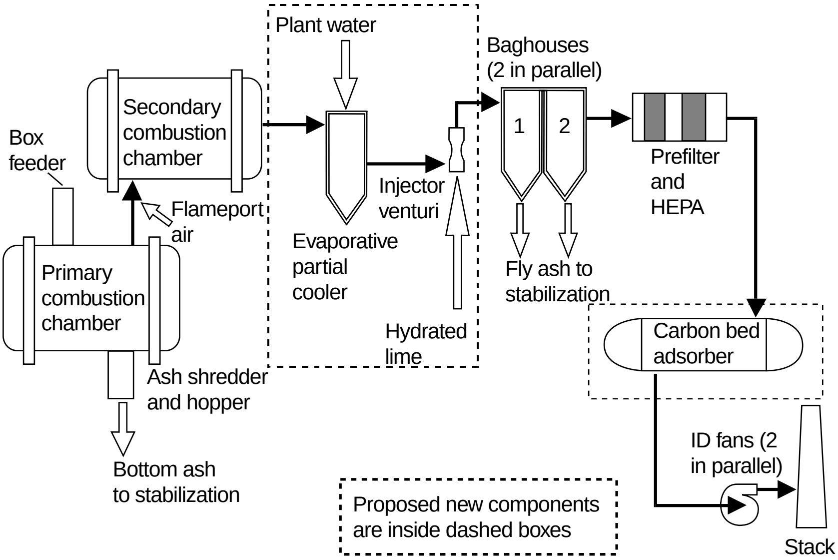

FIGURE 7.5 Proposed off-gas system upgrade design for the WERF incinerator.

how this secondary waste is handled and stabilized. While the hydrated lime could improve the performance of hydraulic cement-based final waste forms, the presence of Cl could impair the performance of many waste forms, including hydraulic cements.

As of 2000, the DOE has determined to close the WERF incinerator rather than modify the system for MACT compliance that would be required to continue operating this incinerator.

Dry-Wet Off-Gas Systems

Examples of dry-wet systems include the off-gas system for the Forschungzentrum Karlsruhe Alpha Waste Incinerator (see subsection entitled "Examples of Existing Off-Gas Systems for Mixed Waste Treatment"), the off-gas system for the U.S. Bureau of Mines (USBM) arc melter demonstration facility (Soelberg, 1996), an off-gas system design initially planned for the proposed AMWTF incinerator (Guay et al., 1998), and one of the system upgrades proposed for the WERF incinerator (INEEL, 1998b). In a dry-wet system, particulate (including most of the toxic metals and radionuclides) is removed from the off-gas to form a dry secondary stream that can be recycled to the primary treatment device or immobilized for final disposal. Acid gases are removed by wet scrubbing following the particulate removal. The dry-wet system can use lower temperature baghouses or high-temperature filters for the initial particulate control, followed by wet acid gas scrubbing. Some designs include reheating and final dry filtration downstream of the wet scrubber, and hence can also be correctly called dry-wet-dry systems.

The general features of dry-wet systems are typified by the USBM arc melter off-gas system (Figure 7.6). Installed in 1995, the performance of this system has been demonstrated in several large pilot-scale tests. In this system, off-gas from the SCC is rapidly cooled using evaporative water spray cooling to around 260°C (500°F), followed by additional dilution air cooling to around 150°C (300°F). This combination of evaporative and dilution air cooling achieves the multiple objectives of (1) rapid cooling to a temperature below the 200–400°C temperature range in which *de novo* D/F formation is known to occur most rapidly; (2) careful control of high- or low-temperature upsets that could cause thermal damage or wetting, blinding, and corrosion in the baghouse; and (3) limiting the increase in total off-gas flowrate that would occur if only air dilution cooling was used. In this configuration, the added cooling air increased the total off-gas flowrate by about a factor of 2, compared to an eightfold increase if only air dilution cooling was used. Five stages of particulate removal are performed in (1) the cyclone

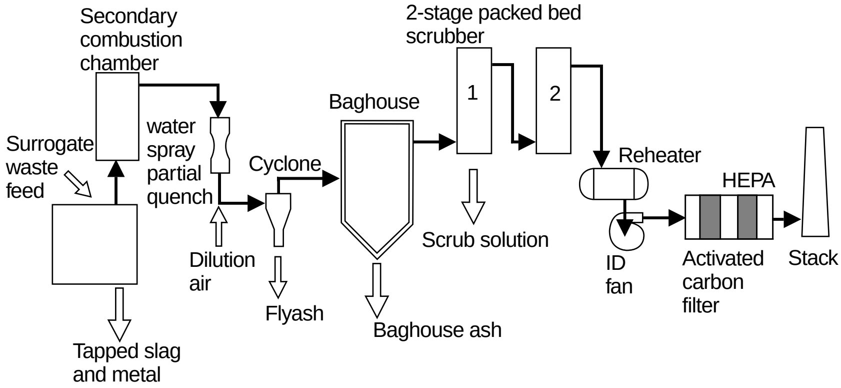

FIGURE 7.6 Schematic of the USBM arc melter demonstration facility off-gas system.

just upstream of the baghouse, (2) the baghouse, (3) and (4) two packed-bed scrubbers in series, and (5) final HEPA filters.

The primary function of the packed bed scrubbers is acid gas control. NaOH is automatically added to maintain the pH of the recycled scrub solution around 8. A portion of the scrub solution is discharged to control the level of dissolved salts in the scrub solution. Because particulate filtration is performed upstream of the scrubbers, the scrub solution stays relatively free of dissolved and undissolved solids. The packed bed scrubbers serve as redundant PM scrubbers and provide some protection for the downstream carbon and HEPA filters in the event of a baghouse failure that would allow appreciable amounts of particulate to pass through the baghouse.

Other features of this off-gas system include a cooler and condenser downstream of the packed bed scrubbers to lower the off-gas temperature to as low as 90°F (and condense water for reuse), and a reheater to raise the temperature of the off-gas above its dewpoint to prevent moisture condensation in the downstream carbon and HEPA filters. The carbon filters were installed to adsorb trace-level gaseous contaminants that are not collected in the HEPA filters.

Wet-Dry Off-Gas Systems

Wet-dry systems are typified by the existing off-gas system for the CIF incinerator (Section 7.4) and the off-gas system for the Mountain States Energy Technology Applications (MSE-TA) Plasma Arc Centrifugal Treatment furnace test facility (Whitworth et al., 1999). In wet-dry systems, the off-gas is rapidly cooled and all contaminants, including PM, radionuclides, toxic metals, and acid gases, are wet scrubbed and produce a single secondary aqueous mixed waste with some suspended and dissolved matter. After wet scrubbing, the off-gas is reheated (to prevent moisture condensation in downstream control equipment) and dry-filtered (to remove trace-level particulate and other contaminants).

Comparisons of Different Wet and Dry Systems

Each of the three general types of off-gas systems has several distinct advantages and disadvantages because of the differences in how each type addresses particulate and acid gas control. These advantages and disadvantages are summarized in Table 7.6. Trade-offs must be considered by system designers and operators when selecting the off-gas system that best suits their off-gas treatment requirements, operating experience, maintenance and ALARA issues, funding for capital and operating expenses, existing facility configurations, and secondary waste requirements and restrictions.

High-Performance Off-Gas System Functional Operations

Functional operations needed for off-gas control for most mixed waste treatment systems are shown in Figure 7.7. Particulate control, acid gas control, Hg and trace organics removal, HEPA filtration, and in

TABLE 7.6 Comparison of Dry-Wet and Wet-Dry APC Systems

Off-Gas System	Advantages	Disadvantages
Dry	No aqueous wet effluent, and no wet scrubber criticality problems.	Potential for dispersible fines in the baghouse catch and potential worker exposure and contamination control issues during baghouse/filter maintenance.
	Lime-based sorbents used for acid gas control may improve hydraulic cement-based techniques for stabilizing the dry particulate secondary waste.	The presence of scrubbed acid gases in the dry particulate secondary waste can impair the effectiveness of downstream stabilizing techniques such as hydraulic cements.
		Moisture, corrosion, or thermal damage in the baghouse/filter can be very severe and costly problems that must be strictly avoided by using accurate and responsive process monitoring and control in the partial quench step upstream of the baghouse/filter.
	Recycling some of the dry particulate can significantly reduce the volume of this waste.	The typical baghouse temperature of ~300–400°F is not cool enough to prevent some D/F formation in the particulate filter according to some recent studies (Soelberg et al., 1996). However, this potential is minimized by using high temperature filtration. Also, if carbon adsorption is used for Hg control, the carbon should remove D/F formed.
	The off-gas system can be more simple, with fewer steps, less or no off-gas reheating, and less auxiliary equiment such as scrub solution pumps, tanks, and piping.	Dry or semi-dry sorbent injection can significantly increase the amount of dry particulate secondary wastes.
		Bags or filters require occasional replacement at considerable expense, resulting in additional secondary waste generation, and potential for worker exposure or environmental release of hazardous or radioactive contamination.
Dry-wet	Separate dry particulate (radionuclide/hazardous metal) and aqueous salt solutions can simplify secondary handling and treatment for each of these streams. The dry particulate can be recycled to another thermal process or solidified in cement technologies such as polyethylene or sulfur polymer cement that do not allow water. The aqueous salt streams with essentially no radionuclides or solids can be treated or disposed of more easily without the radionuclides or toxic metals.	Potential for dispersible fines in the baghouse catch and potential worker exposure and contamination control issues during baghouse/filter maintenance. Moisture, corrosion, or thermal damage in the baghouse/filter can be costly problems that must be strictly avoided by using accurate and responsive process monitoring and control in the partial quench step upstream of the baghouse/filter.
	Wet scrubber criticality is not a concern because, essentially, all fissile radionuclides are removed in the baghouse.	The typical baghouse temperature of ~300–400°F is not cool enough to prevent some D/F formation in the particulate filter according to some recent studies (Soelberg et al., 1996). However, this potential is minimized by using high-temperature filtration. Also, if carbon adsorption is used for Hg control, the carbon should remove D/F formed.
	Volume reduction of the separate dry and aqueous secondary wastes is easier. Recycling dry particulate can significantly reduce the volume of this waste. Evaporation of the scrubber effluent (made more easy by removal of most radionuclides and most particulate) can significantly reduce the volume of this waste.	
	There is still barrier filtration in the event of a power failure.	

TABLE 7.6 (Continued) Comparison of Dry-Wet and Wet-Dry APC Systems

Off-Gas System	Advantages	Disadvantages
Wet-dry	Simpler gas cleaning by rapidly cooling the gas to the dewpoint (or lower, condensing some water out of the off-gas), and combining acid gas and particulate removal functions.	Produces an aqueous mixed waste scrubber secondary stream that could contain fissile radionuclides, toxic metals, and halogen salts, producing more treatment challenges prior to disposal. This lessens the potential for recycling this waste stream to the primary treatment unit or evaporation to reduce secondary waste volume.
	No dispersible fines are produced, unless treatment of the scrubber effluent requires precipitation, filtration, or drying.	The performance of the free-jet scrubber strongly depends on constant off-gas flowrate, composition, temperature, and differential pressure, which may be difficult to control for different heterogeneous waste input streams.
	Minimizes D/F formation by rapidly quenching the off-gas to under 200°F. Marginally better Hg control upstream of the carbon adsorbers because of the initial quench to a lower gas temperature.	Increased potential for problems related to dissolved or suspended particulate in the scrub solution: nozzle erosion/plugging, sludge deposition, nuclear criticality, and residual submicron particulate in the gas remaining from evaporation of scrub solution droplets.
	Stoichiometric caustic agent required for acid gas removal.	A power failure or other upset that affects the scrubber spray can significantly reduce particulate removal capability.

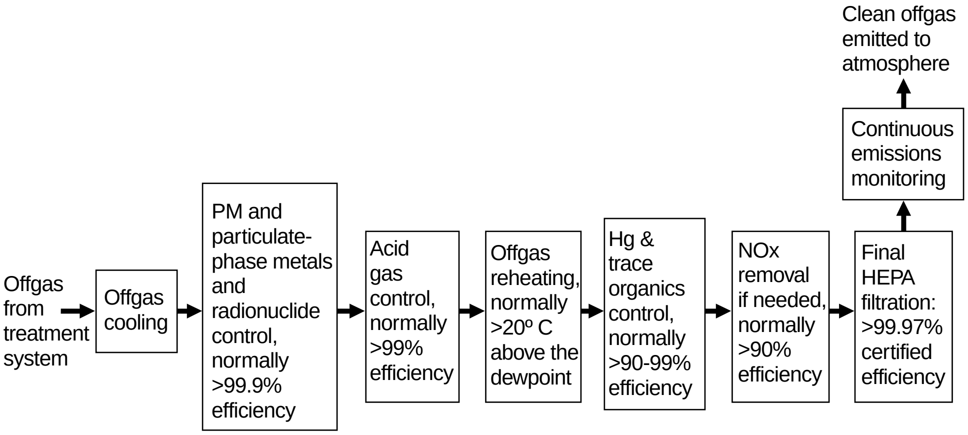

FIGURE 7.7 Functional operations that are required in most mixed waste off-gas systems.

some cases NO_x removal, are needed to comply with the emission regulations listed in Section 7.2. Some conditioning steps are often required to prepare the off-gas for the gas cleaning steps, enable the gas cleaning steps to operate effectively, and prevent damage to gas cleaning and other downstream equipment. Conditioning steps include initial off-gas cooling of hot SCC outlet gas, secondary gas cooling downstream of dry particulate removal in dry-wet systems, and off-gas reheating to temperatures above the dewpoint for final dry HEPA filtration or to reaction temperatures for such processes as NO_x control. The sequence and operating conditions for these various functional operations can vary depending on off-gas system design. Continuous emission monitoring of the off-gas that exits the off-gas system is required to show that emission limits are being met and to indicate when significant changes occur.

Initial Off-Gas Cooling

The high temperature of the off-gas exiting the SCC (usually at least 1800°F) must be reduced to prevent thermal damage of the downstream equipment needed to control PM, metals, radionuclides, and acid gases. Design objectives for off-gas cooling include:

- Sufficient control over the quench process to enable rapid response to temperature, flowrate, and composition variations of the off-gas.
- Quench as rapidly as possible to reduce residence time in the temperature range in which D/F may be formed if D/F precursors are present. D/F precursors, if present in sufficient amounts, can cause unacceptable D/F emissions if allowed sufficient time to form in the temperature window of approximately 200 to 400°C, especially in the presence of significant catalyzing surface area provided by PM deposition in such equipment as heat exchangers, or simply in the PM entrained in the off-gas.
- Minimize the potential for solid or liquid deposits that may impair off-gas cooling or cause flow restrictions.
- Limit amounts of added cooling water or air that ultimately add to the total off-gas flowrate through the remainder of the system.

Heat recovery, although normally a good practice to increase energy efficiency and reduce operating costs for thermal processes including incinerators, is a very low priority for mixed waste treatment. Energy cost benefits and energy efficiencies generally do not justify the added capital costs and potential for maintenance costs, downtime, and worker exposure. Energy costs are generally one of the smallest factors in mixed waste treatment facility operating and life-cycle costs (Feizollahi and Quapp, 1996).

Using gas/air heat exchangers or heat recovery boilers to perform off-gas cooling is not recommended because they add to the potential for process upsets from fouling or corrosion of heat transfer surfaces. Heat exchangers can add capital costs to upfront facility costs. Maintenance that can be performed quickly and inexpensively in nonradioactive processes takes longer, costs more, and has added potential for worker exposures to hazards in radioactive processes. Perhaps most important, heat exchangers can increase *de novo* D/F formation by increasing off-gas residence times and catalytic surfaces in the D/F-forming temperature window.

Depending on the downstream operations, the off-gas can be cooled to a temperature well above its dewpoint (around 300°F for particulate control in a baghouse), at its dewpoint (typically resulting in a saturated gas temperature of around 170 to 180°F), or below its initial dewpoint. The recommended choice for off-gas cooling is direct contact with water or scrubber solution spray in a spray evaporation chamber. Dilution with cool air, steam, or recycled off-gas has been used, but dilution cooling can increase the mass flowrate of the off-gas mixture by up to 10 times, depending on the initial and final air and gas temperatures. The larger total diluted off-gas flowrate would increase the size and performance requirements of downstream off-gas system equipment. Dilution cooling is best used when the off-gas temperature only needs moderate cooling of 100 to 200°F, when the mass increase in the off-gas flowrate is perhaps a factor of 2 or less (Soelberg et al., 1996; IET, 2000).

Cooling the off-gas with a water or scrubber solution spray to a temperature below the initial dewpoint ("subcooling" below the initial off-gas dewpoint) is sometimes desired to (1) reduce corrosion, (2) agglomerate condensed particles for more efficient removal, (3) further minimize D/F formation, (4) improve control efficiencies for hazardous air pollutants, (5) reduce the off-gas volumetric flowrate, (6) reduce moisture condensation in downstream HEPA filter housings and ducting, or (7) condense water vapor that may contain tritium out of the gas stream. Off-gas can be subcooled using additional cool water (and discharging the added heated water), or by a secondary cooling system that cools the quench or scrubber solution. However, energy costs for removing heat of condensation as the off-gas is subcooled, and the potentially increased discharge rates of condensate and scrubber solution, must be compared to benefits achieved by subcooling the gas.

Particulate, Toxic Metals, and Radionuclide Control

Particulate, toxic metals, and radionuclide control are grouped together because most toxic metals and radionuclides exist primarily in condensed aerosol forms at typical cooled off-gas temperatures between 120 and 300°F, and can be removed with efficient particulate control equipment. This temperature range is low enough that even relatively volatile Cs, Co, K, and Zn species are mostly condensed into particulate form. Species of these elements can be concentrated in smaller, sub-micron sized particulate, and control of submicron particulate can be more challenging for the off-gas system. Other challenges include Hg and the radionuclides ^{14}C, ^{3}H, and ^{129}I, which can exist appreciably or entirely as gaseous species at practical off-gas temperatures.

Various radionuclides and their relative volatilities include:

Isotope	Volatility	Comments
^{241}Am	Nonvolatile	Transuranic element
^{238}Pu through ^{241}Pu	Nonvolatile	Transuranic element
^{232}U through ^{238}U	Nonvolatile	Transuranic element
^{137}Ba	Low volatile	
^{60}Co	Low volatile	
^{90}Sr	Low volatile	
^{137}Cs	Semivolatile	
^{90}Y	Semivolatile	
^{65}Zn	Semivolatile	
^{14}C	Volatile as CO_2	
^{3}H	Volatile as H_2O	
^{129}I	Volatile as HI, I_2	

These volatility relationships are qualitative because the actual volatility of any element will vary depending on the speciation of that element between its pure form and compounds such as oxides and chlorides. Metal chlorides are typically more volatile than the elemental or metal oxide species. The speciation of many of these radionuclides can depend on time and temperature history of these elements in the treatment system and the availability of other reactants. Final designs for off-gas systems should be based on waste analyses, modeling, and experimental data to determine metal and radionuclide concentrations and speciation in the off-gas so that the off-gas system can be designed to adequately control such species.

Design objectives for particulate, toxic metals, and radionuclide control include:

1. Meeting expected emission limits by efficiently controlling both gas-phase and condensed or solid-phase metals and radionuclides that may exist in the off-gas. While most metals and radionuclides exist in condensed forms at practical off-gas system temperatures, some may be concentrated in submicron particulate. This submicron PM can form as material volatilized at high temperatures during thermal homogeneously condenses into aerosols at lower off-gas system temperatures. Particulate matter control efficiencies of at least 99.9% are typically required to meet emission limits for particulate and particle-phase metals and radionuclides.
2. Minimizing the amounts of secondary streams that are radioactive or mixed wastes and require further treatment or disposal.
3. Minimizing amounts of dispersible (dusty) secondary streams that can present worker exposure and contamination control challenges.
4. Enabling easier and less costly handling and final treatment/disposal of the secondary streams, including avoiding liquid mixed waste streams and maximizing recycle.

Only high-efficiency particulate control technologies should normally be considered. Figure 7.8 compares generally expected particulate control efficiencies for various control devices. Low-efficiency devices such as stand-alone settling chambers and packed beds have little place in off-gas control

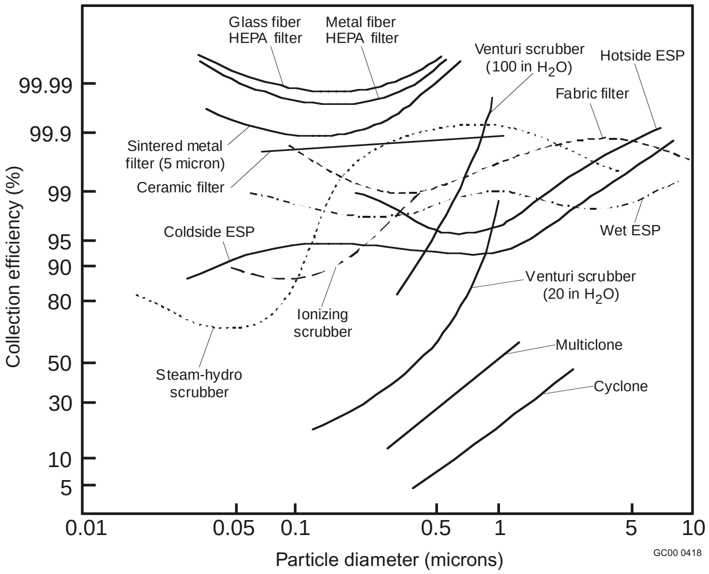

FIGURE 7.8 Relative efficiencies of different particulate control devices. (From EER (Energy and Environmental Research Corporation), 1992, *APC and Monitoring Technologies for Rocky Flats Fluidized Bed Unit, State of the Art Assessment*, EPA Contract 68-CO-0094.)

systems for mixed waste treatment. While they can be relatively inexpensive to purchase and operate, they still require space that can be very expensive in mixed waste treatment facilities. Costs for buildings that house mixed waste treatment facilities can range into thousands of dollars per square foot.

Along with building costs, other cost factors for mixed waste facilities, such as costs for design, associated equipment, inspection, project management, and construction management, can escalate installed facility capital costs 6 to 20 times higher than the actual cost of the control device from the vendor. In addition, at the time of treatment facility decommissioning and dismantlement, treatment facility equipment will need to be handled as radioactive or mixed waste. Worker risk of hazardous and radioactive exposures, and costs for decontaminating or otherwise handling and disposing of contaminated process equipment can be high. The limited performance of relatively low-efficiency control devices is not likely to be worth the capital and decommissioning costs when high particulate control efficiency is ultimately required.

The foremost dry technologies for use when the off-gas temperature is higher than the moisture saturation temperature include pulse-jet baghouses that can operate at off-gas temperatures up to around 500°F, and higher temperature ceramic and sintered metal filters that can operate up to around 1,700°F. Baghouses can require heat tracing and thermal insulation to prevent moisture condensation, and special containment mechanisms to maintain radioactive contamination control during normal operation, upset conditions, and maintenance.

Higher temperature filters have been and are being tested for DOE use (Christian et al., 1978; EER, 1992; MSE-TA, 1995), and have been used in Germany, Austria, and Japan for low-level waste incineration using the Karlsruhe-type shaft incinerator (IAEA, 1989; and Dirks, 1998). High-temperature filters were included in an early off-gas system design for the proposed AMWTF incinerator (Guay et al., 1998). High temperature filters provide advantages of PM filtration before significant off-gas cooling. Removing PM prior to off-gas cooling can make heat recovery in heat exchangers more feasible by reducing the potential for heat exchanger fouling, and by reducing the potential for *de novo* D/F formation catalyzed by PM as the off-gas cools through the *de novo* D/F formation temperature window. High-temperature filtration can also improve overall combustion of organics and soot by holding solid-phase organics and soot on the filter media, thus providing longer residence times for heterogeneous reactions.

Wet scrubber particulate removal efficiency depends primarily on the energy input to atomize and mix the scrubber solution with the off-gas. High energy scrubbers are used to provide better atomization of scrubber droplets and better droplet mixing with the off-gas so that the droplets can more efficiently contact, wet, and agglomerate particulate matter for removal. One example of a high-energy scrubber is a free-jet scrubber. Free-jet scrubbers provide this energy input through the supersonic steam or compressed air-assisted nozzle that atomizes and injects scrubber solution into the off-gas. Free-jet scrubbers are available in various designs for specific performance objectives. This technology has been specified, tested, or implemented in several DOE waste treatment testing and operating facilities, including the Mountain States Energy Technology Applications (MSE-TA) Plasma Arc Centrifugal Treatment furnace test facility (MSE-TA, 1994; 1995), the Savannah River Site (SRS) Consolidated Incineration Facility (CIF), and the Defense Waste Processing Facility (DWPF).

A key, although typically passive, component of wet scrubbers is the mist elimination equipment downstream of the high-energy scrub solution atomizing and contacting section. The free-jet scrubber incorporates dual zones of mixing/wetting and agglomeration downstream of the ejector nozzle, followed by various options or combinations of devices to separate the scrubber solution droplets from the off-gas. Mist eliminator devices include cyclones, chevrons, packed beds, screens, or mesh pads.

Other potential high-efficiency wet scrubbing technologies include high-energy venturi scrubbers and electric charge-assisted wet scrubbers such as wet electrostatic precipitators and ionizing wet scrubbers. Venturi scrubbers require a relatively high pressure drop, sometimes exceeding 60 in. water, for the high efficiencies needed for particulate control in mixed waste treatment.

Acid Gas Control

For this discussion, acid gases include hydrogen halides (HCl, HI, HF, and HBr) and other compounds such as Cl_2, F_2, and SO_2 that are often regulated as hazardous air pollutants. Acid gases are produced when waste materials that contain sulfur or halides are thermally treated. Most sulfur and organic-bound halides evolve to the off-gas system of a thermal treatment process. Design objectives for acid gas control devices include:

- Providing the necessary control efficiency (typically >99%) to meet applicable emission limits based on known or assumed input feedrates
- Operating with acceptably low corrosion, maintenance requirements, and downtime
- Minimizing the amounts of off-gas secondary streams that are radioactive
- Optimizing the treatability of the secondary streams, including avoiding liquid mixed waste streams
- Having minimal impact on system backpressure and flowrates

Acid gas removal technologies include wet scrubbing, semi-dry scrubbing, and dry scrubbing. Wet acid gas scrubbers include the various types of wet scrubbers used for particulate control, and also scrubbers such as packed-bed scrubbers that are commonly used less as stand-alone particulate removal devices. Most acid gases are highly soluble in caustic or pH-adjusted aqueous solutions. Some devices that have relatively low particulate removal efficiency, such as packed-bed scrubbers and low-efficiency venturis, can still have high enough HCl removal efficiencies to satisfy regulatory emission limits. If dry particulate filtration is used for particulate control upstream of acid gas control, then various available acid gas removal options can include wet scrubber options that need not have high particulate removal capability.

If the off-gas system is designed to include wet particulate removal along with acid gas removal, then high-energy scrubbers that can remove particulate matter can also be operated to remove acid gases in the same steps. Free-jet scrubber systems are very efficient for both particulate and acid gases. Other wet scrubbing technologies such as wet electrostatic precipitators may require combinations in series with a unit such as a packed-bed scrubber to provide adequate overall acid gas and particulate control.

For most wet scrubbers, the off-gas is cooled to or below the saturation temperature just prior to the scrubber inlet. This enables the scrubber system to be constructed of corrosion-resistant materials such as fiber-reinforced plastics that cannot tolerate temperatures above around 200°F.

Dry-wet systems that have separate particulate and acid gas removal steps can effectively separate dry particulate and wet secondary streams. This can be attractive in some secondary waste disposal scenarios. Assuming that the initial filtration can efficiently remove particulate and radionuclides, concentrations of these contaminants in the scrubber discharge may be below regulatory limits.

Particulate removal and acid gas scrubbing are both performed in semi-dry (spray-dry) or dry scrubbing systems. Semi-dry scrubber designs use a wet slurry of sorbent media, such as slurried lime, injected in the off-gas cooling step. As the slurry water evaporates to provide the needed off-gas cooling, the solid-phase sorbent absorbs the acid gases. Sorbent particles are collected in a downstream filtering device such as a baghouse. Additional acid gas scrubbing is commonly achieved in the baghouse as the off-gas passes through the filter cake that contains still unspent sorbent. In some cases, most of the acid gas control is in fact achieved in the baghouse, rather than between the sorbent injection point and the baghouse.

Semi-dry scrubbers are typically not as efficient as well-designed and -operated wet scrubbers. The use of semi-dry scrubbing may require extra reagent (that is unused in the process) to achieve adequate acid gas scrubbing. Semi-dry scrubbing can also be prone to process upsets that could cause increased maintenance or loss of scrubbing performance. For example, if the slurry is not completely dry by the time the off-gas reaches the filter media, then the filters could be blinded with moisture. Wetted lime could dry in the piping or equipment, resulting in a difficult-to-remove cemented monolith. In another process upset condition, high temperatures of the off-gas as the wet slurry is injected can reduce the sorbent capability to adsorb acid gases.

Mercury Control

The recently promulgated MACT Rule Hg emission limits are typically 10 to 1000 times lower than prior permitted limits for existing incinerators. Treatment systems that complied with prior permit requirements must now improve Hg control in the off-gas system, or restrict the feedrate of Hg into the treatment system.

Various technologies are in progressive stages of development and application for achieving high off-gas Hg removal efficiencies. The EPA has identified wet scrubbing at low mercury feedrates, as well as carbon adsorption via carbon injection into the off-gas or via flow-through fixed carbon beds, as MACT for controlling mercury emissions from hazardous waste incinerators. Amalgamation of Hg with gold for removal from off-gas (followed by thermal regeneration and recovery) has also been under development and demonstration. Dry particulate removal (such as fabric filters and electrostatic precipitation), the use of various metal oxides and metal ores, and molten gallium filtration have also been evaluated. Because of high vapor pressures of the dominant mercury species (Hg and $HgCl_2$), dry particulate filtration is not expected to provide efficient and reliable mercury control. Some fundamental research on Hg adsorption using metal oxides and metal ores has been performed in the United States and Russia. While molten gallium filtration has been patented as a mercury control technology, only limited information has been found regarding this technology.

More detailed discussion of mercury control technologies for off-gas control in mixed waste treatment is provided in Section 7.6.

HEPA Filtration

Particulate control efficiencies for baghouses and free-jet scrubbers can exceed 99.9%. Other off-gas equipment, including evaporative coolers and acid gas scrubbers, can also exhibit some particulate removal capability. However, in a nuclear facility, final HEPA filtration is normally required to control any small remaining amounts of particulate for radionuclide emissions control.

Spent HEPA filters will be a secondary waste that can be recycled to the primary thermal treatment process, processed in other secondary waste treatment facilities such as chemical leaching or glass melting, or macroencapsulated. Recycle to a melter is possible as long as there is not a large buildup of Hg or difficult-to-control fines in the system. With a high combined particulate removal efficiency for the off-gas system upstream of the HEPA filters, the HEPAs for a well-designed and -operated off-gas system should not require frequent replacement.

NO_x Control

NO, NO_2, and other nitrogen oxide species in off-gas are typically grouped together and identified as NO_x. NO_x in thermal process off-gas is typically 90 to 95% NO, with the remainder being NO_2 and smaller levels of other nitrogen oxides. After exiting the facility off-gas stack, NO ultimately converts to NO_2 in the atmosphere, with a reaction time constant of 1 to 2 min. Most mixed wastes have low nitrogen levels and evolve low NO_x levels during thermal treatment. Most off-gas NO_x from mixed waste processes is "thermal" NO_x, produced when small amounts of N_2 in process air are oxidized at high temperatures to form NO_x. When waste-bound nitrogen is low, NO_x control is not generally required for mixed waste thermal treatment because thermal NO_x formation is typically low in most thermal treatment systems. NO_x emission levels have not been regulated under either 40 CFR Part 264 Subpart O incinerator regulations, nor are NO_x emissions specifically regulated under the MACT standards. NO_x emissions from most thermal treatment processes for most kinds of mixed waste are low enough to avoid triggering other NO_x emission regulations.

While most mixed waste treatment facilities have not emitted NO_x at levels approaching regulatory or public concern, there are some exceptions. Increasingly strict regulations have resulted the inclusion of NO_x control for the recently modified off-gas control system for the Forshungzentrum Karlsruhe alpha waste incinerator. Processes such as plasma torch melters that use air for the torch gas produce appreciable amounts of thermal NO_x, and thus have included NO_x control. There are some wastes that contain sludges of metal nitrates, and some aqueous liquid radioactive wastes contain high levels of nitric acid and metal nitrates. Treating these kinds of wastes that often contain percent levels of nitrates and nitric acid can produce appreciable amounts of NO_x, which can sometimes be mostly NO_2. For example, test results have shown that the off-gas from the calciner system at the New Waste Calcining Facility at the INEEL contains up to 4 vol% NO_x (dry, corrected to 7% O_2) which is 80 to 90% NO_2.

NO_x control technologies can be described as dry or wet processes and catalytic or noncatalytic processes (Dalton et al., 1992). Dry processes convert NO_x to N_2 by reacting the NO_x with other gaseous reagents. Dry technologies include selective catalytic and noncatalytic reduction as well as nonselective catalytic and noncatalytic reduction processes. Selective reduction processes react NO_x with ammonia or other nitrogen compounds. Catalytic processes can achieve a destruction efficiency between 85 and 95% while operating at temperatures between 500 and 800°F.

Noncatalytic processes can normally achieve destruction efficiencies of up to 70 or 80% at temperatures between 1600 and 2200°F. In nonselective processes, a fuel is mixed with gas containing the NO_x and burned to convert NO_x to nitrogen, water, or carbon dioxide. The fuel (such as methane, propane, or other hydrocarbons) is not selective and will react with other constituents, primarily oxygen. In fact, the presence of oxygen is generally required to initiate the NO_x-reduction reactions. Reaction conditions, including stoichiometries, temperatures, mixing, and residence times, need to be carefully controlled to achieve NO_x reduction while also efficiently oxidizing the added fuel.

Continuous Monitoring

Continuous emissions monitoring requirements based on the MACT Rule are shown in Table 7.7. This table also includes some assumed additions to meet expected permit requirements and for some specific process monitoring and control. Continuous monitors that are being developed for such species as Hg, other metals, and D/Fs are not included. While continuous Hg and metals monitors may be commercially available, these are still in field development and demonstration stages. At present, they do not meet reliability requirements, nor do they meet performance specifications in the United States. Operating permits and emission regulations are expected to continue to specify or at least allow the use of feed limits, monitoring and control of key system components, and periodic performance testing (manual sample collection and analysis) in lieu of continuous monitors that are not yet fully developed and demonstrated.

Continuous radionuclide emissions monitoring requirements are not included in Table 7.7. Radionuclide continuous monitoring for DOE facilities, including mixed waste treatment facilities, is assumed to be required according to American National Standard N13.1 revised as of January 1999 (ANSI, 1999). This standard specifies a graded approach for emissions sampling and monitoring. Using this approach, radionuclide continuous monitoring for most mixed waste treatment facilities should include at least two components. The first component is continuous, real-time monitoring using a constant air monitor (CAM) with alarm capability. The CAM should have sensors to detect the presence of all radionuclides (gaseous or aerosol beta, gamma, or alpha emitters) expected to be present in the facility. The CAM provides operators with a real-time indication of any radionuclide emissions above the CAM detection limits.

TABLE 7.7 Continuous Emissions Monitoring for Off-Gas Systems

Parameter	Monitoring Point	Comments
O_2	Near SCC outlet	Continuously monitor excess oxygen in the SCC to show that the SCC outlet O_2 stays above 3% (wet basis).
NO_x	Upstream of NO_x removal	Optional. Included only when the off-gas system has an NO_x removal stage, for process control of that operation, and to determine removal efficiency. Upstream NO_x measurements may not always be required.
Off-gas flowrate	Typically at the stack (or upstream of any other gas flows such as building ventilation air, if vented to the stack)	Continuous off-gas flowrate measurement is required to ensure adequate residence time in the SCC.
O_2		For use in making oxygen correction calculations for pollutant measurements.
CO		The MACT Rule allows continuous CO or continuous THC monitoring. Continuous THC monitoring is typically preferred because CO monitoring is typically less costly and less maintenance intensive.
THC		Continuous THC monitoring may also be required by regulators or may be used for process monitoring/control or for added stakeholder assurance.
PM		Required for compliance to the MACT Rule, but implementation of this requirement is delayed until PM monitors can demonstrate compliance to applicable performance specifications.
CO_2		Primarily for information only, and for determining combustion efficiency.
NO_x		NO_x monitoring is not required by the MACT Rule. If state and local regulations and the operating do not require NO_x monitoring, then this may be eliminated.
HCl		HCl monitors are commercially available and have been used for many years in the U.S. Cl_2 monitors have not yet been accepted by EPA for compliance use in the U.S. The alternative of feedstream Cl limits and monitoring of scrubber and other systems is used instead of total HCl and Cl_2 emissions monitoring. The use of HCl monitoring provides continuous process control data for the acid scrubber and assurance of acceptable total Cl emissions if Cl_2 emissions are low compared to HCl emissions.

CAM detection limits are typically too high to provide a record to show that radionuclide emissions are within regulatory and facility limits. The second component of radionuclide emissions monitoring, which is usually required for mixed waste treatment facilities, includes continuous sampling to collect radionuclides expected to be present in appropriate collection media. High-efficiency filters are used for collecting particulate matter, while other media such as liquid impingers or carbon filters can be used for gasesous radionuclides such as tritium (in water vapor) or radioactive isotopes of iodine or chlorine. Periodic retrieval and offline analysis of these collection media provide a much more sensitive, although time-integrated and time-delayed, record of compliance with radionuclide emission limits.

The use of optional CEMs such as HCl, Cl_2, Hg, and metals CEMs should be considered based on specific advantages and disadvantages. The tangible capital and operating costs may be outweighed by other less tangible issues. These issues include:

- Potential for using some optional CEMs for compliance instead of sometimes restrictive feed limits for total Cl, Hg, and various metals. However, if these optional CEMs are used for verifying compliance, then when these CEMs incur planned or unplanned maintenance, shut-downs, or upsets, the treatment facility would need to automatically shut down. These optional CEMs are generally less well demonstrated, may not meet applicable performance specifications, may not even have approved and standardized performance specifications, and can be more prone to upset conditions or maintenance than more routinely used CEMs.
- Added knowledge of operating conditions for better process control, even if the CEMs are not used for compliance monitoring. This can be useful for facility operators to diagnose system performance and make adjustments to better maintain system performance within operating limits.
- Generation of emissions information on a continuous, ongoing basis for providing to stakeholders, even if the CEMs are not used for compliance monitoring. This potential two-edged sword could improve stakeholder acceptance of the treatment process, but may also cause concern at times when the CEMs are either offline for maintenance or erroneously report higher emissions.

Target: Zero Emissions

Operation of thermal and non-thermal treatment systems with “zero emissions” is not realistically possible using current technologies because of the generation of effluent gas that typically contains at least some amounts of noncondensable gases such as N_2 and O_2, which can contain some contaminants that cannot be 100% removed. The most technically feasible approach for “zero emissions” or “zero uncontrollable emissions” is to minimize the volume of off-gas to the extent possible; minimize the amounts of any organic, metal, and radionuclide contaminants in the off-gas; and then prevent release of the off-gas to the atmosphere until adequate analysis is completed that demonstrates that pollutant emissions are within regulatory limits. Methods that can be used to approach this concept of zero emissions include:

1. Oxygen instead of air for combustion can reduce off-gas flowrates by up to about 75%, by reducing or eliminating nitrogen in the off-gas. This much volume reduction is not feasible for higher-heating-value organic wastes because oxygen-firing can produce temperatures too high for even refractory-lined equipment. O_2-fired combustion can more efficiently destroy organics. The use of O_2-fired combustion or O_2-enriched combustion is commercially available but not in wide-spread use because higher safety hazards and higher costs usually outweigh the benefits of lower off-gas flowrates and improved combustion.
2. Electrical heating or indirect heating for treating low-heating-value wastes can lower off-gas flowrates by up to 50%. This is one of the advantages that the various versions of plasma, electric-arc, and joule-heated melter treatment technologies have over classical incineration systems that co-fire the waste with auxiliary fuel such as natural gas or kerosene. Higher capital and operating costs, and potentially higher emissions of metals and radionuclides that need to be controlled in the off-gas system, can outweigh the benefits of lower off-gas flowrates, but other benefits such as an improved and lower-volume final waste form can increase the desirability of melter technologies.

3. Using highly efficient and reliable off-gas control systems to remove constituents of concern to reduce emissions to orders of magnitude below regulatory limits. This is not generally done because there is no regulatory requirement to incur the added capital and operating costs. However, in cases where there are public acceptability concerns even when the facility meets regulatory limits, lowering emissions to levels well under regulatory limits may be worth the added cost.
4. Segregation of organic waste materials that do not require treatment to destroy the organics can proportionately lower off-gas flowrates. Consequences of this method include increased costs and hazards associated with characterizing and segregating wastes, and larger-volume and less-uniform final waste forms for the organic materials segregated from the feed.
5. Segregation of waste streams or waste items that contain specific contaminants can prevent those contaminants from evolving to treatment system off-gas. These items include elemental mercury, lead shielding, electronic components, and materials that contain tritium or carbon-14. Alternative storage or treatment options for these items may be necesssary.
6. Partial, rather than complete, oxidation of organic material in waste streams can proportionately lower off-gas flowrates. Consequences of this method include larger-volume and less-uniform final waste forms, and an increased potential for residual hazardous materials to be retained in the final waste form.
7. Evaporation of directly injected water spray for cooling, rather than cooling by adding cool air, can reduce off-gas flowrates by up to 90%. Most state-of-the-art designs for off-gas control systems already incorporate water or scrubber spray evaporation for cooling to obtain this and other benefits such as fast temperature quenching to limit synthesis of D/Fs in the off-gas system.
8. Lower-temperature (non-thermal) treatment processes can lower the amounts of hazardous metals and radionuclides that are volatilized from the wastes during treatment.
9. Off-gas retention until analyses verify that off-gas emissions are within regulatory limits will prevent emissions of any uncharacterized off-gas.
10. CO_2 removal from the off-gas via absorption, liquefaction, solidification, or through photosynthesis can lower off-gas emissions by over 90% when used in combination with O_2-fired combustion. This could also lower emissions of ^{14}C, which is not readily controlled by any other commercially available off-gas control technology.

All but two of the above-listed methods to reduce off-gas flowrates are commercially available and demonstrated for mixed waste treatment. Oxygen enrichment has been used in various processes and is technically viable. Electric heat input, such as via indirect heating or through the use of electrically heated melters (joule-heated melters or plasma arc melters), is also technically viable for waste treatment. Waste treatment systems based on electric melters are available from many vendors. Water-spray evaporation for cooling is more commonly used than air dilution cooling, mainly for the obvious reason that off-gas flowrates can be appreciably reduced, lowering the size, footprint, and cost of downstream off-gas control equipment.

The last two above-listed methods for approaching zero emissions (off-gas retention and CO_2 removal) are presently considered to be economically impractical, and have not been proven technically (Soelberg et al., 1998). Two conditions may increase future attention to, or use of, these methods. Increasing public concern over air emissions from waste treatment processes may provide sufficient need to retain off-gas emissions until practical, wider-ranging continuous and noncontinuous analysis can be made that demonstrate compliance to many, if not all regulated emissions. The ever-increasing concern about worldwide anthropogenic CO_2 emissions may eventually necessitate CO_2 removal from the off-gas in addition to or instead of off-gas retention.

Studies have shown, however, that pollutant emissions from hazardous and mixed waste incineration are very small in comparison with emissions from other sources. For example, hazardous waste incineration presently accounts for only 0.1% of the total D/Fs emitted in the United States (Bruce, 2000). Even if all D/F emissions from hazardous waste incineration in the United States were completely eliminated, a reduction in D/F emissions of only 0.1% would be achieved. The technical and cost challenges to further limit pollutant emissions from hazardous and mixed waste treatment need to be evaluated with respect to the potential benefits, as well as with respect to potential reductions in pollutant emissions from other anthropogenic sources such as utility power generation, metals industries, municipal waste incineration, transportation, backyard refuse burning, and even private use of small engines such as lawn mowers.

In the meantime, off-gas retention and CO_2 removal have not been included in mixed waste treatment off-gas systems or any final designs for new facilities. The implementation of a zero emissions philosophy to a degree that includes these methods depends on stakeholder and operator requirements, cost/benefit evaluations, and yet-to-be-proven technical feasibility.

Mercury Emissions Control Technologies for Mixed Waste Treatment

Under the MACT Rule, mixed waste treatment may require more extensive mercury control than has been required in the past or that will be required at most hazardous waste combustion facilities. For this reason, mercury control for mixed waste thermal treatment has recently been specifically evaluated (Chambers et al., 1998; Cole, 2000; Fellows, 1998; Soelberg et al., 1999; Young 1997). Extra attention to mercury control has been given in this chapter compared to control of other pollutants because of this unique need for mixed waste treatment, and because most other off-gas technologies are quite well addressed in other references (see the “For Further Information” section, and in particular Cooper and Alley (1994), Dalton et al., (1992), EER (1992), EPA (1991), Hesketh (1991), and IAEA, (1989).

Mercury is present in many mixed waste streams. Some mixed waste streams contain amounts of mercury used in certain chemical processes. Other mixed waste streams contain elemental mercury from such items as mercury thermometers and mercury switches, or even containers of liquid mercury. Mercury is also sometimes present in such forms as paints and pigments. Because mercury is already present in some mixed waste streams, practices such as limiting feedrates of mercury and limiting the amounts of mercury that are included in waste streams are less practical for mixed waste treatment than for treatment of other hazardous wastes. Mixed waste inventory estimates show that if some mixed waste streams are thermally treated, the off-gas could contain mercury in concentrations ranging up to 500,000 μg/dscm (dry, at 7% O_2). Facilities that need to comply with the MACT standards or similarly strict emission limits may require Hg removal efficiencies ranging up to 99.99% unless strict feed characterization, sorting, and blending are used to used to the limit Hg feedrate.

Several modeling and experimental studies have evaluated mercury speciation in thermal treatment off-gas. Off-gas concentrations of SO_2 and HCl, temperature, residence time, and initial mercury species can affect mercury speciation in off-gas streams. Both SO_2 and Cl can increase the formation of the oxidized species (Lausman and Lavely, 1997). Laboratory tests to investigate the kinetics of reactions of gas-phase elemental mercury with various off-gas constituents showed that elemental mercury was oxidized by HCl, Cl_2, NO_2, and O_2 in the presence of activated carbon (Senior et al., 1997). The same experiments showed that oxidized mercury was reduced back to elemental mercury by reaction with SO_2 and CO as well as steel surfaces. The authors concluded that it was impossible to ascertain how important the reduction reactions would be in a full-scale system.

Off-gas temperature can strongly affect mercury speciation. At gas temperatures above about 550 to 700°C, gaseous elemental Hg is thermodynamically and kinetically favored over all oxidized species, even in the presence of high HCl levels (Gaspar et al., 1997; Soelberg et al., 1997a; Widmer et al., 2000; Young, 1997). Mercury speciation at the outlet of typical secondary combustion chambers that operate at temperatures of 1000 to 1200°C may be entirely elemental Hg. However, some of the elemental Hg may convert to oxidized forms as the hot off-gas is cooled in conventional off-gas systems. At temperatures below 550 to 700°C, $HgCl_2$ is thermodynamically favored, but not kinetically favored, even when there is excess HCl. In contrast, the gas-phase reaction of mercury with Cl_2 is fast even at temperatures as low as 10°C (50°F). In one laboratory study, as little as 2 ppm Cl_2 was enough to oxidize half the elemental mercury in about 1 second, starting with a mercury concentration of 0.012 ppm (100 μg/m^3), (Senior et al., 1997).

Mercury speciation between Hg and $HgCl_2$ can vary widely in different thermal treatment systems because of expected nonequilibrium conditions at temperatures below 550 to 700°C, and because mercury speciation depends not only on temperature and HCl, but also Cl_2 and other gas constituents. Equilibrium models have shown that other species in addition to Hg and $HgCl_2$ (such as HgO) are not thermodynamically favored at most off-gas conditions.

Mercury control technologies addressed in the following subsections include wet scrubbing, adsorption on activated carbon, and removal by amalgamation with gold. The EPA's MACT Rule database and several other references contain some data on efficiencies of mercury removal from hazardous waste incinerator off-gas by wet scrubbers, carbon beds, and carbon injection (Chambers et al., 1998). In addition, some vendor recommendations are available on the use of activated carbon adsorption. Mercury removal efficiency data for the gold amalgamation filter is limited at this time due to the developmental stage of this technology.

Hg Control Using Wet Scrubbing

Wet scrubbing is commonly used in thermal process off-gas systems for controlling particulate matter and acid gases. If wet scrubbers in existing mixed waste incinerator off-gas systems could provide the necessary mercury control with minimal modifications, then major retrofits could be avoided. However, based on data currently available, mercury removal efficiencies for traditional wet scrubbing can vary from less than 10% to over 99% (Table 7.8).

TABLE 7.8 Mercury Removal Efficiencies for Wet Scrubbers

Ref.	Hg Removal Efficiency (%)	Comments
Krause (1995)	30–70	Coal-fired power plants
Chang and Owens (1994)	20–>90	Field measurements at full-scale wet scrubbers
Vidic et al. (1997)	8–72	Removal from flue gas desulfurization (FGD) systems
Siret and Eagleson (1997)	Elemental and ionic Hg removal rates >90%	Wet scrubbing process utilizing 2 scrubbers in series; 1 at low pH and 1 at high pH
Livengood and Mendelsohn (1997)	~10–>80	Field tests conducted by DOE/EPRI in wet FGDs
Meij (1991)	Avg. removal of 52, 60, and 75	Study conducted in the Netherlands, Germany, and Sweden, respectively
EPA (1997a)	20–99.9	APC systems include venturi scrubbers, packed-bed scrubbers, wet electrostatic precipitators (ESPs), and ionizing wet scrubbers
EPA (1997a)	8–94.4	Dry-wet systems that include wet scrubber components and also dry components such as ESPs, fabric filters, cyclones, dry scrubbers, and waste heat boilers
EPA (1997b)	>90	For soluble species of Hg such as $HgCl_2$ and HgO; and for a 3-stage wet scrubbing system
Connett and Connett (1992)	>90	Data from incinerator in Basel, Switzerland (1989)

Such a wide variation in mercury removal performance is possible because many different factors can affect mercury removal thermodynamics, mass transfer, or kinetics for different system designs and operating conditions. Any of several different factors can dominate at different times in different systems. These factors include:

- Hg concentration and speciation in the scrubber inlet gas (which in turn depends on Hg feedrate, gas temperature, cooling rate, composition, etc.)

- Scrubber design (gas and liquid residence time, scrub solution turbulence in scrub tank, etc.)
- Scrubber operating conditions (temperature, scrub solution pH, scrub solution recycle-to-discharge ratios, PM and acid gas concentrations and removal efficiencies, use of reagents and additives, etc.)
- Any treatment or filtration of recycled scrub solution that can affect the solubility of Hg species in the scrub solution or the phase separation of suspended solids or suspended elemental Hg from the liquid water phase

While elemental Hg is thermodynamically favored over other species at elevated temperatures, $HgCl_2$ is favored at low temperatures typical of wet scrubbers when there is sufficient Cl in the waste feed. Most hazardous wastes have sufficient Cl for reaction with Hg to form $HgCl_2$. When the off-gas is quenched relatively slowly, as in a heat recovery boiler, then there may be sufficient residence time at temperatures up to 500 to 750°C such that thermodynamics and kinetics favor conversion of Hg to $HgCl_2$. However, most mixed waste treatment off-gas systems quench the off-gas rapidly, mainly to minimize D/F formation. The rapid off-gas quench slows the conversion of Hg to $HgCl_2$ such that when the off-gas enters the wet scrubber, elemental Hg may still persist rather than react to form $HgCl_2$. $HgCl_2$ is highly water soluble, but Hg is not. Wet scrubbers can have high total Hg removal efficiencies if they follow slow off-gas cooling where the conversion of Hg to $HgCl_2$ is high. Wet scrubbers that follow rapid quench systems may have low total Hg removal efficiencies because of limited conversion of Hg to $HgCl_2$.

Some wet scrubber conditions, such as low pH or oxidizing additives such as sodium sulfide or sodium hypochlorite, may improve the removal of elemental Hg by chemically reacting with Hg to form solid or water-soluble Hg species. Then, the wet scrubber removal efficiency for Hg will depend on the effectiveness of the Hg oxidizing reactions, and on the effectiveness of the scrubber system to separate the dissolved and suspended Hg species from the scrub solution before the scrub solution is recycled back to the off-gas. In radioactive systems, scrub solution discharge-to-recycle ratios are typically very low to minimize the amounts of secondary waste production. Dissolved or suspended Hg species can be re-entrained into the off-gas when the scrub solution is recycled to the scrubber or to the quench, unless the recycled scrub solution is treated or filtered to remove Hg species from the scrub solution.

Hg control by wet scrubbing may only be moderate (ranging from 10 to 90%), unless specific capabilities such as scrub solution additives, low pH scrubbing, or scrub solution filtration are used. Moderate Hg control in wet scrubbing, however, may be adequate for mixed waste thermal treatment for many low-Hg waste streams and when the input waste can be sorted to remove items that contain Hg. Reliance on wet scrubbing for even moderate Hg control is not recommended without facility-specific Hg wet scrubbing efficiency data under expected facility operating conditions, and without some understanding, monitoring, and control of parameters such as those listed above that can affect Hg control in wet scrubbers.

Hg Control Using Carbon Adsorption

Carbon adsorption of mercury can be accomplished by (1) injecting dry carbon with or without other dry sorbents into the off-gas upstream of a PM control device (typically a baghouse), or (2) using a fixed or moving bed of granular carbon through which the off-gas flows. The effectiveness of carbon adsorption depends on many different factors, including mercury concentration and speciation, pre-treatment of carbon (such as sulfur impregnation), operating temperature, sorbent particle size, residence time, and sorbent capacity.

Temperature can significantly affect carbon adsorption. Most carbon injection and carbon bed adsorption studies have shown that the adsorptive capacity of the carbon decreases with increasing operating temperature. Mercury speciation affects carbon adsorption because while carbon readily adsorbs oxidized Hg species, elemental Hg is not readily adsorbed. Impregnation of the carbon with sulfur or iodine allows the oxidation of elemental Hg to improve the total Hg adsorption. Impregnated carbon is limited by temperature even more than untreated carbon because both sulfur and iodine will tend to volatilize at higher temperatures. The temperature effect on impregnated carbon is also influenced by the method of impregnation.

One study determined that the capacity of the carbon increased with the concentration of the mercury in the gas, indicating that there was better carbon utilization when exposed to the greater adsorption driving force provided by the higher concentration (Livengood et al., 1994). The adsorptive capacity of the carbon for mercury at low temperatures and higher inlet concentrations of mercury was nearly double its adsorption capacity at the same temperature but about half the inlet mercury concentration. At low concentrations of mercury in the off-gas, the adsorption process could become mass transfer limited and reduce mercury removal efficiency. When the system is mass transfer limited, using smaller carbon particles can improve mercury removal.

Hg Control Using Carbon injection

Activated carbon injection (ACI) has been used in some waste incineration plants (mainly in Europe) for controlling mercury or D/F emissions. The activated carbon injection and gas flow characteristics must be controlled to allow proper mixing, temperature, and contact time. Baghouse collection of the spent injected carbon affords increased contact time with mercury in the flue gas (thus enhancing removal) because the injected carbon particles that are captured on the bags can continue to adsorb mercury from the gas that flows through the bags. Carbon injection systems can be added relatively easily to off-gas systems that are already equipped with baghouses for PM removal. The addition of carbon injection adds little to the overall pressure drop of a baghouse. These features make carbon injection more attractive than carbon beds for industries such utility power generation where baghouse PM control is common, off-gas flowrates are large, and mercury concentrations are low (thus, removal efficiencies above 90% are not required).

Carbon injection systems typically operate at temperatures between 150 and 200°C (300 and 400°F). Few systems operate at temperatures less than 150°C to avoid moisture condensation in downstream PM removal equipment, and the mercury adsorption capability of the carbon is significantly decreased above 200°C. At temperatures between 150 and 200°C, the Hg removal efficiencies for carbon injection systems can vary from 10 to 100% as shown in Table 7.9.

TABLE 7.9 Reported Mercury Removal Efficiencies for Carbon Injection Systems

Ref.	Reported Hg removal efficiency (%)	Comments
Connett and Connett (1992)	40–94	ACI used at a Zurich, Switzerland, incinerator
Connett and Connett (1992)	>87	Activated carbon injection
EPA (1997a)	97.4–97.9	For dry-wet APC systems that include carbon injection
Krishnan et al. (1996)	>90	ACI followed by a fabric filter in municipal waste combustors (MWCs)
Lausman and Lavely (1997)	Increased removals from 10 to 20%, up to 50–60%	Through addition of carbon injection to an APCS
Lausman and Lavely (1997)	100 and 80, respectively	Injected I- & S-impregnated carbons
Roeck (1996)	At a feed rate of 0.12 lb Hg per hr, a removal efficiency of 97% was achieved with carbon injection system	Extensive testing of carbon injection completed at Waste Technologies Industries, a hazardous waste incinerator in Ohio

The maximum expected capacity of Hg on carbon in carbon injection systems depends on many variables. The maximum design Hg capacity recommended by at least one vendor is 1 wt% (1 g Hg per 100 g carbon) for activated, sulfur-impregnated carbon.

Hg Control Using Fixed-Bed Carbon Adsorption

In a typical fixed-bed carbon adsorption system, the flue gas flows through a vessel packed with a specified depth of carbon granules. The bed and packing are designed to limit the linear velocity of the off-gas in the bed to increase the contact time with the carbon. Due to the increased contact times and typically lower operating temperatures, better removal efficiencies can be achieved than for carbon injection. At a residence time of 10 s in the carbon bed, virtually all of the mercury can be removed (NUCON, 1995). Mercury removal efficiencies of essentially 100% have also been reported by Livengood et al. (1994).

Fixed-bed carbon adsorption is less common than carbon injection, and there is less reliable performance data. Data used to support the proposed MACT Rule ranges from 76.2 to 92.7% mercury removal efficiency for a dry off-gas system that included air dilution cooling, dry sorbent injection, fabric filtration, HEPA filtration, and fixed-bed carbon adsorption (EPA, 1997a). Vendors recommend maximum operating temperatures of around 65°C. Because of the use of pretreated carbons, fixed-bed carbon adsorption is more temperature limited than carbon injection, where carbon pretreatment is less common.

Fixed-bed carbon adsorption is most applicable to processes that generate small off-gas flowrates with high off-gas mercury concentrations, at lower off-gas temperatures. While existing mixed waste incinerator systems have relatively low off-gas flowrates and may have high mercury concentrations, off-gas temperatures are typically higher than vendor-recommended maximum limits. New carbon pretreatment methods have been able to raise recommended temperature limits to over 100°C (Korpiel and Vidic, 1997).

There are several uncertainties or potential limitations that may need to be resolved before using fixed-bed carbon adsorption for Hg control in mixed waste treatment systems. Pressure drop associated with the fixed beds is a necessary evil, but it can be minimized through appropriate design. Other potential limitations to using carbon bed adsorption in mixed waste treatment systems include the initial capital cost, generation of a potentially radioactively contaminated secondary mixed waste (carbon contaminated with mercury, radionuclides, and possibly other hazardous compounds), and installation and operation in a radioactive process.

Carbon bed replacement may be infrequent because of the high expected loading of mercury adsorption on pretreated carbons, as long as carbon life is not limited by other factors. Carbon bed capacity for Hg may even be large enough such that some systems can be sized to last for the planned lifetime of the facility. Factors that might limit the lifetime of a carbon bed to a duration less than expected based on the Hg capacity include (1) depletion of sulfur impregnation over time, (2) physical degradation of carbon particles, (3) buildup of particulate matter in the carbon bed, (4) adsorption of other off-gas contaminants such as trace organics or radionuclides to a limit that is reached before the Hg capacity limit is reached, and (5) regulatorily specified bed replacement frequency that is more frequent than it would be if based on the Hg capacity of the bed.

The theoretical equilibrium adsorption capacity of one type of vendor-supplied carbon is 85 g mercury per 100 g adsorbent (85 wt% capacity). However, achieving that level in commercial applications is impractical because an extremely long contact time would be required for diffusion and adsorption of the mercury into the carbon pellets. Dynamic adsorption capacity data obtained by carbon vendors suggests that a typical design capacity of carbon for mercury is 20 wt% of the carbon. Some facilities have reported over 23 wt% capacity at the adsorber inlet for high mercury concentrations in the off-gas (NUCON, 1995).

Hg Control Using Gold Amalgamation Filter

Mercury can be removed from off-gas streams by reversible sorption of mercury on noble metal sorbents (typically gold) coated on a support media such as alumina. Because of the affinity of gold for mercury (regardless of Hg speciation) mercury removal can be as high as 99.99% (Roberts, 1995; Roberts et al., 1998), and effluent mercury concentrations in the treated off-gas have been reduced to less than 8 $\mu g/m^3$ (Fellows, 1998). Operating temperatures up to 180°C (350°F) are possible, and the pressure drop through the unit can be low. Tests indicate that mercury removal is independent of mercury speciation, water, and HCl in the flue gas. The gold can be regenerated by taking the filter bed offline and thermally desorbing the mercury into a small flowrate of purge gas (ADA, 2000). The purged mercury, at very high concentrations in the purge gas, can be largely recovered as liquid mercury upon cooling. Remaining mercury in the purge gas can be vented through a second gold amalgamation filter that is online while the first filter is being regenerated.

Gold amalgamation appears to be a promising alternative for controlling mercury emissions from mixed waste thermal treatment processes because of the high temperature limit, filter media regenerability, high mercury removal efficiency, and small-volume secondary wastes.

Hg Control Cost Comparisons

Installation, operation, and life-cycle costs were estimated for a hypothetical mixed waste thermal treatment facility so that the different mercury control technologies (carbon injection, carbon bed, and gold amalgamation) could be evaluated on the same bases. Performance and cost comparisons developed here are preliminary, based on the currently available information for the above technologies. Costs are based on a hypothetical mixed waste incineration or thermal processing facility that would operate 4032 hours per year based on operating 24 hours per day, 240 days per year, at 70% availability.

Two different average mercury feedrates to the treatment system were assumed: 10 g/hr and 1000 g/hr. All input mercury fed was assumed to evolve into the off-gas. All of the mercury was assumed to be elemental, although this is an adjustable parameter in the cost calculation spreadsheet. The assumption of 100% elemental Hg represents the most conservative scenario because of the need to use sulfur-impregnated carbon adsorbent, which is 10 times more expensive than untreated carbon. No credit was taken for possible removal of some of the mercury in other off-gas system components, such as wet scrubbers, that may be located upstream of the mercury control technologies evaluated here. Three off-gas flowrates were assumed for sizing the equipment: 5000, 10,000, and 20,000 acfm. These off-gas flowrates encompass typical mixed waste incinerator off-gas flowrates.

The target mercury concentration in the treated off-gas was 10 μg/dscm (at 7% O_2), providing a safety factor of 4.5 below the MACT Rule limit of 45 μg/dscm for new facilities. At lower mercury concentrations, the removal efficiencies may be more mass transfer limited, and at the same time, less mercury has to be removed to meet the target concentration. It was assumed for simplicity that any reduction in removal efficiency at lower concentrations was equal to the reduced removal efficiency needed to meet the target mercury concentration.

Numerous cost estimation factors were employed in the capital cost calculations. These factors, including the adjustments for higher costs for installation and operation of radioactive mixed waste processes at DOE locations compared with nonradioactive commercial facilities, were obtained from Feizollahi Quapp (1996). These factors were percentages of other various cost components. Equipment and installation cost factors were percentages of the equipment purchase cost and included electrical (15%); mechanical support, instrumentation, and installation (30% each); and connecting ductwork (10%). Facility construction costs included a factor for indirect costs at 29% of the building, structure, and equipment costs. Additional facility capital cost factors were percentages of the facility construction costs and included design (25%), inspection (7%), project management (10%), construction management (17%), and an allowance for project scope change or management reserve (10%). An additional factor for contingency was included in the total installed capital cost at 25% of the installed facility capital costs.

Operating costs were estimated based on several components and assumptions. Labor was assumed for all systems to consist of one operator per shift at $140,000 per person-year. The cost for carbon was calculated using $5 per pound for sulfur-impregnated carbon. No consumable materials were included in the costs for the gold amalgamation filters because the gold filters can be regenerated and reused. Annual maintenance, spare parts, and replacement equipment was estimated at 10% of the equipment purchase cost. Maintenance labor was estimated as 250% of the cost for spare parts and replacement equipment. A contingency factor was added in as 25% of the subtotal of all of the other operating costs.

Total life-cycle costs for each of the systems include the total installed capital costs, D&D costs at $450 per square foot of the structure in question, and the total operating expenses over an assumed 10-year operating life. Any handling, treatment, or disposal costs for spent carbon or other secondary wastes that would be generated from these mercury control systems were excluded from these estimates. Spent carbon disposal costs may be significant, but at present are very uncertain because of the potentially mixed waste nature and conflicting waste codes that could be applied.

Carbon Injection Capital Costs

Table 7.10 shows the cost estimates for carbon injection control of mercury for each of the assumed mercury concentrations and off-gas flowrates. The maximum mercury adsorptive capacity of the carbon used in carbon injection was assumed to be 1 wt% of the carbon, per vendor recommendations. The amount of carbon injected did not vary when the mercury feedrate did not vary, although the mercury concentration and amount of mercury that had to be removed to meet the target mercury concentration varied when the off-gas flowrate varied. Therefore, estimated costs were constant regardless of off-gas flowrate for each of the assumed mercury feedrates.

TABLE 7.10 Capital and Operating Cost Estimates for Carbon Injection Adsorber Systems in 1997 U.S. Dollars

Feedrate of Hg to Thermal Treatment System, (g/hr)	10	1000
Flowrate (acfm)	5000–20,000	5000–20,000
Equipment type	Bulk bag	Silo
Equipment cost ($ million)	0.050	0.30
Area of structure (ft)	260	260
Building cost ($million)	0.442	0.442
Total installed capital cost ($ million)	1.5	3.0
Carbon injection rate (lb/h)	3	221
Annual cost for injected carbon ($ million)	0.044	4.4
Annual operating cost ($ million)	0.26	5.9
Carbon waste generated (lb/yr)	12,000	890,000
Total lifecycle cost ($ million)	4.2	62

For the lower mercury feedrate case, a bulk bag carbon storage/addition system was considered adequate. This system had a much lower life-cycle cost compared to the silo carbon storage/addition system that was necessary for the higher mercury feedrate. While the mercury feedrate varied by a factor of 100x for the two cases, the feedrate of carbon changed by only 74x. This is because some of the inefficiencies that limit carbon adsorption were considered relatively larger for the lower mercury feedrate case than for the higher mercury feedrate case. Retrofits of installations that do not already include an adequately sized baghouse for PM removal would require a baghouse, but this was not included in the present calculations. Inclusion of a baghouse would increase the equipment cost by $8/acfm, with associated cost increases factored into other cost components. A baghouse addition to the low mercury feedrate case would increase the equipment costs by 80 to 320%. A baghouse added to the high mercury feedrate case would increase capital costs by 13 to 53%. Operating costs and total life-cycle costs would also increase by varying amounts.

The total installed capital cost for the low mercury feedrate case was $1.5 million, while the total installed capital cost for the high feedrate case was twice as high at $3 million. This installed cost included costs for the carbon injection system (carbon storage unit, structural steel frame, volumetric screw feeder and suction funnel, eductor, blower package, electric hoist and trolley, and standard instrumentation) and costs associated with system design, construction, and installation. The building cost was assumed to be the same for both cases because the footprint of the added equipment was considered equal in both cases. While the cost for injected carbon injection varied in proportion to the mercury feedrate variation (100x), labor costs did not vary proportionately; thus, the annual operating cost for the high mercury feedrate case was only 23x the annual operating cost for the low mercury feedrate case. The total life-cycle costs, over a 10-year life cycle, were \$4.2 million and \$62 million for the two cases, a difference of 15x.

Fixed-Bed Carbon Adsorption Capital Costs

Table 7.11 shows the life-cycle cost estimates for fixed-bed carbon adsorption control of mercury for each of the assumed mercury concentrations and off-gas flowrates. Per vendor recommendation, the maximum adsorptive capacity of the carbon for mercury was assumed to be 20 wt% of the carbon. The number of beds needed and the amount of carbon per bed for each facility were calculated by trying to achieve an adequate residence time, which was calculated as the depth of the bed divided by the superficial velocity through the bed. The beds, based on information from vendors regarding the typical size of beds currently used in industry, were assumed to be housed in cylindrically shaped vessels 10 ft in diameter and 15 ft in length. Each vessel holds approximately 13,500 lb carbon. A minimum residence time of at least 2.5 s was used to calculate the required number of beds needed for a given off-gas flowrate. The lifetime of each bed was calculated based on the rate of mercury throughput.

TABLE 7.11 Capital and Operating Cost Estimates for Fixed Bed Carbon Adsorber Systems in 1997 U.S. Dollars

Feedrate of Hg to Treatment System (g/hr)	10			1000		
Flowrate (acfm)	5000	10,000	20,000	5000	10,000	20,000
Number of beds	1	2	4	1	2	4
Equipment cost (\$ million)	0.15	0.30	0.60	0.15	0.30	0.60
Total installed capital cost (\$ million)	2.3	4.5	9.1	2.3	4.5	9.1
Design velocity (ft/min)	63.7	63.7	63.7	63.7	63.7	63.7
Nominal residence time (s)	2.83	2.83	2.83	2.83	2.83	2.83
Total mass of carbon in beds (lb)	13,500	27,000	54,000	13,500	27,000	54,000
Life of carbon beds (years)	26	53	106	0.26	0.53	1.1
# of times purchase full quantity of carbon over life of facility	1	1	1	38	19	10
Annual cost for carbon (\$ million)	0.007	0.014	0.027	0.26	0.26	0.27
Annual operating cost (\$ million)	0.25	0.33	0.48	0.56	0.63	0.78
Total lifecycle cost (\$ million)	4.9	8.1	14.4	8.0	11.1	17.4

Potential variations such as a separate bed of untreated activated carbon for dioxin and furan (D/F) and other trace organics removal, or using two or three banks of mercury-adsorbing beds in series for better capture efficiencies, were not included in the cost estimates. Other potentially significant cost variations excluded from this analysis were (1) shortened bed life due to factors other than Hg loading and (2) costs associated with treatment and disposal of spent carbon that may be contaminated with radionuclides or hazardous organics such as D/Fs.

TABLE 7.12 Capital and Operating Cost Estimates for Gold Amalgamation Filters Systems in 1997 U.S. Dollars

Off-Gas Flowrate (acfm)	5000	10,000	20,000
Cost for equipment (\$ million)	0.47	0.71	1.1
Installed cost with sorbent (\$ million)	3.7	5.1	7.3
Steam for regeneration (\$/yr)	3,000	35,000	54,000
Operating labor (\$/yr)	140,000	140,000	140,000
Maintenance/parts (\$/yr)	47,000	71,000	110,000
Total operating expense (\$ million/yr)	0.26	0.31	0.38
Annual capital expense (\$ million)	0.37	0.51	0.73
Total life-cycle costs (\$M)	6.4	8.3	11.1

Gold Amalgamation Filter Capital Costs

The estimated costs for the gold amalgamation filter are depicted in Table 7.12. ADA Technologies, Inc., provided cost estimates for a gold amalgamation filter system capable of removing and recovering mercury from 5000 acfm of flue gas. Equipment costs for the 10,000 and 20,000 acfm cases were estimated using the cost for the 5000 acfm case and a 0.6 power scale-up factor. In a parallel configuration that includes at least two filters, the filters can be readily regenerated without removal from the system. Costs per unit were essentially insensitive to the mercury concentration in the flue gas. The effects of entrained droplets of mercury in the off-gas were not considered. Because disposal costs for the mercury desorbed from gold amalgamation are not included in these estimates, there is no difference in the estimated operating costs or life-cycle costs for low and high mercury feedrates.

Secondary Wastes for Hg Control

Carbon injection will generate more spent carbon waste than carbon beds (per gram of mercury removed) because of the lower maximum mercury loading (1 wt% of the carbon) compared to that of carbon beds (20 wt%). In nonradioactive processes, this spent carbon can be retorted and recycled or otherwise disposed, depending on the concentrations of leachable mercury. Spent carbon from radioactive processes would not have the flexibility of retorting and reuse, due to the likelihood of radioactive contamination. This is especially true for carbon injection, wherein the baghouse used to collect the carbon is also the primary PM control device. The fate of spent carbon secondary wastes from radioactive processes is yet to be resolved, and depends on levels and types of radioactive contamination, and levels of other contamination such as from trace organics and metals that may also be collected by the carbon bed over its operating life.

Spent carbon can also contain adsorbed trace organics, including D/Fs. The EPA Phase IV Land Disposal Restrictions (LDR) rule requires that all Underlying Hazardous Constituents (UHCs) meet the applicable low Universal Treatment Standards (UTSs). Therefore, the secondary waste must be characterized to determine the applicable treatment standards and treated accordingly. If the spent carbon is contaminated with D/Fs above RCRA LDR treatment standard levels for D/Fs, the D/Fs in the waste would need to be incinerated, which would release mercury into the incinerator off-gas system, thus “undoing” the previous mercury adsorption process. Alternatively, the D/Fs could potentially be stripped with superheated steam and the effluent passed through an afterburner and then a caustic scrubber to neutralize the HCl. The facility that does this must be permitted for handling this toxic waste.

Secondary wastes from gold amalgamation will consist of recovered mercury and the spent ceramic-based sorbent. The initial sorbent is assumed to last for the lifetime of the facility. Final regeneration of the sorbent is assumed to be able to clean the adsorbent of mercury sufficiently such that the spent sorbent can be categorized as low-level radioactive waste and directly disposed. The recovered elemental mercury would likely be contaminated with radionuclides and would therefore require amalgamation to meet current LDR treatment standards for such waste.

Hg Control Conclusions and Recommendations

Performance data for wet scrubbing and gold amalgamation is insufficient to definitively determine mercury control efficiencies because of numerous parameters that may affect mercury removal in different systems. More information is needed to relate mercury control to potentially controlling parameters such as mercury speciation and concentration, off-gas temperature and composition, wet scrubber design and operation (pH, residence time, reagent additive type and quantity, recycle ratio, phase separation, Hg revolatilization, etc.), and gold amalgamation removal efficiencies and regenerability over many cycles.

Given certain assumptions made in this study, capital costs for carbon injection are less than those for gold amalgamation and carbon beds. Operating costs are lowest for gold amalgamation. At low mercury feedrates, operating costs for carbon injection are lower than for carbon beds; but at high mercury feedrates, operating costs for carbon injection increase significantly above operating costs for carbon beds because of the high usage of carbon in carbon injection. Disposal costs for secondary wastes, such as the spent carbon and mercury desorbed from gold amalgamation, are not included in the present calculations because of their uncertainty. These disposal costs could further increase operating costs of each of the systems, especially for higher mercury feedrates and for the carbon adsorption systems (especially carbon injection).

Estimated life-cycle costs for the different mercury control technologies are compared in Table 7.13. At low mercury feedrates, life-cycle costs for carbon injection were less than those for carbon beds or gold amalgamation; but at high mercury feedrates, life-cycle costs for carbon injection were much higher than those for carbon beds or gold amalgamation because of the large differential in operating costs. Life-cycle costs for carbon bed adsorption were similar to those for gold amalgamation at low mercury feedrates; carbon bed life-cycle costs were higher than for gold amalgamation at higher mercury feedrates due to increased operating costs.

TABLE 7.13 Total Life-Cycle Cost Comparisons for Mercury Control Technologies Systems in 1997 U.S. Dollars

Feedrate of Hg to Treatment Process (g/hr)	10			1000		
Off-gas flowrate (acfm)	5000	10,000	20,000	5000	10,000	20,000
Carbon injection adsorption ($million)		4.2			62	
Fixed bed carbon adsorption ($million)	4.9	8.1	14.4	8.0	11.1	17.4
Gold amalgamation ($million)	6.4	8.3	11.1	6.4	8.3	11.1

Gold amalgamation for mercury control is not yet commercially available with reliable performance data for design and installation. Carbon adsorption systems are commercially available from several vendors, but secondary waste disposal continues to be a major concern — especially for carbon injection. Operating temperature limits can be a concern for treated carbon beds.

The fate of spent carbon that is contaminated with radionuclides, hazardous metals including mercury, and potentially hazardous organics including D/Fs is uncertain at this point, and needs to be more fully addressed if carbon adsorption is implemented in mixed waste treatment off-gas systems.

Off-Gas System Design and Capital Cost Estimates

Off-gas system design must be based on design and performance objectives such as those listed in Section 7.2 and estimates of input off-gas flowrates and compositions such as those tabulated in Section 7.3. Different stages of planning and design require increasingly detailed design information.

Process Simulations

Process simulations using a computational model allow quick comparisons of different design alternatives and evaluations of whether desired objectives can be achieved for a given design early in the design process. These comparisons can be used to assist decision-making, process design, and determinations of technical feasibility, and to identify areas of weakness in the process design. Various commercially available or private consultant/vendor computer models perform simulations based on thermodynamic equilibrium calculations. These models should generally be capable of estimating (1) off-gas system unit operation performance based on input parameters, bounding conditions, chemical equilibria; (2) mass balances that show input and output streams and compositions; (3) equipment size; and (4) energy balances. More advanced or specialized models that include kinetic calculations and non-equilibrium conditions are often necessary because chemical equilibrium conditions are often not achieved in off-gas systems due to kinetic or mass transfer limitations. The ability to link multiple unit operations such as exist in an off-gas system is needed for at least final design and for earlier evaluations of overall system performance. The ability to model solids handling processes such as particulate filtration that are not based on thermodynamic equilibria is also usually necessary.

Many different commercial and private process simulation models exist and have been employed in off-gas system design. Some examples are listed or used in various references (see also the "For Further Information" section) and in particular Dalton et al. (1994), Feizollahi and Quapp (1996), Liekhus et al. (1997), and Soelberg et al. (1998).

Some key results generated from the various process simulations and comparisons with actual performance data are listed below.

1. A well-designed and -operated off-gas system can meet all applicable emission regulations.
2. Equilibrium concentrations predicted by process simulations can be inconsistent with measurements from actual systems. Reactions, especially at low temperatures, are often limited by kinetics or mass transfer from reaching thermodynamic equilibrium in the off-gas system where residence time is measured in seconds or less. In these cases, predictions need to be made to better reflect observed data by limiting the extent of reaction, or by specifying a reaction temperature at which to calculate the equilibrium composition. For example, Hg control performance in off-gas systems suggests that speciation in off-gas often varies and is often not at chemical equilibrium. At temperatures exceeding 550 to 700°C, elemental Hg is thermodynamically favored under typical off-gas conditions. Hg speciation at a secondary combustor outlet, where temperatures can reach 1200°C, is predicted to be almost entirely elemental Hg based on chemical equilibrium. At temperatures below 550°C, $HgCl_2$ becomes thermodynamically favored in the presence of even small amounts of HCl. At temperatures between 400 and 550°C, $HgCl_2$ formation from reaction of Hg and Cl is rapid and can be described by equilibrium calculations, but the reaction is kinetically limited at lower temperatures (Senior et al., 1997). If a process simulation allows the Hg-$HgCl_2$ reaction to reach equilibrium in a low-temperature wet scrubber, then very little Hg would exist, and the process simulation would predict that the total Hg is readily scrubbed in the wet scrubber. However, this is not consistent with empirical data from many sources (Chambers et al., 1998; Soelberg and Chambers, 1997b). To make the process simulation better match reality, the minimum equilibrium temperature for the Hg-$HgCl_2$ reaction can be specified at a higher temperature (e.g., 550°C). The use of the higher temperature for Hg-$HgCl_2$ equilibrium calculations considers the rapid temperature quench and effectively "freezes" a significant portion of Hg as elemental Hg, even in excess Cl when $HgCl_2$ is thermodynamically favored at quench outlet temperatures.
3. The mass flowrate of the off-gas can increase, although the volumetric flowrate may decrease, as the off-gas is quenched from sometimes high secondary combustor temperatures to lower off-gas system temperatures. If water spray quenching is used, followed by moderate hot air dilution reheating, then the mass flowrate of the off-gas may increase by about a factor of 2.
4. Particulate in off-gas results from particles of feed material or fly ash entrained in the off-gas exiting the treatment unit, or condensation of volatile material when the off-gas is cooled in the off-gas system. The most conservative assumption assumes that all particulate formation from condensation occurs by homogeneous condensation, yielding submicron particulate with particle diameters less than 0.5 μm. Chemical equilibria also show that some condensed material can revolatilize if the off-gas is reheated for HEPA filtration. This can be a mechanism that allows some condensible material that would otherwise be retained as particulate matter to pass through typical HEPA filtration at temperatures as low as 100°C.
5. Particulate removal efficiencies should be based on estimated or measured removal efficiencies as a function of particle size. Example design removal efficiencies for an efficiently designed baghouse can range from 99.9% for particles equal to or larger than 0.5 μm particles to 99% for particles less than 0.5 μm.
6. Recycling scrub solution discharge to quench the hot off-gas at the inlet to the off-gas system can reduce the amount of scrub solution that is discharged. However, if the scrubber solution blowdown is not treated to remove dissolved and suspended solids (especially Hg species), then these

contaminants can be re-entrained as very small (submicron) particles when the water droplets evaporate. These small particles are especially difficult to capture in downstream particulate control equipment. The potential to increase emissions of material captured in a wet scrubber system by re-entraining the material into the off-gas should be considered in designs that minimize scrub solution discharge by recycling some of the discharge to the quench.

7. Mercury in the form of $HgCl_2$ can be captured in caustic or acidic wet scrubbers with efficiencies exceeding 99%, although elemental Hg is not very water soluble and not efficiently captured in typical caustic wet scrubbers.
8. Subcooling the off-gas to a temperature below its dewpoint can improve the collection of acid gases, particulate matter, and metals. It can also lower the total freshwater makeup requirements. Excessive off-gas subcooling to temperatures below 45 to 55°C may lead to undesireably high-energy requirements to condense water from the off-gas, and may cause undesireably large scrub solution discharge streams due to large amounts of condensate formed as the off-gas is subcooled.
9. Vendor-recommended maximum dissolved salt concentrations in scrub solution range around 10 wt%. Scrub solution discharge or treatment is necessary to keep the salt concentration below this limit to miminize the potential for solid deposits forming in the scrub system.
10. Off-gas reheating may be limited to a temperature about 20 to 30°C above its dewpoint, not to exceed a maximum temperature of 100 to 120°C, which may be an operational limit for Hg control in carbon beds. Using preheated air to blend with the saturated off-gas for reheating is a unique design that has potential advantages, including elimination of heater elements in contact with off-gas, and lowering of the blended off-gas dewpoint. Potential problems (such as corrosion and fouling from aerosols impacted on the elements) are eliminated when the heating elements are not in contact with the saturated off-gas. Also, any maintenance that is required for the heating elements can be performed in an area of lesser contamination than expected for the off-gas.
11. The use of a coarse prefilter, even after baghouse or wet scrubber particulate control, is recommended to better protect and increase the operating life of downstream HEPAs. A coarse prefilter can have removal efficiencies that range from essentially 100% of particles larger than 2 μm, to 70% for particles smaller than 0.3 μm.
12. HEPA filters can be certified for 99.97% efficiency for removing 0.3 μm particles. However, a more conservative efficiency of 99.9% or less should be assumed for each HEPA filter when there are multiple HEPA filters in series. This more conservative assumption was made to be consistent for multiple filtration steps in series (Burchsted et al., 1979) and to better account for nonidealities such as housing and frame warping, occasional moisture, etc. Even this more conservative efficiency model may be orders of magnitude higher than filtration efficiencies actually measured in some off-gas systems.
13. Properly designed and operated sulfur-impregnated carbon beds may be assumed to remove 99% of the total Hg still in the off-gas at the carbon bed inlet. While there is no data to indicate removal efficiencies for other pollutants, including trace organics and radionuclides, in sulfur-impregnated carbon beds, some removal of these trace pollutants should be expected. This can have the advantage of even lower emissions of these species, and the disadvantage of added contaminants in the carbon that could shorten the carbon bed operating life or complicate final disposal of the spent carbon.
14. Calculated (theoretical) decontamination factors (DFs, or ratios of influent mass to effluent mass) for PM and all metals except mercury can range up to 10^9 when multiple metals and PM removal devices are used in series. Baghouse DFs can range from 100 to 200. Wet scrubber DFs range up to approximately 300. Prefilter DFs range up to 10, and DFs for each HEPA filter for double HEPA filters range up to 1000 for each filter. Actual measurements for operating off-gas systems typically do not indicate such high DFs. The difference between calculated and measured DFs can be due, in part, to the insensitivity of measurements and/or the inability of successive PM and metals control devices to achieve such high DFs when the input concentrations of PM and metals become increasingly small.

15. Calculated DFs for Hg can range from 100 to 10,000, depending on the amount of $HgCl_2$ in the off-gas that can be removed in a scrubber and the use of sulfur-impregnated carbon beds for Hg control.
16. Replacement frequencies for HEPA filters range up to around once per 1000 operating hours (40 operating days for continuous operation).
17. Carbon bed replacement frequency can extend to thousands of operating hours or even for the life of the operating facility, assuming that factors other than Hg capacity of the carbon do not limit the carbon operating life.

Off-Gas System Equipment Size and Cost Estimates

Installed capital costs for the off-gas systems were estimated by Soelberg et al. (1998) for hypothetical high and low off-gas flowrate cases. The hypothetical off-gas flowrates and compositions for these two cases are shown in Table 7.14. The high-flow case is based on off-gas produced from a hypothetical rotary kiln incinerator that would treat mixed waste at a rate of 2150 lb/hr, using auxiliary fuel fired in a secondary combustion chamber and using air for combustion of waste and auxiliary fuel. The low-flow case is based on off-gas produced from a thermal treatment process such as a plasma arc melter that would treat mixed waste at a rate of 2150 lb/hr, using oxygen instead of air for waste combustion. The low-flow case also has assumed concentrations of HCl and SO_2 that are 10 times higher than those in the high-flow case.

TABLE 7.14 Input Off-Gas Conditions at the Outlet of the Secondary Combustion Chamber

Parameter	High-Flow Case	Low-Flow Case
Off-gas temperature (°F)	2200	2200
Off-gas flowrate (scfm)	6715	3429
Off-gas composition (by volume):		
Oxygen (%)	7	14
Nitrogen (%)	74	5
CO_2 (%)	8	30
H_2O (%)	10	48
CO (ppm)	10	10
NO_x (ppm)	4000	4000
HCl (ppm)	2500	25,000
Cl_2 (ppm)	5	100
SO_2 (ppm)	100	1000
Total (%)	100	100

Capital costs were estimated using vendor-provided purchase costs, equipment and system and footprint estimates, and installation cost factors. The estimated costs are expected to be representative but not exact because many design and operating details could not be included without a more specific treatment system scenario. Facility capital costs such as building, design, inspection, electrical, instrumentation, and management cost factors are generally consistent with those used in cost estimates for the ITTS study (Feizollahi and Quapp, 1996).

The capital cost estimates of the APCS alternatives for the high-flow and low-flow cases are shown in Table 7.15. The estimates are organized to separately show the major cost components: purchase costs of major equipment, other equipment and installation costs, building costs, indirect costs, and other facility capital costs. The costs of installation and other equipment and indirect costs are determined using cost factors. While slightly different cost factors and approaches for accounting for indirect and other facility costs can vary for different sites to estimate facility costs, this approach should provide representative cost estimates for planning and decision-making. Consistent with most installed capital

TABLE 7.15 Capital Costs for Conceptual APCS Alternatives in Millions of 1997 U.S. Dollars

Cost Factor	High Flow Case	Low Flow Case
Major equipment purchase cost:		
Partial quench spray tower	0.25	0.19
Baghouse	0.32	0.18
Full quench spray tower	0.04	0.03
Free-jet scrubber	0.16	0.12
Scrubber water chiller	0.13	0.09
Air heater	0.03	0.03
Carbon adsorbers	1.40	0.52
HEPA filtration system (includes prefilters)	0.38	0.19
Reheater	0.20	0.20
NO_x control	0.50	0.40
CEMs	0.17	0.17
Subtotal of major equipment purchase costs	3.58	2.12
Other equipment and installation costs:		
Electrical, 15% of equipment cost	0.54	0.32
Mechanical support, 30% of equipment cost	1.07	0.63
Instrumentation, 30% of equipment cost	1.07	0.63
Installation costs, 30% of purchase cost	1.07	0.63
Connecting ductwork, 10% of purchase cost	0.36	0.21
Subtotal of other equipment and installation costs	4.11	2.42
Building cost (at $1700/ft^2 for alpha-containment):		
Area of building housing APCS (ft^2)	5400	3090
Building cost	9.18	5.25
Subtotal of installed equipment and building:	16.87	9.79
Indirect Costs, 29% of total of building, structure, and equipment costs	4.89	2.83
Total Facility Construction Costs:	21.76	12.62
Other Facility Capital Costs:		
Design, 25% of facility construction costs	5.44	3.16
Inspection, 7% of facility construction costs	1.52	0.88
Project management, 10% of facility construction costs	2.18	1.26
Construction management, 17% of construction costs	3.70	2.15
Allowance for project scope change or management reserve, 10% of construction costs	2.18	1.26
Subtotal of other facility capital costs	15.02	8.71
Subtotal of installed facility capital costs:	36.78	21.33
Contingency, 25% of total installed capital costs	9.20	5.33
Total Installed Capital Cost	45.98	26.66

cost estimates for DOE facilities, the actual major equipment purchase cost is the smallest of all these cost components.

The largest single cost component is the “other facility capital costs” category. This cost category includes five key subcomponents: design, inspection, project management, and construction management. The design subcomponent includes both preliminary design and detailed design and is estimated at 25% of the facility construction cost for an alpha-facility. The inspection subcomponent includes engineering support during construction, and is estimated at 7% of the facility construction cost. The project management subcomponent is estimated at 10% of the facility construction cost and includes project management costs incurred both by the DOE and the site management and operations (M&O) contractor. Construction management (CM) is estimated at 17% of the construction costs, which is the sum of the equipment, building, and indirect costs. Construction management includes material and services procurement and control activities, which are typically handled by the site CM contractor. Allowances for project scope change or management reserve is estimated at 10% of construction costs.

Facility construction costs include the rest of the installed costs and include the purchase cost of equipment, installation costs, building costs, and indirect costs as defined below:

- *Major equipment purchase cost.* Cost estimates for the individual pieces of equipment that comprise the air pollution control system were primarily determined by soliciting budgetary costs from suppliers and vendors. Where this was not a practical option, engineering estimation methods were used and costs were scaled for time and capacity.
- *Other equipment and installation costs.* For systems that involve processing equipment, the allowance for electrical is 15%, mechanical support is 30%, and instrumentation is 30% of the equipment costs. Factors for installation costs and costs for connecting ductwork were also included in the equipment subtotal at 30% and 10% of the purchase cost, respectively.
- *Building and structure costs.* Building and structure costs are estimated by multiplying building unit costs by the space square footage allocated to each process unit. Assumed unit rates are applied to several categories of buildings. The category chosen for this study was that of an alpha waste processing area rated at \$1700/ft^2 for triple-confinement alpha cells. Building unit rates incorporate all material and labor needed for constructing the building shell including utilities, lighting, heating, ventilation, and air conditioning (HVAC), and site development costs.
- *Indirect costs.* Indirect costs, including subcontractor overhead and fee, are estimated at 29% of the total of equipment, building, and structure costs.

Because the costs are a planning-level estimate, a 25% contingency is also included. The contingency is applied to the total capital cost.

Off-Gas System Equipment Sizing Estimates

The major components of the air pollution control system contributing to the size of the housing required to contain the system were the baghouse, the spray quench towers, the HEPA filters, and the carbon adsorbers. All of the other process units were considered small factors in determining the total equipment footprint needed to estimate a building size in square feet. The footprint for the baghouse for the high-flow case was calculated to be roughly 900 ft^2. The baghouse footprint for the low-flow case was determined to be about 500 ft^2.

The estimated footprint for the Flanders HEPA filter system, including prefilters and two banks of HEPAs, was 320 ft^2 for the high-flow case and 160 ft^2 for the low-flow case. The carbon adsorption system using fixed beds in parallel was sized based on vendor information. For the high-flow case, calculations showed that six beds in parallel would be required to handle the gas flowrate, with each bed being 10 ft in diameter and 15 ft long, a footprint of 150 ft^2 per bed, and a total footprint of 900 ft^2. The low-flow case only required three parallel beds of the same size for a total footprint of 450 ft^2.

The partial spray quench tower was 100 ft^2 for the high-flow case and 50 ft^2 for the low-flow case. The estimated footprint for the full quench tower was 30 ft2 for the high-flow case and 25 ft^2 for the low-flow case.

The total footprint for the other pieces of equipment was assumed to occupy roughly 450 ft^2 for the high-flow case and 360 ft^2 for the low-flow case. This area includes the SCR at 150 ft^2; free-jet scrubber at 100 ft^2 for high-flow and 60 ft^2 for low-flow; scrubber water chiller at 100 ft^2 for high-flow and 50 ft^2 for low-flow; and heater and reheater at 100 ft^2 together.

The total equipment footprint was multiplied by a factor of two, to account for such space as the areas needed between each major equipment component, access around the equipment, and filter and adsorbent replacement space. Consideration was not given to how some equipment items may be physically located on decks or structures above other equipment, which may in fact be desirable not only to reduce footprint but also to avoid long or tortuous runs of interconnecting ducting. Costs for non-alpha-containment building space for control rooms, storage, laboratories, maintenance, and other activities were also not specifically itemized, but were be considered to be within the safety factor of two for the alpha-containment space. The total area of the alpha-containment building for the APCS is estimated at 5400 ft^2 for the high-flow case and 3090 ft^2 for the low-flow case.

Off-Gas System Capital Cost Estimates

The purchase costs for major pieces of equipment were based on data supplied by vendors. These costs are itemized below for each major component in the off-gas systems:

Item	Cost High-Flow Case	 Low-Flow Case
Partial quench tower	\$251,000	\$186,000
Baghouse	\$168,000	\$94,000
Full quench tower	\$44,000	\$32,000
Free-jet scrubber	\$160,000	\$117,000
Scrubber water chiller	\$125,000	\$90,000
Air heater	\$30,000	\$30,000
Prefilter/HEPA filters	\$189,000	\$94,000
Fixed-bed carbon adsorbers	\$1,404,000	\$520,000
Reheater	\$196,000	\$196,000
SCR for NO_x control	\$500,000	\$400,000
CEMS	\$166,000	\$166,000
O_2 monitors: \$7000 CO_2 monitor: \$5000 CO monitor: \$6000 NO_x monitor (2): \$20,000 THC monitor: \$12,000 Gas conditioner and pump: \$20,000 DAS: \$10,000 Heated sample line: \$20,000 Flow splitter: \$10,000 Stripchart recorder: \$5000 Regulators, fittings, etc.: \$5000 Instrument racks: \$5000 Off-gas flowmeter: \$1000 Pressure transducer: \$2000 *In situ* particulate matter monitor: \$25,000 Misc. fittings, valves, tubing, gages: \$13,000		

Figure 7.9 shows how each major component contributed to the total purchased equipment cost. The carbon adsorber beds, NO_x control unit, and HEPA filtration system are the largest contributors to the purchased equipment cost. For the carbon beds, the high-flow case was calculated to need six beds in parallel that are 10 ft in diameter, 15 ft long, with a carbon bed depth of 3 ft. The process simulation model assumed that the carbon beds had a removal efficiency of 99%. Thus, it was calculated that there would be 7.75 lb mercury captured in the beds per hour. At this capture rate and an assumed carbon adsorptive capacity of 20 wt%, the carbon beds were calculated to have a lifetime of 1800 operating hours before saturation. The cost of the carbon needed to achieve this removal would be on the order of \$404,000. This cost is rather high because the expected high percentage of elemental mercury dictates the use of sulfur-impregnated carbon. It was assumed that 99.6% of the mercury going to the carbon beds was elemental. The cost of impregnated carbon is about \$5/lb, compared to plain activated carbon which costs between \$0.50–1/lb.

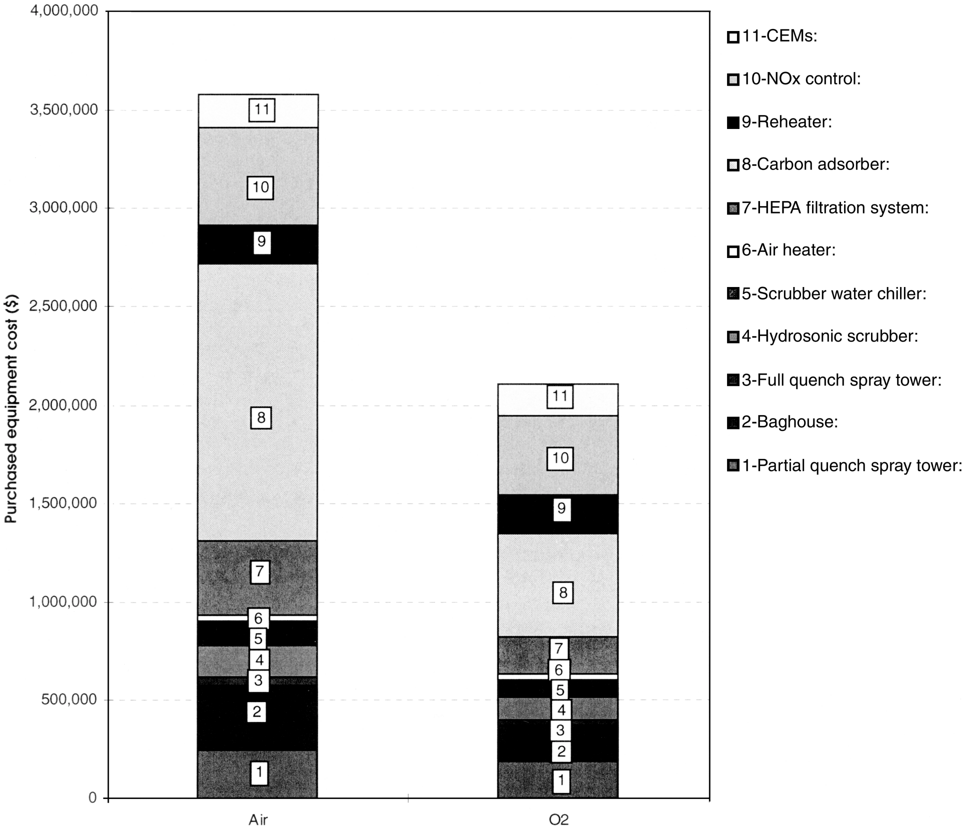

FIGURE 7.9 Breakdown of purchased equipment cost by major process units of the APCS.

The low-flow case, at half the off-gas flowrate of the high-flow case, needed only three beds of carbon of the same dimensions stated previously. The same assumptions of removal efficiency and adsorptive capacity were made as in the high-flow case. For this case, only 0.042 lb mercury would be captured in the carbon beds per hour. At this capture rate, the carbon beds would have a lifetime of 168,000 operating hours. Assuming 4032 hr per year as in the life-cycle costs, the carbon beds would have a lifetime of 42 operational years. The cost of the carbon to achieve this removal would be approximately $20,000. This cost is much lower than that of the high-flow case because much of the Hg was removed in the low-flow case in the scrubber upstream of the carbon beds and because the mercury was assumed to be 100% $HgCl_2$ because of the high HCl levels. Therefore, plain activated carbon can be used instead of impregnated carbon at a cost of about $0.50/lb.

The estimated installed APCS total capital cost for the high-flow case was about $46 million, and the installed APCS cost for the low-flow case was about $27 million.

Figure 7.10 shows the components of the total capital cost for the two systems modeled in this study. The largest cost component is the "facility capital costs" which include design, inspection, project management, construction management, and an allowance for project scope change or management reserve. Contingency and building costs are similar in magnitude and are the second and third largest cost components. The remaining three factors — indirect costs, equipment installation costs, and equipment purchase costs — are also roughly equivalent, although the actual purchase cost of major equipment is the smallest of all cost components.

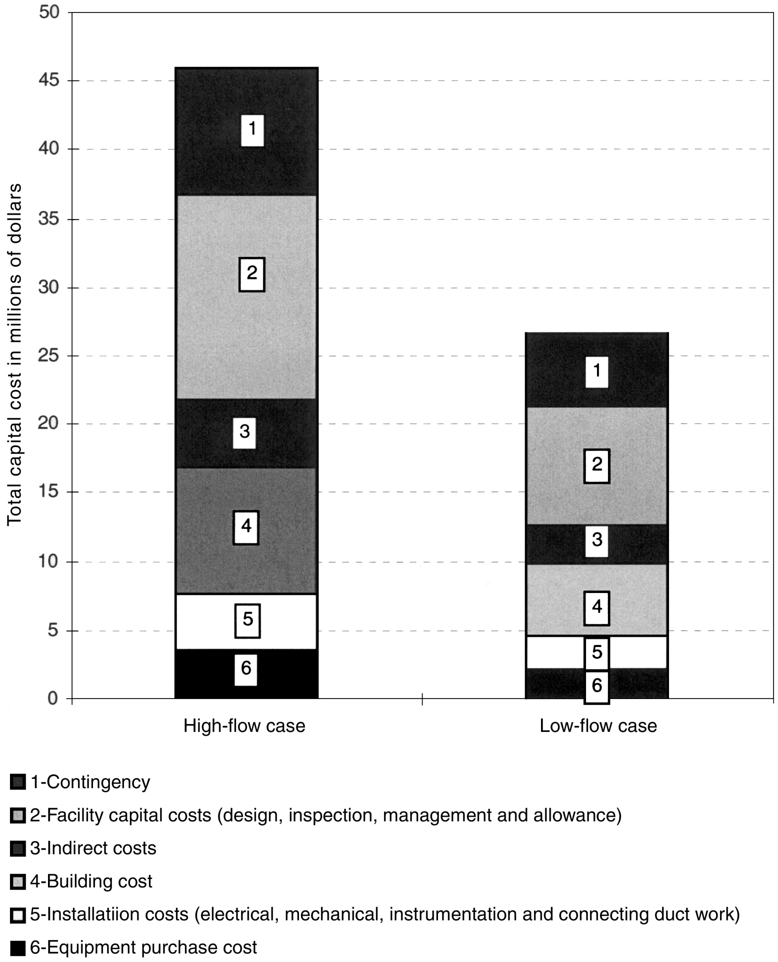

FIGURE 7.10 Breakdown of factors that determine total capital cost.

Capital Cost Sensitivity Studies

Many primary waste treatment processes do not produce large amounts of NO_x, although waste streams that contain some nitrates that can be a source of NO_x. Existing and proposed federal regulations for waste treatment do not include emission limits for NO_x, although state and local regulations can limit NO_x emissions. If NO_x emissions from the treatment process are not regulated or are within applicable emission limits, then the SCR reactor can be eliminated. The SCR is one of the largest single components of the APCS capital cost. Elimination of the SCR will decrease the APCS capital costs by 6 to 9%, as shown in Table 7.15. The capital cost for the high-flow case will decrease from $46 million to about $43 million, and the capital cost for the low-flow case will decrease from $27 million to $24 million.

Sensitivity studies can also show cost savings that would be realized without the carbon bed adsorbers because these are also a major cost item that can be eliminated if other Hg control technologies are available or if Hg control is not required. These savings are shown in Table 7.2 to be $9.3 million (20% of the total cost) for the high-flow case and $3.6 million (13% of the total cost) for the O_2 combustion case.

Conclusions and Recommendations

High-performance APCS designs of several varieties are available to meet performance requirements. Process simulations indicate that pollutant emissions can be controlled to within expected emission limits, and even below expected detection limits for some metals and PM, although Hg emissions control is still not well demonstrated. Many variables, including Hg levels in waste feeds and Hg speciation in the off-gas, can affect Hg control. The performance of Hg control technologies including sulfur-impregnated carbon absorption must be validated to provide the level of Hg control (sometimes up to 99.99%) needed if some Hg-contaminated mixed wastes are thermally treated. If such high Hg control efficiencies are not possible, then the Hg content in waste fed to mixed waste incinerators may need to be significantly limited to meet expected emission limits.

Process simulations are necessary for designing off-gas systems to meet design and performance objectives, determine equipment size and cost, determine masses and properties of influent and effluent streams, and evaluate potential off-gas system variations. Installed capital costs of an APCS for hypothetical low and high off-gas flowrate cases were estimated to be $27 million and $46 million, respectively. These installed capital costs are 6 times higher than the major and other equipment purchase costs, largely because of factors needed to account for costs associated with designing, constructing, and permitting DOE facilities (facility capital costs). The most costly control equipment in these hypothetical systems were fixed-bed carbon adsorbers, followed by the NO_x control unit and HEPA filters.

Issues that should be addressed in future APCS designs include:

1. Hg control technology capabilities and limitations
2. Optimization of off-gas cooling, reheat, and carbon adsorber temperature to prevent moisture condensation in HEPAs and downstream equipment while achieving desired Hg removal efficiency and minimizing secondary wastes
3. Optimization of prefilter, HEPA filter, and carbon bed media replacement frequency
4. Optimization of D/F control
5. Optimization of secondary waste amounts and properties
6. The impact that secondary waste treatment has on off-gas system alternatives
7. Validation of assumptions for PM size distribution and control
8. Validation of metals partitioning and control

Acronyms

ALARA	As Low As Reasonably Achievable
APC	Air Pollution Control
APCS	Air Pollution Control System
ARAR	Applicable or Relevant and Appropriate Requirement
BIF	Boilers and Industrial Furnaces
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CFR	Code of Federal Regulations
CIF	Consolidated Incineration Facility
CM	Construction Management
DF	Decontamination Factor
D/F	Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans
DOE	U.S. Department of Energy
DRE	Destruction and Removal Efficiency
DWPF	Defense Waste Processing Facility
EER	Energy and Environmental Research Corporation
EPA	U.S. Environmental Protection Agency

HEPA	High Efficiency Particulate Arresting (filter), or more commonly, High Efficiency Particulate-Air (filter)
HVAC	Heating, Ventilation, and Air Conditioning
INTS	Integrated Nonthermal Treatment System
ITTS	Integrated Thermal Treatment System
IWPF	Idaho Waste Processing Facility
LMITCO	Lockheed Martin Idaho Technologies Company
LVM	Low Volatile Metals
MACT	Maximum Achievable Control Technology
MEI	Maximum Exposed Individual
M&O	Maintenance and Operations
MSE-TA	Mountain States Energy Technology Applications
NESHAPS	National Emission Standards for Hazardous Air Pollutants
PIC	Product of Incomplete Combustion
POHC	Principal Organic Hazardous Constituent
PM	Particulate Matter
RCRA	Resource Conservation and Recovery Act
SCC	Secondary Combustion Chamber
SCR	Selective Catalytic Reduction
SNCR	Selective Non-Catalytic Reduction
SRS	Savannah River Site
SVM	SemiVolatile Metals
TEQ	Toxicity Equivalent
THC	Total HydroCarbons
TRU	TransUranic
TSCA	Toxic Substances Control Act

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For Further Information

A number of books, reports, and other references have been published over the past decade on off-gas control for hazardous and mixed waste treatment. The intent of this chapter on off-gas control is not to repeat information provided in these other references, but to update, focus, and apply this information and provide new information to aid in state-of-the-art off-gas control system design and operation for mixed waste treatment.

Recent textbooks and handbooks that address off-gas control for mixed waste treatment are listed chronologically as follows:

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The EPA, DOE, and other federal departments and agencies have also funded research, design, and development of off-gas control technologies and systems for mixed waste treatment, especially in the 1990s. The author estimates that total funding by the DOE alone for off-gas control system research and development in the 1990s approached $100 million dollars. DOE programs and projects that included off-gas system research and development were many and diverse. Just a few of these included:

- Pilot-scale tests for the Consolidated Incineration Facility (CIF) incinerator/off-gas system
- The Mixed Waste Integrated Program (MWIP)
- The Buried Waste Integrated Program (BWID)
- The Mixed Waste Focus Area (MWFA)
- The Integrated Thermal Treatment Systems Study (ITTS)
- The Integrated Nonthermal Treatment Systems Study (INTS)
- The Idaho Waste Processing Facility (IWPF) at the INEEL
- The Advanced Mixed Waste Treatment Facility (AMWTF) at the INEEL
- The EPA/DOE National Technical Workgroup for Mixed Waste Treatment

These programs or projects have resulted in several useful references that can be useful in design and operation of mixed waste off-gas control systems. Listed in chronological order, some of these references are:

Dalton, J.D., Gillins, R.L., Harris, T.L., and Wollerman, A.L., 1992, An Assessment of Off-Gas Treatment Technologies for Application to Thermal Treatment of Department of Energy Wastes, DOE/MWIP-1, September.

Energy and Environmental Research Corporation (EER), 1992, APC and Monitoring Technologies for Rocky Flats Fluidized Bed Unit, State of the Art Assessment, EPA Contract 68-CO-0094.

Dalton, J.D., Wolfe, W.P., and Geimer, R.M., 1994, Air Pollution Control System Flowsheet for the Pilot-Scale PHP System, SAIC-94/1042, Science Applications Int. Corp.

DOE, 1994, Technical Area Status Report for Second-Stage Destruction and Off-gas Treatment, DOE/MWIP-5, August.

Eddy, T.L., Raivo, B.D., Soelberg, N.R., and Weirsholm, O., 1995, *Advanced Mixed Waste Treatment Project Melter System Preliminary Design Technical Review Meeting*, INEL-95/0054, Idaho National Engineering Laboratory.

Johnson, S.E., Kujawa, S.T., and Ruschetti, J.S., 1995, Controlled Emissions System Off-gas Component Separation Design Study, MSE Technology Applications, Inc., Butte, MT.

Feizollahi, F. and Quapp, W.J., 1996, Integrated Thermal Treatment System Study — Phase 2 Results, INEL-95/0129, Rev. 1, Idaho National Engineering Laboratory.

Biagi, C., Quapp, W.J., Bechtold, T., Bahar, D., Brown, B., Schwinkendorf, W., Swartz, G., Teheranian, B., and Vetromile, J., 1997, Integrated Nonthermal Treatment System Study, INEL-96-0273, Idaho National Engineering Laboratory, January.

Energy and Environmental Research Corporation (EER), 1997, Demonstration Testing for Mixed Waste Thermal Treatment Technologies, interim final draft, National Technical Workgroup on Mixed Waste Thermal Treatment.

Liekhus K.L., Grandy, J.D., Chambers, A., Soelberg, N., and Anderson, G., 1997, Partitioning Planning Studies: Preliminary Evaluation of Metal and Radionuclide Partitioning in High-Temperature Thermal Treatment Systems, INEL/96-0450, Idaho National Engineering Laboratory.

DOE, 1998, Summary of DOE Incineration Capabilities, DOE/ID-10651, Revision 1, July.

Soelberg, N., Liekhus, K., Chambers, A., and Anderson, G., 1998, High Performance APCS Conceptual Design and Evaluation Scoping Study, INEEL/EXT-97-01138, February.

Soelberg, N.R., Chambers, A., Knecht, M.A., Eaton, D., and Liekhus, K., 1999, MACT System Integration Study, INEEL/EXT-99-00340, June.

There have also been hundreds of conference papers and additional internal reports for DOE off-gas control research and development. These are not listed here, although some are cited as references in this chapter.

Acknowledgments

The contents of this chapter are the products of several different studies and research efforts for the U.S. Department of Energy (DOE). The majority of this work was sponsored by Mr. Carl Cooley of the DOE Office of Science and Technology, and by the DOE Center of Excellence for Low-Level and Mixed Low-Level Waste, through the DOE Mixed Waste Focus Area (MWFA). Personnel who contributed to this work include Andrea Chambers, Dave Eaton, Margaret Knecht, and Dr. Kevin Liekhus of the Idaho National Engineering and Environmental Laboratory.

Chapter Eight

8

Decontamination

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Decontamination Techniques

Decontamination removes substances of regulatory concern, such as noxious chemicals or radioactive material, and renders the decontaminated item "clean" or less contaminated. No single decontamination technique is completely adequate for all decontamination situations, although there may be an optimum technique or combination of techniques for a specific application. It has often been found that the results depend more on the knowledge, skill, and training of those planning and conducting the decontamination operation than on the inherent characteristics and capabilities of a particular technique. It should also be noted that the cost of decontamination should be weighed against its benefit. This is particularly true for nuclear decommissioning activities where decontamination can be an unnecessary step.

When determining the best decontamination technology for an application, several criteria should be taken into consideration, as shown in Figure 8.1. Each criterion can be given a weighting factor to indicate the importance of that category in the determination of the best decontamination technique for a particular application.

The more that is known about the contamination, its chemical composition, structure, and adherence to the base material, the easier it will be to choose the most efficient decontamination method. The types of surface and the materials of construction must also be considered prior to selecting a decontamination method. Most piping and tanks used in the nuclear industries are constructed of stainless steel. However, more exotic materials, such as Hastelloy or titanium, are sometimes used. In addition, secondary waste generation, potential for recontamination, and waste compatibility with disposal facilities can be important factors.

Generally speaking, scale and contamination layers from various nuclear processes differ widely. Those layers in fuel reprocessing equipment and related facilities are usually very different from those in nuclear power reactors. The more accurately the contamination layers can be identified, the easier it becomes to choose an efficient decontamination method. Internal surfaces of reactor coolant piping can have a tightly held contamination layer formed by high temperatures or base metal corrosion with a loose outer layer formed by coolant crud deposition or precipitation. These different types of oxide layers require different decontamination procedures. Radioactive films in Pressurized Water Reactors (PWRs) are more difficult to dissolve than those in Boiling Water Reactors (BWRs) because the insoluble trivalent chromium of the oxide layer formed in PWRs must be oxidized to the hexavalent state before the layer becomes amenable to dissolution by the decontamination solution. The oxide films in BWRs are directly soluble in an appropriate acid.

Fuel reprocessing chemical processes tend to generate a tenacious scale and oxide layer on piping and equipment. Acid etching often causes erosion/corrosion at the metal grain boundaries, which in turn will trap contaminants. The depth of this contamination may prevent decontamination solutions from

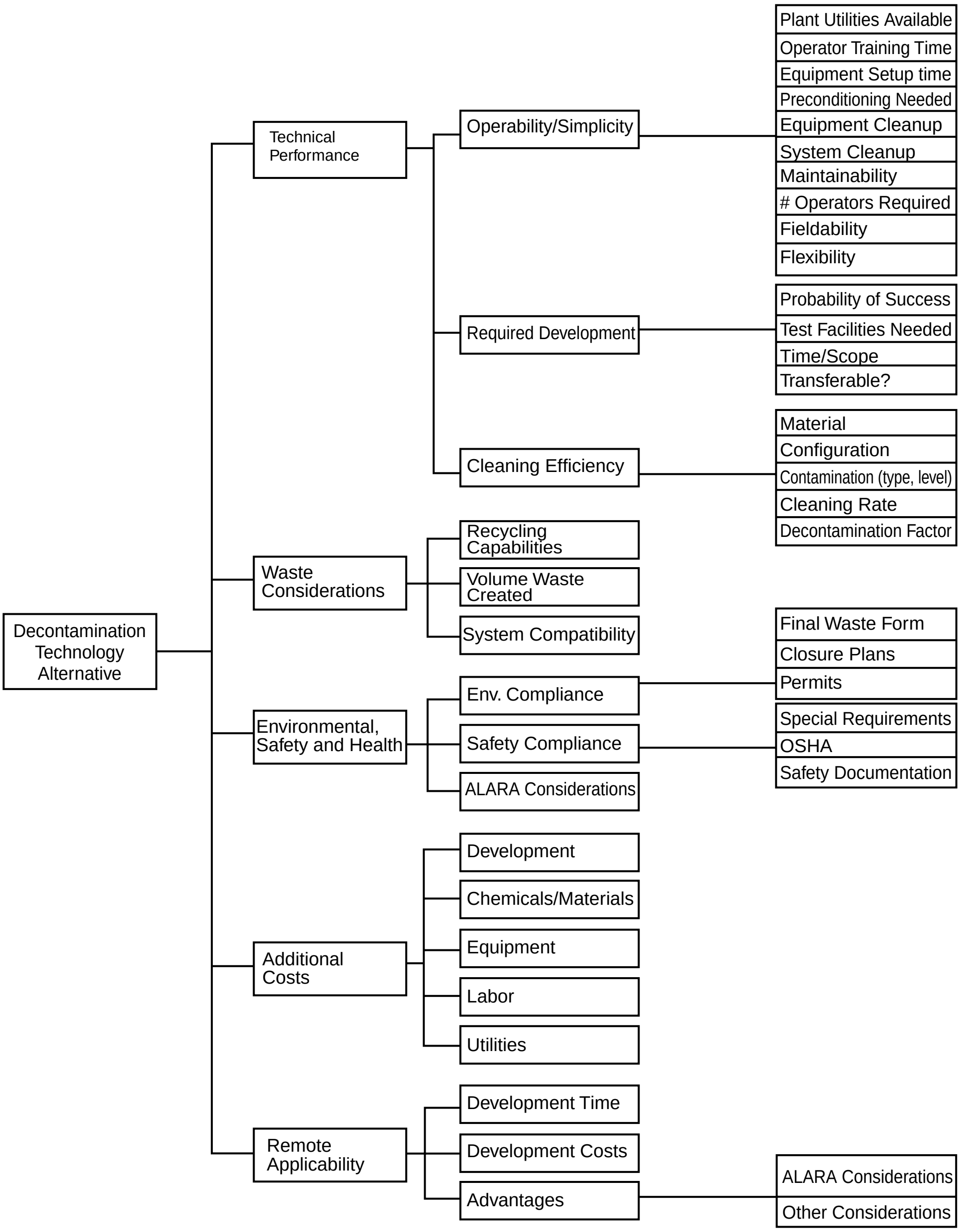

FIGURE 8.1 Criteria tree.

being effective in removing the contaminants. The use of organics in fuel extraction processes leads to the generation of heavy, pasty, tenacious organic degradation deposits in pipes and tanks.

In other types of nuclear facilities, such as hot cells and mixed oxide fuel-fabrication plants, widespread contamination may exist in process vessels, cells, etc. as a result of normal operations. In UO_2 fuel fabrication plants, the processing of UO_2 causes low levels of activity. Where fuels are processed as dry powders, materials settle onto horizontal surfaces and may accumulate in nooks and crannies that are not accessible to routine cleaning operations.

In ventilation systems, the surface contamination is usually loose, although adherence can be increased by oily films or vapors that are often found on the inside of ducts, particularly downstream of fans.

Because the exhaust systems operate at negative pressures, they tend to draw in dust and aerosols that may contain activity. Deposition tends to be heavier in sections of the ducting where the direction or velocity of the fluid changes and at the edges of joints and flanges.

Solutions that dry on a surface account for a great deal of contamination. This type of contamination depends on the solution used in the piping. Solutions that dry on the top inner wall of pipes are the most difficult to remove. Quite often, flushing reaches only the bottom and sides of the pipe.

Decontamination effectiveness has been expressed in the literature by a decontamination factor (DF). DF is defined as the ratio of the concentration of various radionuclides (or exposure, measured in Roentgen or Rem) before and after decontamination. DFs vary widely, depending on the situation, and are most useful when comparing the action of alternate techniques in the same decontamination activity.

Significant progress has been made in the availability and use of non-chemical (or mechanical), decontamination techniques. Mechanical techniques may have unique advantages over chemical techniques for some decontamination tasks. When waste minimization is important, for example, there is a greater potential for waste reduction and ease of waste disposal for these techniques. Some techniques also fulfill particular niches that would otherwise be unfilled. Many of the techniques have virtually no interaction with the substrate, and others can be used to remove large amounts of surface in a short time. Some techniques are very inexpensive and can be very environmentally friendly. As with chemical decontamination, a thorough investigation of the type, process, and criteria for decontamination should be made prior to use.

It should also be noted that decontamination has a different context for the decommissioning of nuclear facilities than it has for nuclear operations. Very harsh, aggressive decontamination technologies or processes can often be used during decommissioning activities, processes that would not be acceptable if continued operation of the facility was the goal. Also, cost/benefit analyses can often be performed which can show that decontamination is not cost-effective, or necessary, for facility decommissioning. It is usually wise to perform a cost analysis before performing any decontamination operation.

Mechanical Surface Removal Methods

Mechanical (or non-chemical) decontamination methods come in a wide variety of types and applications. They can be as simple as brushing a contaminant from the surface and vacuuming it up; or as state-of-the-art as using a laser. The majority of these methods have their basis in physical (mechanical) processes. Abrasive blasting is a simple method that works by brushing or grinding a contaminant from the surface. Laser ablation is a high-technology method that may seem a little mystifying, but uses the simple physical process of thermal shock. Table 8.1 shows the relative performance factors for a number of mechanical cleaning techniques.

Mechanical methods are often used because of liquid waste concerns with the waste from chemical decontamination techniques. The non-chemical methods typically generate less or no secondary waste. Non-chemical waste is usually easier to dispose of than chemical waste. Many have recycling and reuse incorporated into their process for added savings. These systems are more compatible with contaminated materials that can be removed from the process (tools, valves, small equipment, etc.). For "in-place" equipment, advances are being made to use mechanical techniques inside piping and remotely with manipulators or robots.

CO_2 Blasting

CO_2 Pellet Blasting

A CO_2 pellet-blasting system normally consists of liquid CO_2 at 200 to 300 psig, transported through a hose to a pelletizer machine, where rapid expansion of the liquid in the chamber converts the CO_2 to a solid state of dry ice or snow. The snow is then compressed into pellets, which are transported through a hose at 40 psig to a blasting nozzle. At the nozzle, the pellets are entrained in high-pressure air (40 to 250 psig) and propelled from the nozzle onto the workpiece at 75 to 1000 ft/s (Figure 8.2). The CO_2

TABLE 8.1 Relative Performance Factors for Mechanical Cleaning Techniques

Technology Family	Performance[a] Loose Contamination	Performance[a] Fixed Contamination	Types of Substrate	Initial Cost[a]	Production Rate[a]	Decon Item in Place[a]	Availability[a]
CO_2 pellet blasting	H	M-L	Metal, wood, plastic, concrete	H	L	Y	H
Water blasting	H	M	All	M	H	Y	H
Scabbling	H	H	Primarily concrete, metal	L	H	Y	H
Spalling	H	H	Concrete	L	H	Y	H
Abrasive grit	H	H	All	M	H	Y	H
Grinding	H	H	All	L	L	Y	H
Milling	H	H	All	M	L	N	H
Vibratory finishing	H	H	Primarily metal	L	L	N	H
Hand scrubbing	H	M	All	L	M	Y	H
Strippable coatings	M	L	All	L	L	Y	H
Vacuuming	H	L	All	L	H	Y	H
Ultrasonic cleaning	H	H	Primarily metal	L	L	N	H
Turbulator	H	M	Metal, plastics	L	L	N	H
Plasma cleaning	H	M	Primarily metal	H	L	N	M
Light ablation	H	M	Metal, concrete	H	L	N	M
Electrokinetic	H	M	Primarily concrete	M	L	Y	M

[a] All factors are subjective and may change based on application or specific equipment, but should be nearly those quoted here.

Performance factors are based on relative reported cleaning of these methods; High is typically over about 90%, Medium is about 70%, and Low is less than 70%.

Cost is based on initial cost of equipment, High is over about \$100,000, Medium is over about \$50,000, and Low is less than \$50,000.

Production rate is based on a significantly higher or lower rate than 30 ft^3/hr.

Decon item in place is based on whether an item can be decontaminated externally without removal. Availability is based on whether a vendor is currently marketing this equipment or process.

pellet penetrates the workpiece coating (mechanical abrasion), "mushrooms" under the coating as it strikes the substrate, and then sublimes, causing the coating to fall off. This leaves only the coating as waste while the CO_2 pellet returns to its gaseous state. Pelletizer systems are very expensive (\$200K to \$300K) and pellet blasting operations generally require two people, one to operate the nozzle and one to watch gages and control the equipment. In a test at the INEEL (Idaho National Engineering and Environmental Laboratory), the best cleaning results on 304L stainless steel, construction tools and materials with Cs and Zr contamination required blasting pressures of 125 to 150 psi using a 0.08 to 0.125 in. pellet size (Archibald, 1993). Lower pressures of 40 to 50 psi should be used when cleaning soft materials such as lead to avoid damage or driving the contaminants into the substrate. In general, CO_2 pellet blasting is effective at removing loose contamination/materials on a variety of surfaces, but is not abrasive enough to remove epoxy paints or tightly adhered contaminants.

Ventilation and contamination control is the biggest concern with all CO_2 blasting systems. Blasting in confined spaces and pits can lead to the heavier carbon dioxide displacing the air, causing breathing problems for workers. Worker safety should be a primary concern. Shrouded blasting nozzles with HEPA filtration should be considered. Another concern is line freeze-up, which can be solved with an in-line heater without decreasing blasting effectiveness. Moisture buildup (due to condensation from the air) on the item being cleaned can also be a concern. Use of these systems requires hearing protection due to the high noise level.

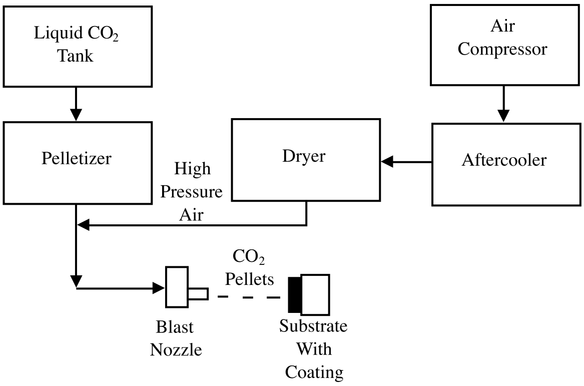

FIGURE 8.2 CO_2 Pellet Blasting System.

CO_2 Shaved Ice

Smaller-scale applications should consider a shaved dry ice blaster that uses blocks of readily available dry ice and shaves off ice particles that are subsequently blasted onto a surface. The shaved ice blasting has been proven as effective as standard pellet blasting for some applications (Archibald, 1997). This equipment is much less expensive ($40K) than the typical large pelletizing units (Demmer et al., 1995).

CO_2 Snowflake

There are also CO_2 "snow" machines used for very gentle cleaning of sensitive equipment such as telescope optics. This blaster uses compressed carbon dioxide to produce a solid CO_2 "snow" under pressure for a gentle cleaning action. It has very limited usefulness in nuclear decontamination because of its gentleness and incomplete cleaning ability, but has been used in areas such as cleaning optical lenses. Hughes Aircraft Co. developed this machine. The device is a handheld "gun-like" trigger mechanism that is easily manipulated and requires only a tank of pure carbon dioxide as supply (Demmer et al., 1995).

Centrifugal CO_2

Centrifugal CO_2 pellet blasting is similar to the compressed air/CO_2 pellet blasting technology. It uses a high-speed rotating wheel to accelerate the CO_2 pellets. With the higher speeds available, the centrifuge technology may enable removal of hard oxide layers from steel, thereby removing both zinc coatings from galvanized steel/sheet metal and nickel plating from brass screws. A brief program with the Air Force at Warner Robins Air Logistics Center demonstrated the removal of the urethane and epoxy paint surfaces from F-15 aircraft at a rate of 120 ft^2/hr for a 15-hp accelerator (Bundy, 1993). Some other sources indicate that the cleaning potential is roughly equivalent to other CO_2 pellet blasting techniques (Archibald, 1997). Generally, a centrifugal unit can be remotely operated with the capability of cleaning 200 to 2000 ft^2/hr depending on the nature of the surface to be cleaned. The cost of the 30-hp machine capable of accelerating 1 ton/hr of CO_2 at speeds up to 400 m/s is ~$200K (Meservey et al., 1994).

Supercritical CO_2

Supercritical CO_2 (above its critical temperature of 87.8°F and at high pressure) is pressurized by an ultra-high-pressure intensifier pump up to 55,000 psi and forced through nozzles, generating high-velocity CO_2 jets at speeds up to 3000 ft/s. The nozzles can be mounted in various types of cleaning heads for contaminated surfaces. The CO_2 jets thoroughly penetrate and remove some surface contaminants. The removed contaminants, any of the substrate surface layer that may be removed, and the CO_2 are captured by a vacuum recovery system. A cyclone separator and a HEPA filter collect the solids and the CO_2 is discharged to the atmosphere or recycled (Meservey et al. 1994; Bundy, 1993).

Cryogenic Cutting Tool

With the cryogenic cutting tool, a very high-pressure jet of liquid nitrogen (up to 60,000 psi) and CO_2 crystals is directed on a workpiece like abrasive blasting. A proprietary ZAWCAD (Zero Added Waste Cutting Abrading Drilling) cryogenic system was developed at the INEEL for cutting and cleaning various materials with zero added secondary waste (Demmer et al., 1995).

Water Blasting

There are many different methods of using water blasting for decontamination. In one, ultra-high-pressure water (up to 55,000 psi) is forced through small-diameter nozzles to generate high-velocity waterjets. The waterjets penetrate and remove surface contaminants, although care must be taken not to damage the substrate. Abrasives can also be added for industrial cutting, milling, or improved decontamination. This operation generates contaminated water as a secondary waste that must be treated. In cleaning concrete, for example, a typical flow rate for one cleaning head would be 3 to 5 gal/min (gpm) at a surface treatment rate of about 1 ft^2/min. Such devices have now been incorporated into remote-controlled deployment devices to allow remote use in hazardous environments.

Superheated water (300 psi and 300°F) can also be blasted onto a surface to remove contamination. The lower operating pressures will only remove surface contamination that is soluble or loosely bound to the surface. The wastewater generation rate for a typical commercial unit ranges from 0.4 to 2 gpm.

The high-pressure water lance, or hydrolaser, consists of a high-pressure pump, 1000 to 10,000 psi operator-controlled gun with directional nozzle, and associated high-pressure hose. A 2000-psi water lance provides a flow of about 8 gpm and a 10,000 psi unit a flow of 22 gpm. Hydrolasers have been successfully used to decontaminate components, structures, walls and floors, and pipe and tank interiors. A variation of the water lance is the "pipe mole" in which a high-pressure nozzle attached to a high-pressure flexible hose is inserted in contaminated pipe runs. The nozzle orifices are angled to provide forward thrust of the nozzle and drag the hose through the pipe. (Bundy, 1993; NEA Group of Experts, 1981).

Hot water at low pressure is also used to flush areas to dissolve readily soluble contaminants or to flush loosely deposited particles to a central area for collection. Flushing with hot water is often used following scrubbing, especially on floors. The effectiveness of flushing is enhanced by the use of squeegees to force the water and contaminants to collection or drain areas.

Steam cleaning combines the solvent action of water with the kinetic energy effect of blasting. At relatively high temperatures, the solvent action is increased and the water volume requirements are reduced compared to water blasting.

Scabblers/Scarifiers

Mechanical impact methods can be used to remove a contaminated surface. Many vendors market units that use high-speed reciprocating tungsten carbide tipped pistons to pulverize protective coatings and concrete substrate in a single-step process. Other types of units such as diamond head grinders, needle scalers, etc. use a shrouded head to remove concrete from edges, corners, and wall surfaces. These units are also used for removing relatively thin layers of lead-based coatings and contamination from steel surfaces. Scabblers have limited use on concrete block because the vibration often breaks the block. The solid debris produced by these mechanical scabbling techniques is normally removed and collected by a HEPA filtered vacuum system. Mechanical scabblers are usually operated manually. The amount of waste generated depends on the depth of the surface layer that needs to be removed to achieve decontamination. Often, several passes will be required to remove embedded contamination. For example, two different commercial units provide removal of concrete at rates of 3 to 4.5 $in.^3$/min (8 to 12 lb/hr) and 60 $in.^3$/min (160 lb/hr) at a removal depth of 1/16 in. per pass. A seven-piston floor unit can remove 35 yd^2 of concrete surface per hour (Bundy, 1993; NEA Group of Experts, 1981).

These mechanical decontamination devices can also be attached to remotely operated vehicles or equipment such that they can be deployed remotely to avoid exposing workers to hazardous environments. A BROKK™ demolition robot has been tested for service in concrete breaking and scabbling at the INEEL. This technique uses a remotely operated, articulated, hydraulic boom to place the operator up to 400 ft away from the scabbling activities. Large units for floor scabbling are also available from various vendors.

Drilling and Spalling

Drilling and spalling is used to remove concrete surfaces to depths of 1 to 2 in. without removing the entire structure. Spalling is little used because of its inherent safety concerns and sluggish production rates. The process consists of drilling 1-in. diameter holes on an 8-in. pitch to a depth of 2 in. into which a spalling bit is inserted. A tapered mandrel is hydraulically inserted in the expandable bit to spall the concrete. The surface removal rate is about 100 ft^2/hr. The drill and spall method is good for concrete only (not concrete block) and is recommended for removing surface contamination that penetrates 1 to 2 in. into the surface. This technique is good for large-scale, obstruction-free applications (Meservey, et al., 1994; NEA Group of Experts, 1981).

There are two types of high-pressure jet spalling devices. One is a compressed gas-actuated piston that forces small quantities of high-velocity water through a nozzle at a rate of 5 shots per second. This unit is usually mounted on a heavy transporter such as a backhoe. The other is a gun that fires glycerin capsules at close range onto a contaminated concrete surface. The glycerin gun can remove a concrete surface at a rate of about 10 ft^2/hr as compared to the other water cannon's rate of about 4 ft^2/hr. The technique is useful in areas of difficult access. The glycerin gun coats the removed dust and particles with glycerin, which contains the contamination. An advantage to the slower water cannon over the glycerin gun is that the cannon can be used for overhead structures such as ceilings (Meservey et al., 1994).

Abrasive Blasting

This technique projects solid particles suspended in a fluid medium at a surface to achieve decontamination by surface abrasion. The medium is typically compressed air or high-pressure water. An option to this basic technique is to utilize a rotating chamber to impart kinetic energy to the particles by centrifugation. The particles can then be discharged onto the contaminated surface without need for supplemental use of a compressed fluid (Wood et al. 1986).

A key factor in achieving successful decontamination without causing deleterious effects on the substrate material is to select the abrasive material and the operating conditions for the application so that just enough surface abrasion occurs to effect the desired decontamination. The prime criteria to be evaluated are hardness of the surface to be decontaminated and degree of degradation of the surface allowed. Any desired action, from general scouring to significant surface abrasion, can be accomplished. Grit blasting is an efficient cleaning method, with high decontamination capabilities.

Abrasive blasting is very versatile and has been heavily used in the nuclear industry in applications ranging from heavily contaminated pipe with the contamination fixed in the oxide to lightly contaminated surfaces. Commercial units are readily available. Typical abrasives include sand, glass beads, plastic beads, metallic beads, sponges with imbedded grits, and soft materials such as nutshells, rice hulls, and wheat starch. The En-Vac™ robotic blasting system is a complete unit to manipulate, vacuum, filter, and recycle an abrasive blasting process. This system can be used to blast and recover abrasive from many kinds of surfaces, including vertical and curved areas. Ice shavings have also been used as an abrasive. Waste production rates, including grit plus filters, could range from 0.005 to 0.1 lb/ft^2, although some systems recycle some durable grits (alumina, steel shot) for reuse to minimize secondary waste generation (Meservey et al., 1994; Demmer et al., 1995; Bundy, 1993).

Shot Blasting

Shot blasting uses mechanically accelerated iron shot to clean the work surface. After the shot hits the surface to be cleaned, it is recovered by a magnetic system and recirculated. There is some concern that shot blasting may drive contaminants into the surface, making it more difficult to remove. Therefore, testing of the particular application is advised. Shot can be recycled many times during cleaning, but ultimately erodes and becomes part of the waste stream at the rate of approximately 0.1 lb/m^2. Commercial units are available that have been used to prepare large areas of concrete floors in one step for painting, for cleaning rust and marine growth from ship hulls, and for cleaning structural steel elements (Meservey et al., 1994; Bundy, 1993).

Sponge Blasting

The sponge blasting system decontaminates by blasting surfaces with various grades of patented water-based urethane foam media using 110-psig air as the propellant. The foam can be used either dry or wetted for a variety of surface contaminants such as oils, greases, lead compounds, chemicals, and radionuclides. Two basic grades of foam cleaning media are used: (1) a nonaggressive grade that is used for surface cleaning on sensitive or otherwise critical surfaces and (2) aggressive grades that are impregnated with abrasives that can remove tough materials such as paints, protective coatings, and rust. Foam blasting media are recyclable in a closed-cycle wash unit. The media typically can be recycled eight to ten times. On the first time through, the sponge-blasting unit uses 6 to 8 ft^3 of media per hour at a surface-cleaning rate of about 1 ft^2/min. Thus, the solid waste produced (foam media, recycled ten times, with the absorbed contaminants) is approximately 0.01 ft^3/ft^2 of surface cleaned. The cleaning heads are similar to those of other blasting technologies and could be readily adapted to a robotic control system (Meservey, et al., 1994; Bundy, 1993).

Hand Grinding, Honing, Scraping – Automated Grinding

Power-driven grinding equipment can be used to remove the contaminated object surface. Operating cost varies with the shape of item being decontaminated and with the location. The heat generated by the grinding operation can cause organic compounds to vaporize and decompose requiring special control (Allen, 1985; Bundy, 1993).

Metal Milling

A metal milling machine is used to shave off the surface layer of metal in this technique. This method is most suitable only when there is a large number of similar items to be decontaminated because there is a 1/2 to 3/4 hour setup time required between differently shaped items. After the equipment is set up and loaded, about 2.5 ft^2/hr can be milled. The waste generated is the metal surface removed (up to 1/8 in.) (Meservey et al., 1994; Bundy, 1993).

Concrete Milling

This equipment is a large vehicle used by paving contractors primarily that is suitable for large-area horizontal surfaces. The top 0.25 to 1-in. of surface is removed. Operating costs in 1980 dollars, not including the cost of hauling away the debris, range from $500K to $1.6M per square mile (Meservey et al., 1994; Bundy, 1993).

Vibratory Finishing

Vibratory finishing employs a rapidly vibrating tub filled with abrasive media, often triangular ceramic or conical plastic impregnated with aluminum oxide, to mechanically scrub contamination and other surface materials such as paint, tape, corrosion products, and soil from almost any item type. The dislodged contamination and surface material is often removed with a flushing solution. No pretreatment is required except for surfaces coated with epoxy paints. The process will decontaminate a variety of materials, sizes, and shapes at the same time, and the secondary waste volume produced is small.

Vibratory finishing is an excellent decontamination technique for tools and large quantities of small items, but larger components require extensive disassembly or sectioning. The maximum size of items that can be processed is about 8 to 12 in. diameter. Up to 300 lb of wrenches, hammers, screwdrivers, and other miscellaneous tools have been successfully decontaminated for reuse within an hour, with minimal operator attention (Wood et al., 1986).

Hand Scrubbing

Hand-scrubbing and related manual decontamination operations are probably the most widely and frequently used of the non-chemical techniques. Contaminated surfaces are wiped or scrubbed, by hand or with a power brush or mop, using cleaning/scouring materials and chemical cleaning agents suited to the specific decontamination requirements. Smearable contamination on a smooth or impervious surface may be removed by simple wiping with a dry or damp cloth, whereas the use of an abrasive pad with an aggressive chemical cleaning agent may be required to adequately remove contamination associated with a corrosion layer or embedded in the surface. Organic solvents and detergents can be employed to remove contamination associated with oil, grease, and various types of surface soil. This is a labor-intensive, but versatile technique. Major concerns and constraints are radiation exposure, possible generation of airborne contamination, and difficulty in removing contamination from crevices and constricted areas (Meservey et al., 1994; Allen, 1985).

Strippable and Fixable Coatings

A strippable coating is applied to a contaminated surface by methods such as spraying, brushing, and rolling (as may be used for paint). During application, the coating migrates into surface microvoids to contact contaminants. While the material is wet, it attracts, absorbs, and may chemically bind the contaminants. During the drying or curing process, the contaminants are mechanically locked into a polymer matrix. After the coating dries, it is either manually stripped from the surface or, in the case of "self-stripping" coatings, it falls off by itself and is collected by vacuuming. The surface contamination is removed with the coating, producing a dry, hard, non-airborne waste product. Water-based strippable coatings are intended for use in decontaminating smooth and semi-rough porous surfaces, including steel, concrete, aluminum, wood, and painted surfaces. The technology has been used for decontamination purposes in applications involving hazardous and radioactive contaminants. Typical coverage would be 30 to 120 ft^2/gal of polymer, and most coatings dry in 4 to 24 hr, depending on temperature and humidity (Tripp, 1996). A strip coat developed at Los Alamos can sense when uranium or plutonium is present and change color (Archibald et al., 1999). Most commercial strippable coatings can be incinerated.

Strippable coatings can also be applied over clean surfaces prior to contamination to provide a protective, sacrificial layer of material, or applied to contaminated surfaces to fix contaminants and inhibit airborne contamination such as asbestos (Bundy, 1993; Wood et al., 1986; Tripp, 1996). They can be difficult and labor intensive to remove on some porous surfaces.

Vacuuming

Loose solid contaminants can be removed using a vacuum cleaner. When significant amounts of solids are present but not loose, they may be broken free by hand scraping or more automated means and then vacuumed by a HEPA filtered vacuum system. Dust-laden areas are also good candidates for vacuuming to control contamination. Vacuuming is usually used in conjunction with various other contamination removal techniques (Bundy, 1993).

Ultrasonic Cleaning

Ultrasonic cleaning utilizes the scrubbing action of liquid excited by ultrasonic frequencies to remove surface deposits of oils, organic and loosely bound solids from metals, plastic, glass, and other solids. The ultrasonic generator and the contaminated item are located in close proximity within a tank geometrically sized for the application. Basic equipment, widely available commercially, consists of a liquid tank with appropriate plumbing, an ultrasonic generator, and vibrating bars (transducers), which are placed in the tank to provide energy to the liquid. Chemical solvents or liquids with added abrasives can be used as the fluid couplant to increase decontamination effectiveness. The generator converts line frequency (50 to 60 Hz) to a high frequency of about 18 to 90 kHz. The transducer converts this impulse to low-amplitude mechanical energy in the couplant. The resulting wave cycle causes the liquid to cavitate and implode. This action serves to scrub the surface being decontaminated. Ultrasonic frequency affects cleaning efficiency by determining the cavity size. Low frequencies generate large but relatively few cavities with high cleaning power. High frequencies generate a large number of small cavities with good penetrating capability. The most important parameters include ultrasonic frequency, power intensity, cleaning-solution viscosity, temperature, and fluid recirculation rate. Achievement of optimum results requires a knowledgeable, skilled operator. It produces no abrasion, distortion, or changes in most things and is ideally suited for delicate or valuable parts and materials that are to be reused (Allen, 1985).

Ultrasonic cleaning is primarily used for small metal parts that can fit into an ultrasonic bath and is particularly effective for crevices or threaded areas. It is not practical for large items that would require size reduction. It is ineffective for tightly bound materials such as paints, varnishes, and other materials that are difficult to remove. The technique can generate secondary wastes that are expensive to manage (such as solvent and detergent solutions requiring processing). The technique is intended for valuable parts that can be recycled “as is” after cleaning. The technique is also good for removing deposits in difficult-to-access places, and it may be useful for electronic parts and electric motors. Using portable transducers, this technology has been used for cleaning the inside of waste storage tanks (although this may not be a cost-effective option). (Meservey et al., 1994; Bundy, 1993; NEA Group of Experts, 1981; Wood et al., 1986; Allen, 1985; DOE, 9.4.2, 1994).

Pulsed Acoustical Technique

Mississippi State University and the Tennessee Valley Authority developed this technology, which is a type of ultrasonic cleaning. Named Tube Cleaning System (TCS), this technique uses repetitive high-voltage electrical discharges in fluids (principally water) to produce acoustic shock waves. The results are removal of scale, silt, and other deposits from ducts, tubes, and pipes with less worker exposure and less secondary waste produced. The process is applied while the pipe is full of water and the insertion of the TCS tip is made in such a way as to preserve the water pressure during cleaning. The high-voltage spark causes water in the area of the electrode to vaporize, thus causing cavitation in the water, which cleans the pipes of surface contamination. The operator controls the amount of cavitation created in the pipe. There is some evidence that cleaning is accomplished more by the shock wave causing compressive and shear stresses than by the cavitation. In tests, the TCS has been used to clean 1-in. pipes in a facility. Further testing and demonstrations are needed (Costley et al., 1997).

Turbulator

A turbulator (Turco Products) is a large tank with propellers that direct the flow of a cleaning solution over and across a component. Square tanks have two propellers, while rectangular tanks have four propellers arranged at 90° angles around the tank. The turbulator is not quite as effective for porous substances as is ultrasonics. It is most effective on nonfixed contamination (i.e., loosely deposited, loosely adhering contamination). It has been used to clean such components as metallic hand tools, pump seals and pistons, valves, seal-injection filters and other filters, and control drive mechanisms (Meservey et al., 1994).

Microwave Scabbling

This technology directs microwave energy at a concrete surface using a specialized waveguide applicator and heats the concrete and the free water present in the concrete matrix. Continued heating produces thermal and steam pressure induced mechanical stresses that cause the concrete surface to burst. The concrete particles from this steam explosion are small enough to be removed by a vacuum system, yet less than 1% of the debris is small enough to pose an airborne contamination hazard. The process is fast, dry, generates little dust, and avoids mechanical impacts. The microwave applicator head can be manually moved about on the concrete surfaces being decontaminated. Because the rate and depth of surface removal depend on the applicator translation speed, remote operation is desirable. At microwave frequencies of 2.5 and 10.6 GHz, continuous concrete removal rates of 1.1 cm^3/s at 5.2 kW and 2.1 cm^3/s at 3.6 kW, respectively, were obtained. The Japanese reported that up to 1-in. of surface can be removed; however, no microwave frequencies or power were reported (White et al., 1992; Yasunaka et al., 1997; Meservey et al., 1994; Bundy, 1993; DOE, 1994).

Plasma Torch

The plasma torch uses an inert gas passing through a high-power dc or RF arc discharge to produce a very-high-temperature gas stream that is capable of melting nearly all uncooled materials. Such torches are used in plasma synthesis and decomposition of materials. Potential uses in decontamination of materials include breaking down oils and PCBs into less harmful or harmless substances, rapid spalling of concrete, and using the difference in coefficient of thermal expansion to delaminate contaminants from underlying substrates. The torch's inert gas creates no additional waste stream of its own compared to the smoke, CO_2, and NO_x product created by a combustion torch (Meservey et al., 1994).

Emerging Technologies

Laser Ablation

When a focused laser beam irradiates a metal surface, the surface will absorb a fraction of the incoming photons and, when the laser irradiance is sufficiently great, material will be ejected from the surface by a combination of processes that includes vaporization and ablation. Decontamination is achieved by removing contaminated surface layers and then capturing the ejected material before redeposition can occur. Decontaminating a large surface area with a laser in a reasonable amount of time requires that either the laser beam be sufficiently intense to achieve useful irradiance values over a large area or that the laser operate at a very high repetition rate. In either case, the laser beam needs to be rastered quickly across the surface to achieve large-area decontamination.

Some laser coating removal systems are designed to "strip" relatively soft coatings from a substrate without damage to the substrate. A prototype paint-removal system was built by BDM International and tested by the U.S. Air Force. The system removes a 2-mil-thick coating of paint at a rate of about 2.5 ft2/min. Other systems are designed to remove contaminants that are embedded within the metal surface itself. Laser light ablation for removal of metal surfaces uses a high-power, pulsed laser beam. The system generates irradiance levels sufficient to remove microns of metal from a surface and an off-gas system prevents the material redeposition. Monitoring the laser-generated plasma produced during laser surface ablation may assist process control.

Many laser-based technologies developed for decontamination rely on CO_2 lasers that may be difficult to transport to remote locations and have instrumental characteristics more compatible with the removal of surface coatings, such as paints, than removal of the metal substrate itself. Only short-pulse lasers can ablate materials without causing surface melting, which could entrain contaminants within the bulk. Of course, lasers capable of removing metal substrate can also remove coatings such as paints and oils (DOE, 1994; Tripp, 1996; Bundy, 1993; Archibald et al., 1999).

Lawrence Livermore Laboratory has a portable laser that is able to clean a 5-ft swath on 600 ft of wall in about 1 hr. This laser cleans by photoacoustic stress waves using a 100-watt Nd:YAG beam, pulsing up to 1000 times/second. When the beam hits the painted surface, part of the beam energy is converted into sound waves. The sound hits the underlying hard surface and rebounds. When the echo interacts with incoming sound waves created by the laser, the result is a miniature explosion that pulverizes and removes the paint as a fine dust. Each laser, with its accompanying safety equipment and pointing devices costs about $250,000.

A collaboration between Ames Laboratory and Lockheed Martin Idaho Technologies Company (LMITCO) resulted in the development of an acousto-optic q-switched, fiber optically delivered Nd:YAG laser cleaning system that can remove both surface contamination and metal substrate. This patented technology has been licensed to a vendor for commercialization.

International Technical Associates (InTA) have used lasers for paint and concrete surface removal (up to 1/4 in.). They use a Nd:Yag or a pulsed CO_2 gas laser. Their products include a system specifically designed for the removal of graffiti, paint, organic corrosion, and contamination products from a wide range of surfaces such as street signs, buildings, walls, and vehicles without damaging the base materials. They have another product to remove paint from aircraft without harm, even when the skin is made of graphite-epoxy composite.

Flashlamps and Photochemical Destruction

Radiological decontamination using high-energy xenon flashlamps is an emerging light ablation technology. Flashlamps are being used to clean organic contamination from valuable objects such as artwork, ship hulls, and precious metals. Several flashlamp-based systems are in use in locations around the world. The primary application for flashlamp cleaning is when surface areas need a high degree of decontamination with the absolute minimum amount of waste generation. These systems tend to be rather slow and are not considered large production techniques. The technology produces as waste only the material that is removed from the surface (all the vaporized material is collected in a filtration system) (Bundy, 1993).

A related technique of photochemical degradation matches the UV light frequency to specific hydrogen donors. When the UV light is pulsed, the hydrogen donor and the contaminant react and the contaminant is destroyed. Effective for many organics, this technology shows great promise in hard-to-reach places, but is virtually useless when the contaminant is in dense particulate matter such as soil. The UV light must reach the contamination to be successful. Photochemical degradation is potentially applicable to all surfaces, although best results can be expected on smooth surfaces.

In ultraviolet/ozone treatment, UV light is absorbed by oxygen molecules to form ozone which dissociates to form atomic oxygen. The contaminant molecules are also excited and/or dissociated by the absorption of UV. The excited contaminant molecules and the free radicals react with atomic oxygen to produce simpler, volatile molecules, such as CO_2, H_2O, and N_2O. Used widely in the semiconductor industry, it has not yet been proven in the nuclear industry but may work well for some metal and cleaning. Because inorganic dust and salts are not removed, precleaning is necessary (Meservey et al., 1994).

Plasma Surface Cleaning

Plasma surface cleaning methods by glow discharges are commonly and effectively used for cleaning high-bonding-energy contaminants from surfaces of metals, metal oxides, and glasses. Plasma cleaning is performed in vacuum chambers for accelerators and magnetic fusion devices. Plasma processes of etching and deposition are also used in material processing and microelectronic manufacturing in industry. Extrapolating these plasma-cleaning techniques for decomposing and destroying oil and PCB contaminants in metal process equipment is feasible. Based on known plasma-assisted etching rates, decontamination rates by reactive plasmas are expected to be higher than that by gas-phase decontamination methods. Moreover, the plasma-cleaning process provides a means of separating and recovering uranium from the mixed uranium contaminants, recycling the process equipment, reducing the volume of generated secondary wastes, and helping to minimize the final waste deposition cost. Although additional radio frequency or microwave power is required, the plasma-cleaning techniques will be approximately a factor of ten cheaper and faster than gas-cleaning techniques. Together with a scrubber, the supporting equipment used for the gas-phase decontamination system, including thermal management system, vacuum system, computer control, and monitors, can be used for the waste generated in plasma-cleaning methods (Bundy, 1993).

A device (called the plasma car wash) developed at Los Alamos National Laboratory (Svitil, 1997) allows plasma to survive at room temperature outside a vacuum. This device runs on 300 watts, weighs less than 80 lb, and looks like a leaf blower. It essentially consists of a tank of pressurized gas (the type of gas used depends on the application) that is pumped into a 6-in.-long tube housing two concentric cylindrical electrodes. As the gas shoots between the electrodes, the electric field pulls off its electrons, creating the charged ions of the plasma. The plasma then boosts the energy of other gas molecules in the tube, which shoot out the nozzle and react with other molecules they encounter — like paint in graffiti — by either pulling them apart or stealing their electrons. Most plasmas operate at extremely high temperatures, but the plasma car wash may be able to operate at temperatures below 400°F.

Plasma etching can be done using a fluorine plasma discharge. Volatile fluorides are produced, along with chemically reactive fluorine atoms that promote rapid etching. The contaminated metal surfaces are exposed to energetic ions, electrons, and photons, these greatly enhancing the decontamination rate. Plasma etching and fluorination technology can be developed for *in situ* decontamination (Bundy, 1993).

Water-based reactive plasma uses a water vortex to generate a reactive plasma to destroy hazardous and inert organic fluid wastes. A plasma jet discharging through the high-velocity water vortex will heat feed materials in excess of 2500K. Water is dissociated into O +, O_x, + OH, H, and H_2 reactive species, which then attack and destroy organics. A base can be added to the vortex to remove halogens (O'Brien et al., 1993).

Electrokinetic Techniques

This technique uses an electrical field to cause contaminants to move through concrete pores into the surrounding solution. At the INEEL, concrete decontamination testing was performed by Dry-Tec of North America. Copper-coated steel rods were used as the cathodes and titanium bars as the anodes and were positioned across a concrete slab. When the electrical circuit was connected, a controlled cyclical voltage was applied to the system to cause osmotic migration of water in the concrete from the anode to the cathode. As the moisture was either pushed or pulled out of the concrete, contamination was also pushed or pulled through the concrete. This method is probably more limited to small areas than large production applications. The test results indicated some migration of contaminants with further testing needed to refine the technique (Tripp, 1996).

Oak Ridge National Laboratories has developed a portable electromigration decontamination technology that can be used on a localized concrete area. It uses an electrolytic solvent and electricity to cause the contamination ions in the concrete to migrate to the surface. Electromigration is a slow but very inexpensive process. Because it works best in high electric fields, if either the solvent or contaminant is very conductive, the process is slowed down (Bundy, 1993).

Chemical Decontamination

Chemical decontamination is probably the most universally used system for the decontamination of metal surfaces. Solvents can be used to dissolve the contamination film (non-destructive) or the base metal itself. Chemical decontamination can usually be performed with the least amount of process changes, personnel interaction, and direct operator exposure.

The advantages of chemical decontamination solutions include:

- Used for inaccessible surfaces
- *In situ*

- Less labor
- Used remotely
- Reduce airborne hazards
- Readily available
- Wastes remotely handled
- Allows recycling of solutions

The disadvantages of chemical decontamination solutions include:

- Not usually effective on porous surfaces
- Large volumes of secondary waste
- Possible mixed waste
- Corrosion possible
- Safety hazards
- Chemical makeup and storage
- Criticality concerns

It should be noted that the generation of "mixed wastes" (i.e., a mixture of hazardous and radioactive materials) creates special problems for decontamination processes. Because of the difficulty of disposing of mixed wastes, there are generally severe restrictions on their generation. Because mixed waste disposal sites are few and expensive, all mixed wastes generated must be either treated immediately or stored until such treatment technologies can be developed and made available. Thus, special care must be given when selecting chemical decontamination technologies such that a mixed waste by-product is not inadvertently created.

Table 8.2 shows the relative performance factor for several chemical decontamination technologies. This table gives the relative cleaning efficiency, waste generated, applicability, and general chemical type that characterize each of the chemical decontamination processes. A general discussion is given of each chemical type with some examples given in the text that follows.

Water Methods

Water can be an excellent decontamination agent for many jobs. It is readily available at all facilities and can be used to dissolve or simply flush away various contaminants. However, if a contaminant is deposited in an oxide layer, particularly in a high-temperature process such as a reactor, then pure water is not going to perform well. Detergents and surfactants are often added to aid in contaminant removal. Water is often combined with another technique such as scrubbing or as a flush between chemical treatments.

The method of decontamination by steam provides a mixture of water, steam, and a decontaminating solution. The method is intended for decontamination of tanks and extraction equipment, pipelines, and movable (demountable) equipment. The preparation of steam mixtures is carried out in special devices, using saturated and superheated steam (Tikhonov et al., 1998).

Organic Solvents

Solvents are used in decontamination for removing organic materials, grease, wax, oil, paint, etc. from surfaces and for cleaning clothes (dry cleaning). Some typical organic solvents are kerosene, 1,1,1-trichloroethane, trichloroethylene, xylene, petroleum ethers, and alcohols. Advantages are that where organic solvents can be properly handled, less secondary waste is generated than using water and detergents. The solvents are more effective than water for organic compounds. Disadvantages of organic solvents are they are limited to specific materials (normally plastics must be avoided), are hindered by the presence of water, often do not remove water-soluble stains, are generally flammable and toxic, and

TABLE 8.2 Relative Performance Factors for Chemical Decontamination Technologies

Process or System Name	Description of Process	Type of Chemistry	Type of Materials	Chemicals Used	Relative Efficiency of Process[a]	Relative Amount of Waste	Type of Waste
AP	Alkaline permanganate	Oxidation	Stainless and carbon steels	$KMnO_4$, KOH, NaOH	Low	High	Salt solutions, resins
TURCO 4502	Proprietary AP						
APAC	AP followed by ammonium citrate (AC)	Oxidation/ reduction	Stainless and carbon steels	KMnO4, KOH, NaOH, ammonium citrate	Medium	High	Salt solutions, resins
APACE	APAC with EDTA	Oxidation/ reduction/ complexing	Stainless and carbon steels	$KMnO_4$, KOH, NaOH, ammonium citrate EDTA	Medium	High	Salt solutions, resins
APOX	AP followed by oxalic acid	Oxidation/ reduction	Stainless steel	$KMnO_4$, KOH, NaOH, oxalic acid	Medium	High	Salt solutions, resins
AP-citrox	AP followed by citric and oxalic acids	Oxidation/ reduction	Stainless steel	$KMnO_4$, KOH, NaOH, citric acid, oxalic acid	Medium	High	Salt solutions, resins
Alkaline persulfate, citrox	AP with persulfate, followed by citrox	Oxidation/ reduction	Stainless steel	$KMnO_4$, KOH, NaOH, potassium persulfate, citric acid, oxalic acid	Medium	High	Salt solutions, resins
APSul	AP followed by sulfamic acid	Oxidation /reduction	Stainless and carbon steels	$KMnO_4$, KOH, NaOH, sulfamic acid	High	High	Salt solutions, resins
MOPAC (APAC/ APOX)	Proprietary system from Siemens, AP followed by citric acid, oxalic acid, EDTA with Fe(III) inhibition	Oxidation/ reduction/ complexing	Stainless and carbon steels	$KMnO_4$, KOH, NaOH, citric acid, oxalic acid, EDTA	High	Medium	Salt solutions, resins
NP	Nitric acid and potassium permanganate	Oxidation	Stainless steel	HNO_3, $KMnO_4$	Medium	Medium	Salt solutions, resins
LOMI	Proprietary system from EPRI, AP, or NP, followed by low oxidation metal ion (vanadous formate)	Oxidation/ reduction	Stainless steel, Inconel	AP or NP with vanadous formate and picolinic acid	High	Medium	Salt solutions, resins
CANDECON	Proprietary system from AECL; can be used with AP and NP	Reduction/ complexing	Stainless steel	Citric and oxalic acids with EDTA	Medium	Low	Resins

TABLE 8.2 (Continued) Relative Performance Factors for Chemical Decontamination Technologies

Process or System Name	Description of Process	Type of Chemistry	Type of Materials	Chemicals Used	Relative Efficiency of Process[a]	Relative Amount of Waste	Type of Waste
NS-1	Proprietary system from Dow Chemical	Complexing	Stainless steel	Unknown, complexing agents and inhibitors	High	High	Salt solutions
CANDEREM	Proprietary system from AECL; can be used with AP and NP	Reduction/ complexing	Stainless steel	Citric acid and EDTA	Low	Low	Resins
HP/CORD	Proprietary system from Siemens; permanganic acid, reduction with organic acids	Oxidation/ reduction	Stainless steel	Permanganic acid, oxalic acid; hydrogen peroxide	High	Low	Resins
POD	Reduction chemistry; can be used with AP and NP	Reduction/ complexing	Stainless steel		Medium	unknown	Salt solutions, resins
OZOX-A	Proprietary system of Kraftwork Union AG	Reduction	Stainless steel	Oxalic acid	Medium	Medium	Salt solutions, resins
OPP	One-step oxidizing agent	Oxidation/ reduction	Stainless and carbon steels	Oxalic acid, hydrogen peroxide	Medium	Medium	Salt solutions, resins
Hydrochloric acid	One-step, very corrosive system	Dissolution	Stainless and carbon steels	HCl	Medium	High	Salt solutions
Nitric acid	One step	Dissolution/ oxidation	Stainless steel	HNO_3	Low	Medium	Salt solutions
Sulfuric acid	One step	Dissolution/ oxidation	Stainless and carbon steels	H_2SO_4	High	Medium	Salt solutions, resins
Phosphoric acid	One step	Dissolution	Stainless and carbon steels	H_3PO_4	Medium	Medium	Acid solutions
Sulfamic acid	One step	Reduction	Carbon steel and copper	Sulfamic acid	Low	Medium	Acid solutions
Nitric and hydrofluoric acids	One step	Dissolution	Stainless steel	HNO_3, HF	High	Low	Acid solutions (complexed)
Nitric and sulfuric acids	One step, very corrosive	Dissolution, Oxidation	Stainless steel	HNO_3, H_2SO_4	High	Medium	Acid solutions

TABLE 8.2 (Continued) Relative Performance Factors for Chemical Decontamination Technologies

Process or System Name	Description of Process	Type of Chemistry	Type of Materials	Chemicals Used	Relative Efficiency of Process[a]	Relative Amount of Waste	Type of Waste
Fluoroboric acid	Proprietary system from ALARON Co., one step, very corrosive	Dissolution	Stainless and carbon steels, nickel alloys	HBF_4	High	Medium	Acid solutions (complexed)
Oxalic acid	One step	Reduction/ complexing	Stainless steel	Oxalic acid	Medium	Medium	Acid solutions
Citric acid	One step	Reduction/ complexing	Stainless steel	Citric acid	Medium	Medium	Acid solutions
Nitric and hydrochloric acids	One step	Dissolution	Stainless and carbon steels	HNO_3, HCl	Medium	Medium	Acid solutions
Ce(IV) process I	Proprietary system from PNNL (Battelle); one step, very corrosive	Dissolution	Stainless steel	HNO_3, $Ce(NO_3)_4$	High	Medium	Acid solutions
Ce(IV) process II	Proprietary system from PNNL (Battelle); one step, very corrosive	Dissolution	Stainless steel	H_2SO_4, $Ce(NO_3)_4$	High	Medium	Acid solutions
Ce(IV) process III	Proprietary system from PNNL (Battelle); one step, very corrosive	Dissolution	Stainless steel	HNO_3, $Ce(NO_3)_4$, KF	High	Medium	Acid solutions
Ag(II) process	Proprietary system from PNNL (Battelle)	Oxidation	Stainless steel	HNO_3, $K_2S_2O_8$, $AgNO_3$			Acid solutions

This table adapted from “A Survey of Decontamination Processes Applicable to DOE Nuclear Facilities, ANL-97/19, (Chen et al., 1997).

[a] All factors are subjective and may change based on application or specific equipment, but should be nearly those quoted here.

Performance factors are based on relative reported cleaning of these methods: High is typically over about 90%, Medium is about 70%, and Low is less than 70%.

Waste factors are based in relation to standard APOX-type application, which typically contains greater than 20% salt content.

Cost is not typically a significant concern except for processes that are vendor supplied or proprietary; then cost may be an issue

because many contain chlorine, they are not used around stainless steel (Meservey et al., 1994; DOE, 1994). Because many organic solvents can generate mixed waste, care should be exercised when using chemical decontamination solutions to avoid the generation of radioactive mixed wastes.

Oxidizers

The most common chemical decontamination method (next to water flushing) is oxidizing chemistry. Oxidizers are chemical compounds that remove electrons from other molecules, causing them to increase in positive charge. A higher oxidation state is often more soluble. Almost since the beginning of the nuclear industry, it was recognized that an oxidizing solution, usually an alkaline permanganate, was very effective in removing contaminants. In more recent times, the concept of a chromium-rich oxide (crud) layer, and the subsequent requirement to dissolve and disrupt this layer, began to gain acceptance in the decontamination profession (Pick, 1982). This description appears to explain the alkaline permanganate systems, as well as other oxidizers. A chemical theory was developed to explain this according to the reaction:

$$2MnO_4^- + Cr_2O_3 + 2H_2O = 2MnO_2 + 2HCrO_4^- + 2H^+ \tag{8.1}$$

The $HCrO_4^-$ is more soluble than Cr_2O_3. Disrupting the metal surface film releases the trapped radionuclide particles and decontaminates the metal. This is often the first step in the two-step alkaline permanganate/oxalic acid process. The second step uses oxalic acid ($C_2H_2O_4$), or another suitable reductant, to reduce iron oxide, disrupting this strongly held oxide. The alkaline systems are often called APAC (for alkaline permanganate, ammonium citrate) or APOX (for alkaline permanganate, oxalic acid) (Torok, 1982). Cycling the decontamination chemistry from oxidative to reductive solutions is more effective than either chemistry alone. A novel method used by Siemens Co. uses permanganic acid, instead of potassium permanganate, which generates less waste (Bertholdt, 1998).

Nitric acid-potassium permanganate (NP) decontamination solutions have also been used with success. Decontamination factors (DFs) for the NP system at the Ringhals 2 (Sweden) nuclear reactor system were 6.4 to 7.3, while the AP DF stood at 1.9 to 2.3 (Pick, 1982). NP systems have also been successfully used in the Eurochemic Reprocessing Plant in France, and in the Tokai Reprocessing Facility in Japan (Van Geel et al., 1971). A newer method of chemical oxidation, using cerric (IV) nitrate, was developed by engineers at Battelle Pacific Northwest Laboratories (PNL), Richland, Washington (Bray, 1988). This method involves controlled milling of a stainless steel surface using the strong oxidizing effect of the Ce (IV) ion, which is highly corrosive. A substantial amount of development work was conducted for West Valley Nuclear Services by PNL during the late 1980s employing this method to decontaminate glass canisters. The corrosion potential of the cerric (IV) nitrate waste can be reduced with the addition of a small amount of hydrogen peroxide to produce a noncorrosive cerrous(III) nitrate.

Reductants

Reductants perform a different, although complementary, function with the oxidizers. Reduction occurs when a compound donates electrons to a molecule and lessens it positive charge. Some molecules are rendered more soluble as reduced ions. Most of the organic acids — including oxalic, citric, tartaric, and formic acids — are good reductants. They are also usually good chelating agents (Demmer, 1996).

Oxalic and citric acids are the most commonly used reductants, and have been combined for use in the Citrox and Citrosolv reagents, and in dilute quantities in the Candecon and Canderem processes (Wood and Spalaris, 1989). The reduction typically proceeds according to the (oxalic acid) reaction:

$$Fe_2O_3 + C_2H_2O_4 = 2FeO + 2CO_2 + H_2O \tag{8.2}$$

The FeO is more soluble than the Fe_2O_3, and some oxide is dissolved and disrupted. Because it proceeds as a reduction, the process is generally less corrosive, and creates less waste, than an oxidizing chemistry. Reductants are also often used during the treatment of spent oxidizers.

Another example of the reduction chemistry is the Low Oxidation Metal Ion (LOMI) process (Bradbury et al., 1983). This chemistry uses a vanadous formate solution, dissolved in picolinic acid, to cause the reduction. This is a very powerful reactant, so much so that the vanadous formate can be rapidly oxidized by air. It requires isolation of systems, nitrogen blankets, licenses for use, and is, in general, a fairly complicated and expensive process. It is, however, a very appropriate process when all these criteria are available. It shows good decontamination results with very low final waste quantities. LOMI has been used with good results at the Yankee Rowe facility during decommissioning activities.

Acids

Dissolving materials in acid is an ageless process. The variety of reactions that take place when mineral acids (nitric, sulfuric, hydrochloric, hydrofluoric, phosphoric, etc.) are used in dissolution and decontamination are beyond the scope of this discussion. Some of the reactions are acid-base reactions, complexation, and corrosion of the substrate. Virtually all of the mineral acids have been used in decontamination at some time. They produce relatively low secondary waste, but some (particularly HCl) have serious corrosion concerns. Nitric acid (HNO_3) is one of the most commonly used decontamination processes, partly because of its compatibility with stainless steels. Solutions of 3.5 M HNO_3 and 0.04 M HF have long been used as cleaning/etching solutions on stainless steel (Rankin, 1992). Another common acidic decontamination solution used at the INEEL is a solution of 3.5 M HNO_3 with 0.5 M oxalic acid. Combinations of several organic acids and mineral acids (citric and oxalic acids with nitric acid) have been documented (Zohner, 1996). Organic acids add an extra dimension because they serve as acids, reductants, and usually chelants.

Fluoroboric acid (HBF_4) is an excellent decontamination reagent with extremely high decontamination factors. A commercial vendor, ALARON Co., reports decontamination factors of 50 to 100 using the fluoroboric acid process (Rollar, 1993). ALARON also uses a process for recycling and regenerating fluoroboric acid that decreases the amount of fluoroboric acid that goes to waste (Figure 8.3). This DECOHA technology has been proven in laboratory tests and has been used at the damaged reactor at Chernobyl (Beaujean et al., 1991). While not a perfect "closed-loop" system, DECOHA offers capabilities that would provide significant recycling benefits. The Electric Power Research Institute (EPRI) has also developed a more harsh fluoroboric acid method, known as decontamination for decommissioning (DFD). This method has been used at Big Rock Point for decommissioning (Rollor et al., 1997).

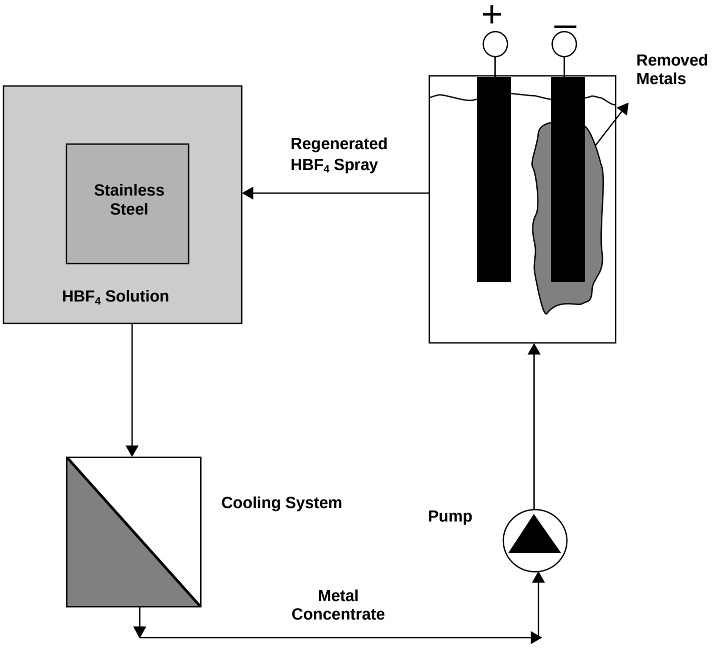

FIGURE 8.3 DECOHA™ acid recycle.

Another effective decontamination method is the TechXtract process, provided by the private decontamination firm EET of Bellaire, Texas. The TechXtract chemistry is a patented process that combines some 25 different chemicals to incorporate dissolution, oxidation, reduction, hydrolysis, decomposition, wetting, complexation, microencapsulation, and flotation chemistry principles (Bonem, 1996). When complete, the process produces a nonhazardous matrix that contains only the waste codes of the contaminants of the original target material. The INEEL has used the TechXtract process to decontaminate both concrete slabs and miscellaneous tools containing fission products (Bonem, 1994). EET has also successfully demonstrated the removal of technetium and uranium from nickel-plated components at the Oak Ridge National Laboratory K-25 gaseous diffusion plant.

Chelants

Chelating agents (chelants) decontaminate materials by surrounding and absorbing (complexing) the contaminant, making it more soluble. Many of the organic acids, as well as some mineral acids, have the ability to complex contaminants. Citric and oxalic acids are two very good chelants. Typically, however, the best chelants are large organic molecules such as ethylenedinitrilotetraacetic acid (EDTA). These chelants are usually used in a system, along with acids, oxidizers, or reductants, to improve the overall decontamination performance.

Two commercially available chelant systems have shown good results in tests at the INEEL. CORPEX 921 is one such reagent available from the CORPEX Co. It has a unique formula, which is superior in decontamination to other common chelants previously used. Hanford, Oak Ridge, and Peducah DOE sites have used it with good results (Coleman, 1997). Thermally unstable complexing solutions (TUCS) are also effective chelating reagents. Ionquest 201 is a strong complexing reagent marketed by the Albright and Wilson Chemical Company. This is a proprietary chemical that is an organic phosphonic acid. It was developed to extract chemical species, notably uranium and some actinides, from nuclear processes (Balint and Beyad, 1993). Used with a catalyst, it has the capability of removing contaminants from the metal surfaces.

Alkaline Reagents

Alkaline reagents include potassium hydroxide, sodium hydroxide, sodium carbonate, trisodium phosphate, and ammonium carbonate and can be used to remove grease and oil films, neutralize acids, act as surface passivators, remove paint and other coatings, remove rust from mild steel, solubilize species that are soluble at high pH, and provide the appropriate chemical environment for other agents. They are often used alternately with strong acids to clean materials. Alkaline solutions can be used on all nonporous surfaces except aluminum and magnesium, which react with strong bases. Only moderate quantities of waste are produced and simple neutralization and precipitation has been the traditional treatment (Meservey et al., 1994; Tripp et al., 1999).

Special Chemical Decontamination Processes

Explosive

Explosive decontamination can be used to remove the top 3 or 4 in. of concrete by detonating carefully placed and timed explosive charges. Capital costs are estimated to be under $50K, with operating costs of $\$5/\mathrm{ft}^2$. Safety concerns need to be resolved; and care must be taken to contain the dust and to prevent structural damage to both the building being decontaminated and the surrounding structures. Improvements in the methods of applying explosives and in the uniformity of the detonation are needed. The explosion can generate toxic organic vapors. The technology to control these vapors must be developed and demonstrated (Meservey et al., 1994; Bundy, 1993).

Electropolishing

Electropolishing is an electrochemical decontamination technique that removes a thin layer, approximately 0.002 in. (0.5 μm), from the surface of contaminated metals. The process establishes an electrical potential between the contaminated item (the anode) and a cathode in an acid electrolyte. Any contamination on the surface or in the pores of the surface is removed and released in the electrolyte by the surface dissolution process. Electropolishing can achieve very high decontamination factors and could be considered for special applications in a decommissioning program (e.g., salvage of a valuable component whose size is consistent with available electropolishing tank systems). Electropolishing has been carried out with various electrolytes, including phosphoric, nitric, sulfuric, and organic acids. The ability to remove contamination from deep cracks, crevices, holes, and other areas that are shielded from the cathode is limited, unless the geometry is favorable for the use of an internal cathode. The surfaces to be decontaminated must be conductive, and should be free of paint, grease, tape, heavy layers of corrosion products, and any other surface material that might inhibit the electropolishing action. Because of electrolysis of the electrolyte, hydrogen can be generated during the process, creating an explosion hazard which can be eliminated by proper forced ventilation of the area [Bundy, 1993; Demmer, 1998).

The electropolishing process can now also be applied to large metal surfaces through the use of close-proximity nozzles to spray the charged electrolyte over the contaminated surface. This and the use of electrolyte-charged sponges can be used to minimize the volume of electrolyte required by eliminating the need to flood (or submerge), the component.

Supercritical Fluid Extraction

Supercritical fluid extraction (SFE) uses the properties of a solvent (typically carbon dioxide) under high pressure to remove contaminants. Under these conditions, the solvent is as efficient at extracting the contaminants as more hazardous solvents. Supercritical extraction by carbon dioxide (SC-CO_2) has enabled the extraction of 75 to 97% of air dry uranyl, plutonium, and americium nitrates from stainless steel, rubber, and asbestos surfaces (Skobcov et al., 1997). It has found only limited adoption in radioactive decontamination because of the need for high pressures and temperatures. In comparison with washing of surfaces by acid and alkaline solutions of oxidizers and complexing agents, SFE reduced the amount of secondary waste without using hazardous chemicals, and without the risk of flammable and/or corrosive chemicals.

Gels and Foams

Foams and gels are used as a method to enhance chemical decontamination by improving coating contact time and surface area covered per volume. Reagents can be mixed in a gel medium and used for decontamination. This approach significantly reduces the quantity of liquid waste normally generated in a cleaning bath or water jet. Gels that have been tested include organic, inorganic, and inorganic modified by organic additives (include glycerophatic, glycerophosphoric, silica and diopside gels). Gels are compatible with most decontaminants. The gel coating can be applied by paintbrush, spray gun, or dipping. Depending on type, the gel is removable by mechanically stripping, dissolution in water, or drying to a powder and removing with a vacuum. The cleaning effectiveness of this method is equivalent to conventional liquid processes and is less costly both in chemical reagents and required labor. They are best for *in situ* removal of smearable contamination over large or odd-shaped objects (Bundy, 1993; Meservey et al., 1994; Demmer, 1998).

Chemical foams are used to increase solution contact time with contaminated items. Foam is used as a carrier of a chemical decontamination agent, and is applied in a thin layer (1 to 2 in. thick) to a surface in any orientation. The foam is produced by injection of air with a foaming agent into the decontamination solution in a pressurized applicator. The solution is sprayed on the surface, foams, and is subsequently rinsed off. Surfactants can be obtained that have various foam breakdown times and that can decompose. Decomposition is necessary to prevent foaming problems in downstream waste processing equipment such as evaporators. Testing has indicated that a liquid chemical waste reduction of 70% is possible. Acid volume requirements decreased by a factor of 20 to 50. More recently gels have been preferred for equipment exteriors, and foams are utilized by circulating in pipes and systems *in situ* (Meservey et al., 1994).

Gas-Phase Decontamination

This long-term, low temperature process of gas-phase, *in situ* decontamination of equipment employs the fluorinating agents ClF_3 and F_2 to remove uranium contamination present on diffusion cascade equipment. The gaseous diffusion process for uranium enrichment employs an isotopic separation barrier arranged in diffusion cascades to increase the assay of the fissionable isotope ^{235}U to levels suitable for use in commercial nuclear power reactors (Riddle, 1998).

Biological Decontamination

Nature provides an environmental microbiological resource that has numerous potentially useful bioprocessing applications. Sulfur and nitrogen oxidizing microbes are of potential interest for concrete surface removal applications. The biodecon (biodecontamination) process is based on the use of naturally occurring microbes. A concrete degradation phenomenon occurs in nature and is illustrated in degraded concrete pipelines, bridges, and other structures where microbial activity is stimulated by optimum moisture and nutrient conditions. Concrete sewer pipes have been the most frequently attacked structures. A reduced form of sulfur is the usual environmental nutrient. The basis of the effect stems from production of sulfuric acid by the microbes, which in turn dissolves the cement matrix of the concrete. Several types of bacteria are known to promote degradation of concrete. Sulfur-oxidizing bacterial strains of *Thiobacillus thiooxidans* have been selected for the biodecontamination process. *T. thiooxidans* bacteria are the most aggressive concrete degraders. Concrete surface materials are loosened as a result of their metabolic processes. These naturally occurring, nonpathogenic, ubiquitous bacteria oxidize reduced forms of sulfur (H_2S, S, $S_2O_3^{-2}$, $S_4O_6^{-2}$) to sulfuric acid. They stick to the surface by producing, at the microscopic scale, a biofilm or adhesive. This acid at several "microsites" loosens the surface. The bioprocess produces no effluents because the microbes produce the acid at numerous microsite locations on the concrete surface. This microbially produced acid is neutralized during the concrete surface loosening process. The dissolution of cement at these microsites results in loosened concrete surface that can be collected for special disposal. The depth of concrete surface removal has been observed to be between 2 and 8 mm/year. The *T. thiooxidans* bacteria show no ionizing radiation effects in tests conducted thus far and are not expected to show any effects in most biodecontamination cases being contemplated (Johnson et al., 1996).

Microbially induced degradation (MID) has been shown to be effective on floors and small concrete chambers. Walls and ceilings pose other problems. Tests indicate that the process involves the removal of calcium from the concrete. In tests at the INEEL, fixed contamination on the treated surfaces showed significant decontamination. The surface activity before application was 600 to 900 cpm, after 5 months of treatment when the surface was scraped to remove the organisms, the surface readings were just slightly above background (Rodgers et al., 1997).

Bulk Decontamination

Contamination resulting from neutron activation of elements or impurities present in the materials itself is called bulk contamination. One of the primary sources of bulk contamination is the material containing activation products (cobalt, iron, nickel, zinc) from reactor facilities. Surface decontamination technologies will not be effective for bulk contaminated materials.

Thermal/Melt Refining

Thermal processes are used throughout the metals industry for processing ores and metal reprocessing. A number of different furnace technologies have been used, but induction and resistance furnace technologies are the most applicable to processing of radioactively contaminated metals, due mainly to the increased ability for maintaining contamination control and proper atmospheric processing environments.

Key parameters in melt refining include type of metal, types and concentrations of radioactive contaminants, the partitioning of the radionuclides between the slag and ingot, the compatibility of slags and refractory materials, melting techniques, and flux chemistries. Melt refining does not remove radionuclides (such as cobalt, iron, nickel, and carbon) that are part of the initial metal alloying elements. Most uranium and transuranic isotopes and their daughter products can be removed, with the exception of technetium and strontium. However, a number of studies indicate low decontamination factors. To increase separation efficiencies, various types of fluxes and slag compositions can be used (Heshmatpour and Copeland).

The Center for Nuclear Studies at Saclay, France, reported that it achieved a separation of cobalt from the other elemental constituents of a mild steel type C 1023. The melting process operations were carried out with liquid/liquid, liquid/solid, and solid/solid systems. The best results were obtained in the solid/solid phase at 1000°C in an oxidizing atmosphere using a slag containing barium, that resulted in approximately 84% of the contained cobalt being separated. The purpose of this program was twofold: to reduce the volume of waste for burial and to permit recycled use of the metal in either controlled or uncontrolled applications (NEA Group of Experts, 1981).

Catalytic Extraction Process (CEP)

The catalytic extraction process uses an induction or electric arc furnace to form a molten metal bath. The catalytic extraction process uses the molten bath not only as a means for metal purification, but also as a high-temperature, high-energy density medium for more effectively reducing hazardous waste materials such as PCBs, hydrocarbons, and cyanide to nonhazardous material. The molten metal at about 3000°F provides much more effective contact with the material in a smaller volume than possible with the hot gases in a conventional incinerator.

A CEP was developed by a commercial vendor to use standard off- the- shelf steel industry equipment. It is unique concerning the use of a molten metal bath to more effectively disassociate hazardous materials with potential recovery of valuable of usable constituents. If oxygen is needed by the waste being processed, it is added as pure oxygen rather than air. Off-gases are 1/5 to 1/50 the volume created in an incinerator for the same amount of material processed. Capital costs are estimated at 1/2 that of an incinerator and operational costs are estimated at 1/3 those of an incinerator. It is estimated that ~50 lb of slag would be generated per ton of scrap metal processed by smelt purification. However, unless a suitable fluxing agent can be demonstrated to remove radionuclides, the process may find little use in decontamination work. If the problem of removing radionuclides is corrected, then the recovery of nickel alone could possibly pay for the process (Meservey et al., 1994).

Defining Terms

ALARA	As Low As Reasonable Achievable
ANL	Argonne National Laboratory
AP	Alkaline permanganate
APAC	Alkaline permanganate ammonium citrate
APACE	Alkaline permanganate ammonium citrate EDTA
APOX	Alkaline permanganate oxalic acid
APSul	Alkaline permanganate sulfamic acid
BWR	Boiling Water Reactor
CEP	Catalytic Extraction Process
DF	Decontamination Factor
DOE	Department of Energy
EDTA	Ethylenedinitrolotetraacetic acid
ft.	Feet
GHz	GigaHertz

H	High
HEPA	High Efficiency Particulate Air
HP	Horsepower
hr	Hour
in.	Inch
INEEL	Idaho National Engineering and Environmental Laboratory
InTA	International Technical Associates
L	Low
lb	Pound
LMITCO	Lockheed Martin Idaho Technologies Co.
LOMI	Low Metal Oxidation Ion
M	Medium
m	Meter
MID	Microbially Induced Degradation
min	Minute
N	No
NEA	National Engineering Academy
NP	Nitric permangante
OSHA	Occupational Safety and Health Administration
PCB	Polychlorinated biphenyls
PNL	Pacific Northwest Laboratory
psig	Pounds per square inch
PWR	Pressurized Water Reactor
SFE	Supercritical Fluid Extraction
TCS	Tube Cleaning System
TUCS	Thermally Unstable Complexing Solution
UV	Ultraviolet
Y	Yes
yd	Yard
ZAWCAD	Zero Added Waste Cutting Abrading and Drilling

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Chapter Nine

System Integration and Deployment

9.1

The Integration of Mixed Waste Treatment into an Environmental and Quality Management System

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Introduction

This section discusses the role of modern methods in mixed waste treatment (MWT) technology as part of a systematic approach of integrating this technology into an environmental management system (EMS) or a quality management system (QMS), with environmentally sustainable development (ESD) — or environmental sustainability — as a performance goal. A brief background on the two major international standards (ISO 9001:1994 and ISO 14001:1996) as templates for quality and environmental management systems is provided.

Because MWT technology is a broad area, the emphasis in this section is on the planning aspects and major questions a professional should consider when deliberating the successful integration of MWT technology into an EMS and QMS. Planning aspects should encompass key areas such as human health toxicology, human health risk assessment, and ecotoxicology. The principles of this section can also be used for any type of waste, mixed as well as non-mixed.

This section will help prepare the reader so he/she can choose the best MWT technology for a particular need, thereby attaining or approaching environmental sustainability. Texts and references listed at the end of the section provide further detail about the QMS, EMS, and ESD.

What Is Environmental Sustainability and its Relationship to MWT?

Environmental sustainability and sustainable development are terms sometimes used interchangeably. Without splitting hairs, one might say that sustainable development leads to environmental sustainability. To explain more precisely what these concepts mean, and how crucial they are for MWT technology, a short history of their evolution is beneficial.

In 1987, the United Nations (U.N.) World Commission on Environment and Development (Brundtland Commission) coined “sustainable development” in its report entitled “Our Common Future.” This report, which emphasized the need to balance environmental protection and economic growth, defined sustainable development as “development that meets the needs of the present without compromising the ability of future generations to meet their needs." This perhaps is the earliest modern use of the term and the simplest definition.

In 1991, the International Chamber of Commerce (ICC) created the *Business Charter for Sustainable Development.* The ICC Charter is composed of 16 principles for environmental management that foster sustainable development. The principles in this document include some of the basic elements of environmental management systems still in use today.

In 1992, the U.N. Conference on Environment and Development (UNCED) was held in Rio de Janeiro, Brazil. The conference, also known as the Rio Summit or Earth Summit, resulted in two important documents: "Agenda 21" and the "Rio Declaration." "Agenda 21" is a comprehensive guidance document for sustainable development, and the Rio Declaration provides a set of 27 principles for achieving sustainable development.

The progress of the "Agenda 21" initiatives was evaluated in a follow-up summit in June of 1997. The goals of this follow-up summit were to assess progress, share best practices, evaluate gaps in financial and economic terms, and build better infrastructure toward "Agenda 21" sustainable development objectives. The summit results indicated:

1. An increase in global warming from greenhouse gases such as carbon dioxide
2. A growing presence of toxic chemicals in the environment
3. A growing scarcity of freshwater and a loss of productive farmland
4. Growing marine pollution and a loss of viable fisheries
5. Continued destruction of forests.

Also in 1997, at a global warming convention in Kyoto, Japan, consensus was reached on cutting back on greenhouse gases to various degrees in various regions of the world, and timetables to achieve these cutbacks were set. At the time this section was written, the U.S. Congress had not ratified the Kyoto agreement and was not expected to do so. But its impact has been felt in many U.S. industrial sectors, and voluntary compliance with carbon dioxide reduction levels has gained momentum. Carbon dioxide production — and the growing need to reduce it — affects MWT technology decisions now and will continue to do so in the future.

In May 1999, the U.S. President's Council on Sustainable Development released "Towards a Sustainable America: Advancing Prosperity, Opportunity, and a Healthy Environment for the 21st Century — Final Report of the President's Council on Sustainable Development." This report concluded that moving environmental management into the 21st century required:

- A broader understanding of the nature, source, and linkage of environmental problems and recasting of potential solutions
- A system that is goal-, performance-, and information-driven; is attuned to natural ecological cycles; incorporates the values of community and place; is sensitive to variations in the business sector and changes in the economy; and increases outside participation in decisions that affect the environment and neighboring communities
- Continued refinement of traditional environmental management tools, while encouraging development of new tools and collaborative strategies.

The President's Council outlined many goals defining environmental sustainability; the four most important relating to MWT are listed below:

> **Goal 1: Health and the Environment.** Ensure that every person enjoys the benefits of clean air, clean water, and a healthy environment at home, work, and play.
> **Goal 2: Economic Prosperity.** Sustain a healthy U.S. economy that grows sufficiently to create meaningful jobs, reduce poverty, and provide the opportunity for a high quality of life for all in an increasingly competitive world.
> **Goal 3: Equity.** Ensure that all Americans are afforded justice and have the opportunity to achieve economic, environmental, and social well-being.

> **Goal 4: Conservation of Nature.** Use, conserve, protect, and restore natural resources, land, air, water, and biodiversity in ways that help ensure long-term social, economic, and environmental benefits for ourselves and future generations.

The first three goals outline what has been called the three Es of sustainable development: environment, economics, and equity. The last goal addresses the broad definition of environmental sustainability that can be summarized as "leaving the earth in at least as good a condition for future generations as was received by ours."

These national and international initiatives on sustainable development have marked the dawn of a new age in environmental protection. The initiatives directly impact MWT as the last link in a technical *system* chain (or *system*) leading to the environment. The growing societal expectation in the past decade, which will likely continue in the 21st century, is for the public and private sectors to operate sustainably. Technically, this forces two modes of operation: either a closed-loop *system* with no impact on the environment — of which MWT will be one facet of that cycle — or an open *system* that involves MWT as the last link to the environment.

For open *systems*, defined as a system in which the material at the end of the treatment process will be released to the environment, the mixed waste treatment chosen must have scientific assurance (through risk assessment and other means) that the environmental products released will be reincorporated renewably into the environment, be economically feasible, and equitable for the community. In short, if an MWT *system* is not closed, the MWT technology model used will have to limit disposal within the assimilative capacity of the air, water, and soil. Examples of these technologies are described elsewhere in this Handbook.

The term "system" was highlighted above (in italics) to underscore the importance of its ability to demonstrate accountability and verification of MWT technology in relation to environmental performance and sustainable development. For the remainder of this section, the ISO standards for quality (ISO 9001:1994, Specification for a Quality Management System (SQMS)) and environmental (ISO 14001:1996, Specifications for an Environmental Management Standard (SEMS)) will be used as templates for integrated quality and environmental management. These standards, the most globally accepted of their kind, outline the concepts common to all good quality and environmental management systems.

What Are ISO and ISO 9001 and ISO 14001?

The International Organization for Standardization (ISO), founded in 1946, is responsible for the development of the ISO 14000 series of international quality and environmental management standards. ISO, based in Geneva, Switzerland, has developed international voluntary consensus standards for manufacturing, communication, trade, and management systems. Its mission is to promote international trade by harmonizing international standards and developing new ones when there is a need. More than 100 countries have national standards bodies that are members of ISO, although only a few are voting members (called participating, or P, members) with the power to vote on ISO standards.

The American National Standards Institute (ANSI) is the U.S. representative to ISO, voting on ISO standard matters on behalf of the United States. ANSI was formed in 1918 to develop U.S. consensus standards and to coordinate this nation's involvement in international standards. ANSI consists of representatives from industry, government, consumer organizations, professional societies, labor, and other groups and represents a wide berth of American stakeholders. All voting within ISO is on a one-country, one-vote basis; the size of a nation's market, geographical area, or population is not a factor. ANSI is the only private-sector, nongovernmental voting member within the ISO and reflects the United States' dedication to private-sector control of voluntary standards related to trade and other matters.

ISO produces specification standards, which have certain elements that must be implemented as requirements if one is to conform to the standard. Through an internal or external auditing process, parties demonstrate conformance to a specification through a registrar or other recognized standards body. The ISO also produces guidelines, which are not requirements and may not be audited; however, these guidelines provide users with internationally agreed-to definitions, interpretations of elements of a standard, and helpful advice with implementation.

Development of ISO 9000 Quality Management Standards

The ISO 9000 series of international quality management standards was published in 1987 after nearly a decade of back-and-forth negotiation. These standards were created to promote consistent quality practices and to facilitate international trade. The ISO 9000 series has been adopted by more than 80 countries and is used as a benchmark for quality management by industry and government bodies worldwide. In some cases, ISO 9000 registration has become a prerequisite for doing business, both domestically and internationally. In North America alone, more than 25,000 companies are registered to ISO 9000 — and the number is growing.

The QMS framework can serve as a foundation for environmental management systems and for their integration. In essence, an EMS is the application of QMS principles to the management of environmental affairs. ISO 14001 was drafted with language to provide consistency between standards, and although ISO 9000 and ISO 14001 have different focuses, they share many similar requirements.

The three specification documents for the ISO 9000 series are ISO 9001, ISO 9002, and ISO 9003. The key differences between ISO 9000 and ISO 14001 is that ISO 14001 requires planning steps to identify environmental aspects and significant environmental impacts that become the basis of an organization's objectives and targets. For ISO 14001, an organization is responsible for setting its own environmental objectives and targets; for ISO 9000, quality objectives are contractual agreements between an organization and its customer(s).

Development of the ISO 14000 Series Environmental Management Standards and their Relationship to MWT

In June 1991, the ISO formed the Strategic Advisory Group on the Environment (SAGE). SAGE assessed the need for international environmental management standards and recommended that ISO move forward with their development. In January 1993, the ISO formed Technical Committee 207 (TC 207) and charged it with the development of the ISO 14000 series of standards. TC 207 is composed of various subcommittees and working groups. Representatives from the ISO member countries contribute their input to TC 207 through national delegations.

In 1996, TC 207 developed the ISO 14001 standard, which specifies requirements for an EMS. The ISO 14001 standard is the only one within the ISO 14000 series that is designed to be audited — a true "specification standard," as mentioned elsewhere. ISO 14001 contains 17 elements that comprise an EMS.

In addition to ISO 14001, TC 207 is also developing several guidance documents. ISO 14001, ISO 14004 (an EMS guidance document), and three environmental auditing guidelines (ISO 14010, ISO 14011, and ISO 14012) were published in September 1996. At the time this section was written, other documents covering environmental labeling, life-cycle assessment, and environmental performance evaluation were being developed. Published ISO standards must be reviewed and revised every 5 years.

ISO 14000 is a series of internationally recognized standards for structuring an organization's EMS and managing the environmental performance of the system to effect environmental improvement and cost savings. The ISO 14000 series includes standards for EMS (14001, 14004), auditing (14010, 14011, 14012), labeling (14020, 14021, 14024), environmental performance evaluation (14031), and life-cycle analysis (14040).

ISO 14001 is the cornerstone document of the ISO 14000 series of standards, and is modeled after the highly successful ISO 9000 QMS standards. It is the document used for registration. ISO 14001 requires a company to:

1. Develop an environmental policy with a commitment to compliance, prevention of pollution, and continual improvement
2. Conduct planning that identifies environmental aspects of an operation and legal requirements, sets objectives and targets consistent with policy, and establish an environmental management program

3. Implement and operate the program to include defined structure and responsibility, training, communication, documentation, operational control, and emergency preparedness and response
4. Implement checking and corrective action to include monitoring, corrective and preventive action, and auditing
5. Establish management review

MWT technology has a major role in all five of these standard elements, as will be discussed in detail later in this section. Because MWT technology is chosen and implemented primarily for environmental concerns, the major elements of the ISO 14001 standard are overviewed and related to quality.

Elements of the ISO 14001 Standard

First, an overview is needed of the major elements of ISO 14001:1996, (SEMS). The elements listed here also have many parallels to ISO 9001:1994 (SQMS). MWT technology will be heavily concerned with the functioning of an EMS, so this overview sets the stage for comparison.

- *Environmental policy.* Develop a statement of the organization's commitment to the environment. At a minimum, the organization must commit to three things in its policy: compliance with regulations, prevention of pollution, and continual improvement of the management system. The policy acts as a framework for planning and action.
- *Environmental aspects.* Identify environmental attributes of the organization's products, activities, and services. Determine those that could have significant impact on the environment.
- *Legal and other requirements.* Identify and ensure access to relevant laws and regulations (and other requirements to which the organization adheres — e.g., responsible care).
- *Objectives and targets.* Establish environmental goals for the organization, in line with its policy, environmental impacts, views of interested parties, and other factors.
- *Environmental management program.* Plan actions to achieve environmental objectives and targets.
- *Structure and responsibility.* Establish roles and responsibilities, and provide resources to attain environmental objectives and targets.
- *Training, awareness, and competence.* Ensure that employees are trained and capable of carrying out their environmental responsibilities.
- *Communication.* Establish processes for internal and external communications on environmental management issues.
- *EMS documentation.* Maintain information on the EMS and related documents.
- *Document control.* Ensure effective management of procedures and other system documents.
- *Operational control.* Identify, plan, and manage operations and activities in line with the organization's environmental policy, objectives, and targets.
- *Emergency preparedness and response.* Identify potential emergencies and develop procedures for preventing and responding to them.
- *Monitoring and measurement.* Monitor key activities and track environmental performance.
- *Nonconformance and corrective and preventive action.* Identify and correct problems and prevent recurrences.
- *Records.* Keep adequate EMS performance records.
- *EMS audit.* Periodically verify that the EMS is functioning as intended.
- *Management review.* Periodically review the EMS with the goal of continual improvement of the management system.

In the list above, if the word "quality" were substituted for "environment," it would closely parallel what is required in an ISO 9001 quality management system. ISO 9001 and ISO 14001 each encompass a "say what you will do, do what you will say, and document it" philosophy. The standards outline a process, not a technology-specific course of action. This is important for our discussion of MWT technology and systems integration because it allows greater flexibility in selecting the most appropriate MWT technology.

What Is Integration?

Integrate is defined as "to make whole or complete by adding or bringing together parts." This concept is especially important because, too often, MWT has been viewed as a necessary evil or as an overhead cost, entirely separate from the quality functions. The lack of integration of MWT into quality and environmental management has caused problems in selecting the technology that best met all of the stakeholders' needs (the community as well as the environment) or in satisfying the three Es of sustainable development. Integration solves this problem by linking QMS and EMS, where possible, to save cost, time, and effort and to satisfy all stakeholder needs through communication, efficiency, and performance.

How Does One Achieve Integration of MWT with ISO 9001 and ISO 14001?

The ISO 9001 QMS and the ISO 14001 EMS standards share many parallel elements, which makes it easy to link them together. The means advocated here to achieve MWT technology integration is twofold:

1. Use the process outlined by these system standards to examine quality and environmental needs and goals side by side, considering quality and environmental concerns.
2. Ask the right questions to ensure that each element is satisfied for both quality and environmental concerns with a goal of attaining environmental sustainability.

To do this more effectively, a primer on human toxicology, human health risk assessment, and ecotoxicology is provided in other chapters of this Handbook. Life-cycle analysis is also examined to help evaluate economic impacts that will prove useful when canvassing MWT options and deciding the best means to achieve quality and environmental sustainability outcomes.

Step-by-Step Integration of MWT into an ISO 9001 Quality and ISO 14001 Environmental Management System

This subsection outlines the major questions on integrating MWT into an organization's quality and environmental management systems. There is not enough space for a detailed discussion of all elements of the ISO 9001 and ISO 14001 standards requirements as they relate to MWT technology, but all elements are covered in some fashion, and helpful suggestions are provided. When reviewing this subsection, it is recommended that the reader have available a copy of the ISO 9001 and ISO 14001 standards, along with their guideline documents.

Policy

An organization's policy with respect to quality and the environment is fundamental to frame the context of MWT technology selection and how it will be integrated into these systems. The goals set out in the policy drive performance, and the remainder of the system (including MWT technology) must support policy.

A fundamental question is: What is the organization's commitment to environmental sustainability? If there is a commitment to ESD, then the MWT technology chosen to be integrated in the systems must be made with this policy goal in mind. If there is no commitment to ESD, one might ask whether it could be. In the near future, environmental sustainability may be an external requirement — it would be wise to consider this as a policy goal even if one's organization does not presently require it.

Remember that, at a minimum, ISO 14001 requires that an organization's environmental policy be appropriate to the nature, scale, and environmental impacts of its activities, products, and services. There should also be a commitment to pollution prevention, legal compliance, and related matters, and continual improvement over the ISO 9001 QMS goals of meeting customer quality expectations is desired.

A separate environmental policy with these elements could be promulgated. Insertion of these statements in the quality policy is also a means of achieving QMS and EMS systems integration. The commitments made in policy will provide clear direction for MWT technology selection.

Planning

Planning is the most important element in integrating MWT into a quality and environmental management system. It is necessary to understand the difference between an environmental aspect and an impact as defined by ISO, and then build the planning process around identification of these as they relate to the MWT technology being considered.

Section 3.3 of ISO 14001 defines an environmental aspect as "an element of an organization's activities, products and services which can interact with the environment." An environmental impact is defined in Section 3.4 of ISO 14001 as "any change to the environment, whether adverse or beneficial, wholly or partially resulting from an organization's activities, products or services." The organization is required under this standard to identify "significant" aspects. The organization determines what is significant and all of the aspects to be addressed by the system. A minimalist view would be environmental or occupational health regulatory compliance. Regulatory compliance may be adequate for sustainability in some cases, if such compliance meets the criteria for sustainable development. An environmentally sustainable definition of "significant" would be a documented, scientifically sound risk to ecological or human health for this or future generations.

The planning elements in the ISO 14001 standard strongly parallel design requirements under ISO 9001. For any integration of MWT technology into an ISO QMS and EMS system, the potential and actual causes (aspects) of such technology should be identified, as should the potential effects (impacts). Proper MWT selection is significant because it brings us front and center to human and ecotoxicology risk assessment paradigms and involves the economic elements (satisfying customer needs at a reasonable cost) and community concerns (equity) essential for environmental sustainability. All must be considered and satisfied.

One of the paradigms to examine when planning is:

> Poor Quality • Poor Yield • Waste • Negative Environmental Aspects • Negative Environmental Impacts • Reduced Profits, Adverse Worker and Community Health Risk or Outcomes, and Long-Term Environmental Damage

The reverse and positive side of this planning paradigm is:

> Good Quality • Good Yields • Minimal to No Waste • Minimal to No Environmental Aspects Minimal to No Environmental Impacts • Maximum Profits, Minimal to No Adverse Worker or Community Health Risk or Outcomes, Minimal to No Environmental Damage, Possibly Demonstrated Environmental Improvement

It is important to remember that living systems operate in an environmentally sustainable fashion. In nature, all waste materials are recycled in a manner that is consistent with the capacity of the environment. A major industrial design consideration for MWT is to achieve this performance characteristic as much as possible. The planning process will involve — and ISO 14001 requires — consideration of legal and other requirements, which, combined with the human toxicology and ecotoxicology risk assessments, will help set priorities, objectives, and targets for planning MWT integration.

The simplest model for MWT integration planning is to look at all MWT in a linear fashion as follows:

> MWT Input → MWT Process → MWT Output

Examining MWT technology in a linear fashion, yet applying a systematic approach, allows use of a logical planning process to achieve quality and environmental system integration. Although it is displayed linearly for simplicity, this is actually a cycle with the endpoint (MWT output) representing a reintroduction of material — as an input to production or sustainable commerce, or as an input to the environment for complete assimilation.

MWT Input Planning

Input is the first area to consider in planning MWT. Questions that can be asked include:

1. What waste stream(s) will the MWT be treating?
2. What volume of waste over what period of time will be treated?
3. Will the mixed waste stream be of a consistent quality or will it be variable?
4. What are the physical, chemical, and biological characteristics of the mixed waste material to be treated?

In quality and environmental management terms, the importance of knowing what type or types, how much, and the properties of the waste to be treated cannot be over-emphasized. MWT input must be estimated as accurately as possible when planning appropriately for quality and environmental management system integration.

"Why?" is another important input question, and the answer is more complex than it might seem at first. When considering input for MWT, one should examine opportunities to reduce pollution at the source. Questions that can be asked include:

1. Can a design change be made upstream that will produce the product or service so that MWT can be avoided entirely?
2. Can there be process changes to prevent pollution or minimize the waste to be treated?

If waste can be reduced at the source, it extends the life of the equipment. Alternatively, the MWT process can be avoided entirely, thus eliminating the risk to human health and ecological destruction altogether, which would be the optimal environmentally sustainable option.

Other chapters in this volume that deal with industrial waste classification, waste characterization, and *in situ* and laboratory techniques for characterizing wastes will help answer questions about MWT technology input.

Three Environmentally Sustainable Options for MWT Process Planning

Once the input or the mixed waste is characterized adequately (including the estimated mixed waste volume), the next step is planning for the MWT process.

To achieve total environmental sustainability, there are three possibilities for MWT technology:

1. Transformational reprocessing of mixed waste into something that can be reintroduced to production or sold to a customer.
2. Transformational reprocessing of mixed waste for release to the environment with no human toxicological or health risk, or ecotoxicological impact or risk.
3. Transformational reprocessing of mixed waste for release to the environment with minimized impact and risk to human toxicological or health risk, or ecotoxicological impact or risk.

The first two possibilities listed above are the superior choices, of course. They are examples of a MWT closed-loop system process, where treated mixed waste is recycled into something that is used, remanufactured or sold, or is rendered into a material that has no negative impact on the environment or possibly even has a positive impact (e.g., waste biotransformation or composting). The third option is an open system process, where some potentially hazardous material is released to the environment, preferably at levels well below human and ecological risk.

An open system could be sustainable if the amount released to the environment does not impoverish the utility and productivity of an ecosystem for this and future generations — a process that requires scientific risk assessment, economic analysis, and multiple impact analysis to prove substantially and beyond a reasonable doubt that it is harmless. Open system environmental sustainability is possible, and for some mixed waste streams it may be the only practical option available.

Examples of mixed waste processes that can be used for transformation/reprocessing for recycling, reuse, and possible reintroduction to the economy are as follows:

1. *Separation techniques.* The systemic question is: Can the mixed waste be unmixed easily, or not mixed to begin with, to permit production of a useful product? The MWT professional, working with the design team to separate waste streams as far upstream as possible in the manufacturing system so that waste products remain simple or more pure, is an example of good quality and environmental management system planning for MWT. Gravimetric settling or filtration processes are also possible MWT techniques that could be used to separate materials for reuse or resale.
2. *Concentration techniques.* The systemic question is: Can the mixed waste be processed in a way that captures and concentrates the waste material to permit production of a useful product? The MWT professional is looking for a means to concentrate the hazardous material before it reaches the environment, and thus produce a useful material. An example of this technique is to capture hazardous materials from a waste stream and re-release them into a manufacturing process, such as using activated carbon to capture solvents from wastewater and then using thermal desorption to release them to a processing stream. Another example would be to use a cationic resin to capture low levels of heavy metals from a wastewater stream and then release the metals from the resin in an acid bath that could be turned over to a plating operation. Yet another example would be to use a condenser column to capture unpolymerized monomer (e.g., butadiene or styrene) from a synthetic rubber operation and then reintroduce the captured material to the polymerization operation. In all of these situations, the waste is captured and concentrated as part of the treatment process to produce something useful for manufacturing and not introduced into the environment.
3. *Select thermal techniques.* The systemic question is: Can the waste material be transformed chemically and physically through heat to permit production of a useful product? A good example is the steam gasification of fossil fuel and carbon-containing wastes described by Dr. Terry Galloway elsewhere in this handbook. Using this technique, high sulfur coal and solid waste can be transformed into carbon disulfide, middle distillates, and asphalt and other hydrocarbons without combustion or carbon dioxide generation. This technique is especially useful for complicated carbon-containing wastes.

   Wet air oxidation, hydrothermal oxidation, and molten salt oxidation, also discussed elsewhere in this handbook, offer the means to be able to transform materials with some energy expense into other materials that may be useful or reduce and eliminate environmental impact.
4. *Select non-thermal treatment technologies.* The systemic question is: Can the waste material be transformed chemically and physically to permit production of a useful product? Dehalogenation of, for example, a large concentrated pool of polychlorinated biphenyls from transformers is an example of this process. Electrochemical and direct oxidation are other examples. These MWT processes are described in more detail elsewhere in this handbook.

Examples of mixed waste processes that can be used for transformation/reprocessing for recycling, reuse, and possibly for release to the environment are as follows:

1. *Select thermal techniques.* The systemic question is: Can the mixed waste be transformed through heat into a material that will not pose a human or ecological health or toxicity risk and can be assimilated by the environment with no negative impact? The two primary techniques would be plasma transformation or incineration; both are discussed elsewhere in this handbook. In some situations, it may prove technically and economically infeasible to process the material into something useful; thus, transforming it into a simple material (e.g., carbon dioxide or carbon monoxide, totally assimilated by the environment) may be the best or only option. If the volume of waste processed is low, this may prove to be a sustainable option given the toxicity of the starting mixed waste material. With carbon dioxide reduction becoming a greater priority, however, careful consideration should be given to this option. Perhaps the carbon dioxide produced from the incineration could be concentrated or sequestered in some fashion by a secondary treatment to provide a closed system.

2. *Select non-thermal treatment.* The systemic question is: Can the mixed waste be transformed through chemical or biological means into a material that will not pose a human or ecological health or toxicity risk and can be assimilated by the environment with no negative impact? Biological destruction, discussed elsewhere in this Handbook, is an example of transforming materials using the nanotechnology of life forms to produce material that can be composted or easily assimilated into the environment without impairment. Key factors to consider are the type of material to be biologically decomposed, what it becomes in the organism, the time for this transformation to take place, and the volume of mixed waste materials to be processed. Biological transformation, for example, might produce compost, fertilizer, or even foodstuffs as a side benefit from chemically transforming mixed waste material. Ozonation, photolysis, gas-phase destruction, inorganic decomposition, and radiation-induced oxidation — discussed elsewhere — are other processes in which waste is chemically transformed into environmentally benign materials.
3. *Stabilization and solidification technologies.* The systemic question is: Can the mixed waste be transformed through physical means into a material that will not pose a human or ecological health or toxicity risk and can be assimilated by the environment with no negative impact? In this option, the mixed waste material becomes, at best, a diluted material that uselessly occupies space, posing a reduced or negative environmental impact. For some mixed waste, such as highly radioactive isotopes, vitrification — the dilution of the radioactive material into a solid solution (e.g., glass) — may be the only and best long-term solution if the material cannot be recycled, concentrated, or reused. If radioactive wastes can be diluted to an extremely low concentration (i.e., vitrified), lower in radiation than naturally occurring radioactive ores, then an environmentally sustainable solution has been reached. The difficulty is that the energy and material costs to conduct environmentally sustainable vitrification are high. The cost and technical challenges, as well as opportunities, for vitrification and other solidification MWT technologies are discussed elsewhere in this handbook.

The processing techniques cited above represent transformational reprocessing of mixed waste for release to the environment with minimized human toxicological, human health, and ecotoxicological impact or risk. The processing questions are the same — it is the totality or degree to which they are satisfied that makes the distinction between minimal environmental impact and sustainable operation. A key point is whether there is low risk at a scientifically acceptable level (i.e., no negative environmental impact now or for future generations), indicative of assimilation into the environment or sustainability, or whether the MWT technology is operated at some risk above the scientifically verifiable level but within regulatory and legal standards.

Output

For planning purposes, try to begin here: examine MWT and rank the value of planned technology against meeting EMS policy objectives and the three Es of sustainability. At this point in the planning process, the design considerations should review legal and regulatory requirements. The following are the types of questions that should be considered when examining the MWT output in an ISO 9001 and ISO 14001 context.

1. Will the planned MWT produce an output that:
    a. Will stimulate new environmental aspects and impacts, through release of matter or energy to the environment?
    b. Will change positively or negatively a current quality or environmental aspect or impact?
    c. Will involve new or different legal and regulatory rules?
    d. Can be sold or reintroduced to production?
    e. Can be reintroduced to the environment with no negative aspect or impact to this or future generations?

2. Will the output:
    a. Be classified as hazardous (i.e., ignitable, reactive, corrosive, toxic)?
    b. Produce a substance that will be harmful to the employees working with it?
    c. Generate a hazardous air emission?
    b. Generate an ozone-depleting substance?
    e. Produce a substance subject to land disposal restrictions?
    f. Produce a substance subject to water emission restrictions?
    g. Produce a material requiring special labeling or packaging requirements?

In examining MWT output, the chapter in this volume dealing with the laws and regulations governing MWT technology listed national and international regulatory bodies and various regulations that should be referenced and consulted; thus, information will not be repeated here. At this stage, however, the linear analysis of MWT technology ends and we return, if needed, to the beginning of a cyclic planning process. If the answer to any of the MWT output questions posed above is “Yes,” other MWT technologies or means to minimize human and ecological health risks should be weighed. Careful consideration should be given to manufacturing or service process modification to ensure that everything has been done technically and feasibly to develop the most effective MWT technology for your quality and environmental goals. In short, return to the beginning of the planning process and weigh the risks and benefits of the MWT chosen.

The systemic question for planning in MWT technology is:

1. Is there a negative aspect or impact?
2. If so, what is its type, magnitude, duration, and potential cost to the environment in equity and economic terms?
3. Is this aspect or impact controllable through substitution, prevention, or further MWT?

Ask these questions at the beginning and the end of a planning circle to identify cost-efficient environmental improvements before new MWT technology is implemented. Then evaluate the MWT options identified against policy and the three Es to identify the best one, or combination, to meet your system’s needs.

MWT, by definition, is an “end-of-pipe solution” that must be planned and implemented when all other technological means have been exhausted to prevent “waste” or non-useful product from being introduced into the environment. The systemic planning paradigm for sustainable development advocated in quality and environmental management is to view all waste as unused resources. The unused resource then requires developing a plan for a useful purpose for it. If MWT can be planned as a transforming technology, in which waste is reintroduced as a useful product or introduced at environmentally benign levels, the more MWT integrates itself into a system of economically and environmentally value-added technology.

The planning component outlined here also provides a link back to quality and environmental policy. The inputs, process, and outputs of the chosen MWT will determine objectives, targets, and programs needed for consistent operation of the MWT within a quality and environmental management system. The objectives will be the overall integration of the MWT technology as related to the three Es; the targets will be the measurable milestones indicating positive progress toward objectives; and the programs will be the means by which the objectives and targets will be achieved.

Program Elements

Policy and planning define the needed programs and what they will achieve. The next areas discussed — implementation and operation, checking and corrective action, management review, and continual improvement — are the “how-to” elements for integrating MWT into environmental and quality management programs.

Implementation and Operation

Once the objectives and targets for MWT technology have been defined through the policy and planning process, a roadmap exists to assist in defining the program that puts the MWT in place (implementation) and for its ongoing performance in attaining targets and objectives (operation).

Six elements form the focus for implementing and operating MWT technology within an integrated ISO 9001 quality and ISO 14001 environmental management system:

1. Structure and responsibility
2. Training and competence
3. Communication
4. Documentation
5. Operational control
6. Emergency preparedness

Structure and Responsibility

ISO 9001 and ISO 14001 both require management to ensure that the organization is capable of meeting all the requirements of these systems. Management must commit resources, align (integrate) environmental management with other management systems, define responsibilities and accountability, build awareness and motivation for quality and environmental goals, identify the knowledge and skills needed, establish processes for communication and reporting, and put in place operational controls for its EMS and QMS systems as a whole. These structure and responsibility areas need to be included for MWT technology.

Critical questions to ask when integrating EMS and QMS are:

1. What is the relationship between an individual's performance, quality responsibility, and environmental responsibility with respect to MWT technology?
2. How do personnel who are accountable and responsible understand the consequences of MWT technology failures or noncompliance?
3. How do personnel who are accountable and responsible anticipate, recognize, document, and provide feedback about quality or environmental improvement opportunities or problems with MWT technology?
4. How do personnel who are accountable and responsible initiate action to comply with quality and environmental policy, programs, objectives, and targets for the MWT technology?

By asking these questions and using the ISO 14001 and ISO 9001 standards and their guidelines for comparison, one can easily identify structure and responsibility gaps between how MWT technology is managed now and how it is planned to be managed. According to Section 4.4.1 of ISO 14001, the roles, responsibilities, and authorities shall be defined, documented, and communicated in order to facilitate effective environmental management. MWT technology would need to be included in this. A solution would be to ensure a chain of responsibility for MWT technology throughout the organization, including roles for quality and environmental management representatives.

Training and Competence

ISO 9001 and ISO 14001 both require that training needs be identified and that employees receive training commensurate with their function. Element 4.4.2 of ISO 14001 is more specific and requires that employees at each relevant function be aware of:

- The importance of conformance with environmental policy and procedures
- The significance of actual or potential environmental impacts and the benefits of improved personal performance
- Their roles and responsibilities
- The potential consequences when operating procedures are not followed

Competency is based on education, training, and/or experience. To be compliant with ISO 14001, training procedures with the goals listed above must be in place.

The following training factors are designed to link MWT technology with quality and environmental sustainability objectives. They should be examined and included when necessary:

- Specific regulatory requirements
- Relevant corporate policy, goals, objectives, and/or industry standards
- Data collection and input, process, and output measurement techniques
- Safety and health factors for workers, the community, and the environment
- Normal operations and maintenance
- Upset situations

Because many accidents result from human error, effective employee education in MWT technology is critical when trying to minimize failures. Once MWT technology has been planned, it is important to ensure that a training needs analysis, a documented training implementation plan, and an evaluation of the training program's effectiveness are performed.

Communication

Internal and external communication is important when integrating MWT technology into a quality and environmental management system. Internal communication is essential so that MWT technology operates efficiently within the entire quality and environmental management system. External communication is necessary to satisfy the equity and right-to-know inquiries of other stakeholders.

The recent trend has been for greater knowledge and transparency for environmental, health, and safety issues and their impact on the community. Societal growth toward sustainable development will make open, clear communication about MWT even more important in the future. Communication with both internal and external parties is important because of the role of MWT technology in pollution prevention and in minimizing the health risks to workers, the community, and the environment for this and future generations.

ISO 9001 and ISO 14001 have overlapping internal communications requirements for the quality and environmental elements. These are important when integrating MWT technology communication. These requirements include:

- Policy
- Management reviews
- Results of audits
- Results of monitoring, measurement, and control of suitable process activities
- Roles and responsibilities
- Training requirements
- Operational and process controls
- Corrective and preventive actions
- Objectives and targets

ISO 14001 also requires internal communication for environmental aspects and emergency response procedures. These last two are particularly important for MWT technology due to its endpoint nature and its potential connection to workers, the community, and the environment.

One procedure could handle internal communication requirements for both the quality and environmental systems. This procedure could also be used for external communication. Not all of the nine elements listed above are required to be communicated by the ISO standards. Environmental aspects, the EMS itself, and the quality and environmental policy are required public communications, and a procedure for receipt, documentation, and response to relevant inquiries from interested parties is also required. Because MWT technology can directly impact the environment and the public, areas of public inquiry regarding MWT could focus on:

- Worker, community, and environmental aspects and impacts
- How the MWT recycles material
- How MWT prevents pollution
- Consequences of MWT technology failure when there is an upset condition

External communications about these questions and other questions deemed relevant should be addressed as part of the integrated communication process.

Documentation

Review of the ISO 14001 and ISO 9001 standards indicates that both standards are heavy on records and documentation to support quality and environmental actions. ISO 14001 is somewhat less documentation-intensive than ISO 9001. ISO 14001 does not require an EMS manual, whereas ISO 9001 does; however, most clients implementing both systems tend to develop an EMS manual because it is valuable as a directory or map to the system. In fact, revisions of ISO 14001 in 2001 might require an EMS manual.

Even if one were to choose not to use the ISO systems, U.S. regulatory standards and concerns about legal liability with regard to MWT technology would almost certainly require a significant effort to document planning, operations, maintenance, and other activities. Both the ISO quality and environmental management standards have been designed to provide at least the minimum information needed to support an independent audit. And, given today's electronic information systems, maintaining and changing the documents to a system are far easier than in the past.

Because documentation is essential in any quality or environmental management system, Tables 9.1.1 and Table 9.1.2 list all sections in the ISO 9001 and ISO 14001 standards where written records or procedures are required. The tables provide a roadmap to the formal documentation process required for quality and environmental management standards. For a system to be completely integrated, all of these documentation requirements must be satisfied.

Not all documentation requirements are specific to MWT technology. For example, a policy might not specifically mention MWT directly. An audit of MWT technology, however, will likely be a required record in the system if the waste treated is on the list of significant environmental aspects and impacts chosen by the company. MWT elements in the table that are more important for ISO QMS and EMS system documentation are in bold type.

For definition, documentation refers to written procedures for ensuring that the environmental and quality management process meets the criteria of the ISO standards as well as regulatory and legal requirements, voluntary codes for quality and environment, and ultimately the policies set forth by the organization. Records are the written objective evidence that the procedures are carried out as specified and are effective.

The systemic question for documentation is to review ISO 9001 and ISO 14001 system requirements with respect to the MWT technology being implemented and ask:

> *What documentation, procedures, and records are required within our system to meet the environmental and quality policy, objectives, and targets?*

A practical suggestion would be to merge or embed MWT technology documents within the four levels of documentation that emerge in the document hierarchy for an ISO QMS or EMS. This hierarchy is:

> QMS/EMS Policy → QMS/EMS Manual → Standard Operating Procedures → Work Instructions → Records

All documentation leads back to the QMS and EMS policy and the commitment to environmental sustainability. All of the documentation elements help demonstrate the value and performance of MWT as a part of the QMS and EMS system.

TABLE 9.1.1 ISO 14001 Documentation Requirements with Emphasis (bold) on Elements of Particular Importance to Mixed Waste Treatment

Section	Documentation
4.2	Documented environmental policy
	Records indicating communication of policy to employees
4.3.1	**Procedure for identifying aspects**
4.3.2	**Procedure for identifying and accessing legal and other requirements**
4.3.3	**Documented objectives and targets**
4.3.4	Documented environmental programs
4.4.1	**Documented roles, responsibility, and authority**
4.4.2	**Procedure for identifying training needs**
	Records indicating communication of impact of work activities and consequences of departing from operating procedures
4.4.3	**Procedure for internal communication**
	Procedure for external communication
	Records for consideration of external communication of significant aspects
4.4.4	Information on core elements of management system
4.4.5	Procedure for controlling all documents
4.4.6	**Identification of operations and activities associated with significant aspects**
	Procedures covering situations where absence could lead to deviations from policy, objectives, and targets
	Procedures related to identifiable aspects of goods and services used
4.4.7	**Procedure to identify potential and response to emergency situations**
4.5.1	**Procedures to monitor and measure key characteristics of operation**
	Recording of information to track performance, relevant operational controls, and conformance to objectives and targets
4.5.2	**Procedure for defining responsibility and authority for handling and investigating nonconformance, taking action to mitigate impacts, and initiating and completing corrective and preventive action**
	Record of any changes to documented procedures
4.5.3	**Procedure to establish and maintain records**
	Document retention times
4.5.4	**Procedure for audits**
	Records of audits
4.6	**Records of management reviews of:**
	– Environmental management system
	– Possible changes to policy
	– Possible changes to objectives and other elements of EMS
	– Audit reports

Operational Control

The overarching question for operational control of MWT technology within an integrated QMS and EMS system is:

> *Are procedures, work instructions, and records developed and put in place to ensure that quality and environmental objectives and targets are continually met?*

Emphasis on operational control will be placed on standard operating procedures for MWT work instructions and on records to objectively demonstrate performance (or lack of it). A practical recommendation is to establish an operations manual that contains the needed SOPs, work practices, and records for the MWT technology chosen. This MWT operations manual must be constructed for consistency with the program policy, goals, objectives, and targets. In the electronic information age, the operations manual could be linked or embedded in many ways in the overall QMS and EMS manuals and easily updated as necessary with existing documentation and records intact.

Maintenance procedures, work practices, and records for MWT technology should be included in the MWT operations manual. It should contain schedules and anticipated and actual aspects of, and impacts to, the environment.

TABLE 9.1.2 ISO 9001 Documentation Requirements with Emphasis (bold) on Elements of Importance to Mixed Waste Treatment

Section	Documentation
4.1.1	Documented quality policy, objectives, and commitment to quality
	Records indicating communication of policy to employees
4.1.2.1	**Documented responsibility, authority, and interrelation of personnel**
4.1.2.2	**Identify resource requirements**
4.1.2.3	Identify management representative
4.1.3	**Records of management reviews of:**
	– Quality management system
	– Possible changes to policy
	– Possible changes to objectives and other elements of QMS
	– Audit reports
4.2.3	**Document how the quality requirements shall be met**
4.3.1	Documented procedures for contract review
4.3.3	Identify how a contract is amended
4.3.4	Records of contract reviews
4.4.1	**Documented procedure to control and verify design of product**
4.4.2	**Documented plans of design and development activity**
4.4.3	**Identify organizational and technical interfaces**
4.4.4	**Identify and document product requirements**
4.4.5	**Documented design output**
	Documented reviews of design output documents
4.4.6	**Records of design reviews**
4.4.7	**Record of design verification**
4.5.1	Documented procedure to control all documents and data
4.5.2	Documented procedure identifying current document revision status
4.5.3	Records of document and data changes
4.6.1	**Documented procedure to ensure purchased product conforms to requirements**
4.6.2	Records of acceptable subcontractors
4.6.3	Records of purchase documents
4.6.4.1	Records of product verification and release
4.7	Documented procedure for control of customer-supplied product
4.8	**Documented procedure for identifying product receipt, delivery, and installation**
	Documented procedure to identify individual product or batches
4.9	**Documented procedures defining manner of production, installation, servicing**
	Records of compliance with standards/codes, etc.
	Records of process parameter monitoring and controls
	Identification of requirements for any process qualifications
4.10.1	**Documented procedure for inspection and testing activities**
4.10.2.2	Recorded evidence of time exercised at subcontractor premises
4.10.2.3	**Records of incoming product released for urgent production**
4.10.5	Records providing evidence that product is inspected and/or tested
4.11.1	**Documented procedure for control, calibration, and inspection of measuring and test equipment**
	Records of inspection for test software or comparative references
4.11.2	**Identify all inspection, measuring, and test equipment**
	Identify process employed
	Identify inspection, measuring, and test equipment calibration status
	Records of calibration
	Records of out of calibration
4.12	**Identify inspection and test status of product**
4.13.1	**Documented procedure for handling nonconforming product**
4.13.2	Identify responsibility for review and authority for dispositioning nonconforming product
	Record of customer acceptance of nonconforming product
4.14.1	**Documented procedure for implementing corrective and preventive action**
	Records of changes to procedures resulting from corrective and preventive action
4.15.1	Documented procedure for handling, storage, packaging, preservation, and delivery of product
4.16	Documented procedure for identifying, collecting, indexing, access, filing, storage, maintenance, and disposition of quality records

TABLE 9.1.2 (Continued) ISO 9001 Documentation Requirements with Emphasis (bold) on Elements of Importance to Mixed Waste Treatment

Section	Documentation
4.17	**Documented procedure for internal quality audits**
	Records of the internal quality audits
	Records of follow-up audit activities and implementation of corrective action
4.18	**Documented procedures for identifying training needs**
	Records of training
4.19	**Documented procedure for performing, verifying, and reporting servicing**
4.20.1	**Identify the need for statistical techniques**
4.20.2	**Documented procedure to implement and control the application of statistical techniques**

Emergency Preparedness

Emergency preparedness is one of the elements of ISO 14001 that is unique (i.e., not part of ISO 9001). Emergency preparedness is also vitally important for MWT technology. In many cases, MWT technology will be implemented to prevent occurrence of a serious environmental consequence; and, therefore, it will be imperative that the consequences, response, and corrective action needed when an MWT technology fails to be considered and planned for. Procedures should also be developed to guard against any unintended disruption in service.

According to Section 4.4.7 of ISO 14001, "The organization shall establish and maintain procedures to identify potential for and respond to accidents and emergency situations, and for preventing and mitigating the environmental impacts that may be associated with them. The organization shall review and revise, where necessary, its emergency preparedness and response procedures, in particular, after the occurrence of accidents or emergency situations. The organization shall also periodically test such procedures where practicable."

The effort that went into planning will be of great use here. All environmental aspects and impacts of the mixed waste that will be treated should be considered. Failsafe systems or backups should be devised and implemented, as necessary, in case of MWT technology failure.

Some local, state, and federal regulations (U.S. EPA SARA Title III) may contain specific requirements for accident prevention, planning, and disclosure; and, when MWT technology is implemented, these regulations will need to be consulted and incorporated into the emergency preparedness portion of the integrated EMS and QMS. Emergency preparation for an MWT technology accident could include training, hazard evaluation, scenario development drills, and emergency system evaluation. In the United States, with the advent of local emergency planning committees (LEPCs) and state emergency response committees (SERCs) under EPA SARA Title III, required emergency planning affords an opportunity to involve the community and provides another avenue to impart understanding of the value of MWT technology in meeting the environmental and equity goals of sustainable development.

Checking and Corrective Action

The purpose of checking and corrective action from an EMS, QMS, and ESD perspective is threefold:

1. *Monitoring and measurement.* This involves input, process, and output measurement, including the analytical and calibration techniques needed, to prevent a negative impact to the workers, the community, and the environment from MWT operation.
2. *Identification of nonconformance for corrective and preventive action.* Data developed from monitoring and measurement will trigger action to ensure that MWT technology is operating efficiently and reliably with expected performance.
3. *Records.* Checking and corrective action activities develop performance records of MWT technology that may be used for management review and internal or external auditing purposes.

Monitoring and Measurement

The ISO 14001 standard, under Section 4.5.1, requires that an organization establish and maintain documented procedures to monitor and measure key characteristics of its operations that might have a significant impact on the environment. A similar requirement under ISO 9001 is Section 4.20, under statistical techniques, requiring the establishment, control, and verification of process capability and product characteristics (if needed).

Referring to the linear flow diagram for MWT technology, it is suggested that a monitoring and measurement program be examined and established for the following three areas:

1. MWT input
2. MWT process
3. MWT output

Depending on the MWT technology chosen, the input characteristics of the mixed waste stream (e.g., state of matter, toxicity, flammability) and whether there is a health or ecotoxicology risk to the environment from the MWT output, MWT output monitoring may only be needed to demonstrate quality and environmental performance. Developing data and records for all three may be superior for identifying improvement opportunities and regulatory requirements, and documenting performance and conformity with ISO standards.

Previous sections in this Handbook have discussed industrial waste classification and waste characterization, including laboratory and *in situ* techniques. These techniques are useful primarily in determining the qualitative aspects of the mixed waste stream for QMS and EMS system input. Additional sections in this handbook describe measurement and sampling techniques, including statistical inferences and analytical instrumentation. These techniques are especially useful for quantitative monitoring of input, process, and output from MWT technology.

For MWT technology, several monitoring and measurement approaches are recommended and useful for tracking progress toward quality, environmental, and sustainable development goals within an integrated system. These approaches monitor:

1. Total mass or volume of emissions to the environment per unit time. Examples would be pounds per month from a MWT technology to the air, soil, or water.
2. Total mass or volume of waste treated per unit of production. Examples would be pounds or liters of waste generated per unit of production or some set number of production units.
3. Total mass or volume of potential waste material recycled into production or transformed into other useful product per unit of production or some set number of production units.
4. Energy consumed per mass or volume of waste treated or transformed per unit of production or some set number of production units.

The first is a direct measure of MWT technology impact on the environment; the second is an estimate of input to MWT technology; the third is a measure of transformational capability of MWT technology, including a means to measure pollution prevention through MWT technology use; and the last is a measure of the energy needed for MWT technology operation. Setting up monitoring and measurement processes using some or all of these approaches can easily be used for financial analysis of MWT technology and provides linkage to the quality of actual production processes.

The overarching question with respect to monitoring and measurement is:

> *Are MWT technology monitoring and measurement methods adequate to prevent a negative impact from the MWT operation to workers, the community, and the environment; ensure that MWT technology is operating efficiently, reliably, and with expected quality performance; and develop records for MWT technology performance useful for management review and auditing purposes*?

In some cases where sustainable development is approached or attained, monitoring and measurement may actually demonstrate environmental *improvement*.

Identifying Nonconformances and Specifying Corrective and Preventive Action

A perfectly designed and maintained system will never experience a breakdown; however, the real world suggests that disruptions might occur and perfect operation of a system might not be 100%. Nevertheless, perfect operation should always be an ultimate goal and, guided by ISO 9001 and ISO 14001, can be approached and attained for MWT technology. The overall record of safety would likely demonstrate that MWT technology within a quality and environmental management system has an excellent performance record with few accidents and failures. Earlier we discussed failsafe and backup systems as a part of the system to prevent negative environmental impact should MWT technology fail. Identifying nonconformances, correcting them, and instituting preventive action are the keys to ISO 9001 and ISO 14001 continual improvement activities. To comply with the standards, a learning organization using an ISO systematic approach to quality and environmental protection must incorporate these processes for MWT.

A nonconformance is the failure to comply with some criteria or standard. In this case, it would be the failure to comply with one of the numerous "shall" requirements in the ISO 9001 and ISO 14001 standards. A nonconformance can either be minor or major under an ISO inspection regimen. A minor nonconformance is some portion of the ISO 9001 and ISO 14001 systems that objective evidence would show is not being followed. A major nonconformance is the complete absence of one of the elements of the ISO 9001 and ISO 14001 standards, leading to a potential or actual breakdown in the quality or environmental management system. It may also be a series of many minor nonconformances that constitutes a potential or actual breakdown. If an organization is seeking or has attained ISO 9001 and ISO 14001 certifications, then ensuring that nonconformances do not result when MWT technology is applied — especially major nonconformances — becomes a critical matter.

The corrective and preventive actions for both quality and environmental concerns are fairly straightforward in the ISO 9001 and ISO 14001 standards. In short, they help in establishing a procedure for handling and investigating nonconformities. This includes assignment of responsibility, evaluation of the severity of the problem caused by the nonconformity, determining the corrective action needed to mitigate the impacts caused, initiating and completing the corrective action, ensuring that the corrective action is sufficient to eliminate the cause of quality and environmental nonconformance, and recording the changes in procedure resulting from the corrective action.

MWT can be considered a subset or one of the many processes within the system that would need to convey a corrective and preventive action procedure. Some ISO registrars and companies use specific system corrective action forms as part of their registration process or systems. For professionals responsible for MWT technology, the elements listed above must be satisfied — and will be with an integrated procedure for corrective and preventive action. Some of the recommendations for further reading at the end of this section supply sample forms, procedures, and letters for satisfying corrective and preventive action documentation requirements for the ISO 9001 and ISO 14001 standards.

Records

ISO 9001 and ISO 14001 have similar requirements for records. The documentation tables above (Tables 9.1.1 and 9.1.2) list record-keeping requirements for these standards. As mentioned earlier in this section section, electronic communication greatly facilitates efficient handling of this type of information. Section 4.5.3 of ISO 14001 requires that an organization "establish and maintain procedures for the identification, maintenance and disposition of environmental records." Given the MWT role as the negative environmental impact prevention mechanism at the end of a production process cycle, developing procedures for record-keeping within an ISO 14001 and ISO 9001 system is especially relevant.

The overarching records question for MWT technology integration is:

> *Are MWT technology records adequate and complete to verify compliance with all elements of the environmental and quality management system (ISO 9001 and ISO 14001, if applicable) and do they demonstrate performance toward attaining sustainability goals set forth in the policy, aspects, impacts, objectives, and targets?*

Note that at this point MWT technology records are linked all the way back to policy. At the end of the workday, and during auditing and management review, a record of MWT technology performance is useful in demonstrating that policy goals (and the MWT objectives and targets developed during the planning process) are ultimately met. Records support the claim that the procedures in the system work.

Audits

Auditing for the QMS and the EMS provides a tool for integrated quality assurance, verifying that technical and management practices exist and are used to achieve an organization's quality and environmental goals. If environmental sustainability is the goal of a chosen MWT technology, the audit can determine whether that goal is attained. The audit, through examination of a process and how it operates — alone and as part of the system — provides objective evidence that the stated quality and environmental goals and conformance with the ISO 9001 and ISO 14001 standards have been achieved. The objective evidence attained through an audit is then used for the management review and continual improvement cycles described below.

Two types of audits are important to MWT technology to determine its functionality within a quality and environmental management system. The first is an internal audit, or first-party audit. Internal audits can be focused on either an area or an entire system in which MWT technology operates. Internal audits are required by both ISO 9001 and ISO 14001, and a program must be in place to ensure that they occur. They are an integral part of ensuring that a chosen MWT is functioning properly within a QMS and EMS system.

A third-party audit, or external audit, is the second type of audit important to MWT technology. An objective external party always conducts this audit for ISO 9001 or ISO 14001 certification. It may be conducted by an ISO registrar or a representative from another body, such as the Chemical Manufacturers Association (CMA), as long as that body subscribes to the Responsible Care Program.

Regulatory compliance inspections, such as by EPA and OSHA authorities in the United States, are another example of an external audit. While such audits are usually focused and narrow, they are important to MWT technology. Because ISO 14001 requires a commitment to regulatory and legal requirements and because a procedure must be in place to identify what those requirements are, integrating MWT into an ISO 14001 EMS should assist in meeting these requirements.

The second-party audit, or supplier audit, may be required if an external party supplies mixed waste material for processing. For a professional MWT processing plant, this type of audit would be necessary to evaluate consistent quality of material furnished to the MWT process by suppliers.

An audit, whether internal or external, will try to establish objective evidence that what is said to be done is, in fact, being done. Objective evidence can take the forms of records, written procedures, SOPs, manuals, and policies, auditor observations, and documented/corroborated witness accounts of activities.

If one subscribes to ISO 9001 and ISO 14001, Tables 9.1 and 9.2 in this section (referring to documents and procedures most applicable to MWT technology) double as a preliminary audit checklist. As mentioned, the need for this documentation will vary with the MWT chosen and its overall place in a quality and environmental management system, but the elements highlighted in the tables are the suggested emphasis areas. During a systems audit, the auditor must be provided with written or observable proof that these elements are in place and functioning.

Alternatively, the MWT professional should be prepared to answer an auditor's inquiry to demonstrate that a certain element is covered by another part of the QMS and EMS system. In other words, show that a specific procedure or record is not applicable for the MWT technology or that there is a link to other aspects of the QMS and EMS system elsewhere.

A good experience is to put yourself in the auditor's place:

> *What would you need to see to feel confident in asserting that the MWT technology audited is a functioning and integral part of the QMS and EMS?*

It is highly likely that MWT professionals will be part of internal audit teams, so this question can be answered through experience.

Readers are urged to examine the elements presented in this section and compare them with the MWT technology planned or in use. This will determine what is needed to demonstrate conformance to the ISO standards. Ensure that regulatory and legal requirements are met, and that quality and environmental goals are attained. The resources at the end of this section provide detailed checklists of questions encompassing all of the QMS and EMS auditable elements. In addition, if one seeks accreditation through an ISO registrar, he or she will usually provide guidance helpful for preparing for a formal ISO 9001 and ISO 14001 registration audit.

Management Review and Continual Improvement

Management review and continual improvement are the end and the beginning of the quality and environmental management cycles. Management review permits one to reflect on performance, and continual improvement consists of decisions made about future steps needed to improve performance.

The ISO 9001 and ISO 14001 standards are similar in that management review is a requirement, with ISO 14001 somewhat stronger because continual improvement is also required. In both standards, top management personnel are obliged to collect information and conduct the review at selected intervals they determine are adequate. For integration purposes, both standards require a record of management review of:

- The EMS and QMS system
- Possible changes to quality or environmental policy
- Possible changes to quality and environmental objectives and targets
- QMS and EMS audit reports

Management review identifies opportunities, needs, and inspirational ideas for continual improvement. Continual improvement is defined by Section 3.1 of ISO 14001 as the "process of enhancing the environmental management system to achieve improvements in overall environmental performance in line with the organization's environmental policy." According to Section 5.5(c) of the ISO 9004 quality guidance document, "Review and Evaluation of a Quality Management System," "reviews should consist of well structured and comprehensive evaluations which include: considerations for updating the quality system in relation to changes brought about by new technologies, quality concepts, market strategies, and social or environmental conditions."

Although ISO 14001 is more explicit about continual improvement, the spirit of ISO 9001 is also directed toward that concept. The revised ISO 9001:2000 more strongly encourages continual improvement. Continual improvement should be seen as a vehicle for attaining the environmental improvement, equity and economic performance, the pillars for sustainable development mentioned previously.

What areas of management review and continual improvement would be particularly important to MWT technology? Here are some questions that might be asked and answered:

1. *Environmental performance.* Is human health and ecological risk reduction at a scientifically demonstrated and defensible level of no-harm or eliminated entirely by use of MWT technology? Are the organization's legal and regulatory requirements met or exceeded by the MWT technology in place?
2. *Pollution prevention.* To achieve quality and environmental ends, are energy and material for operation of MWT technology (inputs, process, outputs) reduced or optimized to the maximum level possible?
3. *Cost-effectiveness and profitability.* Does the MWT technology employed operate at the most cost-effective level possible? Does it produce products that are recyclable, capable of being reintroduced to commerce, and that positively affect the financial bottom line? Does it reduce insurance and liability risk? Does it develop new market opportunities? Does it contribute sufficiently to financial performance to positively affect stock performance?

4. *Benefits for community and equity.* Does the MWT technology improve the health and well-being of workers and the community? What community benefits are derived beyond environmental performance by MWT technology (e.g., jobs, positive public relations, educational opportunities)?

If the management review can answer "Yes" to all of these questions, an optimum MWT technology for achieving quality and environmentally sustainable goals has been attained, or close to it. An answer of "No" or "None" to any of these questions should spur a discussion about the need to change existing quality and environmental policies and the goals, objectives, and targets. Is it feasible? How does one make it happen? Discussion of these types of open-ended questions provides the basis for new ideas, allows one to move closer to an environmentally sustainable operation, and tests the limits of technology and its creative application. Management review and the opportunities for continual improvement that stem from it takes us right back to policy and planning for quality and environmental management systems. The circle is closed, ready to begin anew, with MWT technology an integral part.

The Future of MWT Technology and Integration in Quality and Environmental Management Systems

At the time this section was written, ISO 14001 and ISO 9001 were heading into their 5-year mandatory review cycles. It is expected that requirements will become more harmonized between the two standards to allow ease of integration and reduction of effort for their implementation. The automotive industry in the United States, most notably Ford and General Motors, is requiring suppliers to become ISO 14001-certified in the near future. Already, ISO 9001 has thousands of registrations worldwide and its acceptance as a necessary trade requirement is growing. It appears that ISO 14001 may well do the same through private-sector initiatives.

Looking to the workplace, Occupational Health and Safety Management System (OHSMS) standards are emergent in certain nations (Great Britain BS 8800, BSI OHSAS 18001) with the possibility that some international consensus standards may emerge or may be needed in the future. The American Industrial Hygiene Association (AIHA) published an OHSMS guidance document in 1996, consistent with ISO 9001 and what was then a draft version of ISO 14001, to allow ease of integration of OHS management with quality and emergent environmental management systems. The British Standards Institute (BSI) OHSAS 18001:1999, an occupational health and safety management system specification, and the guidance document OHSAS 18002:2000 are very similar to ISO 14001 in structure and form to allow ease of integration. These documents are not British standards. OHSAS is an acronym for an Occupational Health and Safety *Assessment Series*. These documents provide a means to register a system and allow third-party recognition of an OHS system. OHSAS are documents prepared by registration bodies, BSI, and others, but have not undergone the voluntary adopted national or international standard process and as such are not true standards. The OHSAS documents follow closely in form to a standard and may provide a template upon which national or international occupational health and safety management standards can be built.

In the United States, ANSI is granting a secretariat for the development of an occupational health and safety system in 2000. It is likely that in the next few years the trend of writing national and international standards for occupational health and safety management systems will grow and mature. All of these documents are leaning toward harmonization of management systems and integrating health, safety, environment, and quality.

BSI is working on an environmental sustainability standard that may be published in 2 years and another guidance document for implementing ISO 14001 in a few easy steps for small and medium-size employers. The recommendations found in the U.S. President's Council on Sustainable Development's Final Report of May 5, 1999, may well prove a significant driver for sustainable development in the United States and the use of management systems as a means to attain that end. Because other nations around the world are beginning to realize the importance of operating in an environmentally sustainable manner, this will inexorably drive the need to integrate MWT technology into the quality, health, safety, and environmental aspects of all management systems.

Many of the technologies described in this Handbook are state-of-the-art and provide the technical solutions to the new social, economic, and environmental challenges encompassing sustainable development in the near future. It is our hope that the description of MWT technology integration in this section will prove helpful to professionals in this area, both now and in the future.

Recommended Reading

Culley, W.C., 1998. *Environmental and Quality Systems Integration*. Lewis Publishers.

ISO 14001, Environmental Management Systems — Specification with Guidance for Use; International Organization for Standardization, Geneva, Switzerland; 1996.

ISO 14001, Environmental Management Systems — General Guidelines on Principles, Systems and Supporting Techniques; International Organization for Standardization, Geneva, Switzerland; 1996.

ISO 14010, Guidelines for Environmental Auditing — General Principles; International Organization for Standardization, Geneva, Switzerland; 1996.

ISO 14011, Guidelines for Environmental Auditing — Audit Procedures, Part 1: Auditing of Environmental Management Systems; International Organization for Standardization, Geneva, Switzerland; 1996.

ISO 14012, Guidelines for Environmental Management Systems — Qualification Criteria for Environmental Auditors; International Organization for Standardization, Geneva, Switzerland; 1996.

ISO 14024, Environmental Labeling — Guidance Principles, Practices and Criteria for Multiple Criteria-Based Practitioner Programmes (Type 1) — Guide for Certification Procedures; International Organization for Standardization, Geneva, Switzerland; [Draft stage].

ISO 14031, Environmental Performance Evaluation; International Organization for Standardization, Geneva, Switzerland; 1999.

ISO 14040, Life Cycle Assessment — Principles and Guidelines; International Organization for Standardization, Geneva, Switzerland; [Draft stage].

ISO 9000, Quality Management and Quality Assurance — Guidelines for Selection and Use; International Organization for Standardization, Geneva, Switzerland; 1994.

ISO 9001, Quality Systems — Model for Quality Assurance in Design, Development, Production, Installation and Servicing; International Organization for Standardization, Geneva, Switzerland; 1994.

ISO 9002, Quality Systems — Model for Production, Installation and Servicing; International Organization for Standardization, Geneva, Switzerland; 1994.

ISO 9003, Quality Systems — Model for Final Inspection and Test; International Organization for Standardization, Geneva, Switzerland; 1994.

ISO 9004, Quality Management and Quality Assurance Elements, Part 1 — Guidelines; International Organization for Standardization, Geneva, Switzerland; 1994.

Ritchie, I. and Hayes, W., 1998. *A Guide to the Implementation of the ISO 14000 Series on Environmental Management*, Vol. 1. Prentice-Hall, Englewood Cliffs, NJ.

Towards a Sustainable America: Advancing Prosperity, Opportunity, and a Healthy Environment for the 21st Century, May 1999. http://whitehouse.gov/PCSD/Publications/tsa.pdf.

9.2

Risk Analysis and Toxicology

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Introduction

The purpose of this section is to provide an introduction and overview of risk assessment and toxicology as they apply to mixed waste management. This section presents the basic risk assessment approach, principles, and vocabulary for the working professional in waste technologies, chemical engineering, environmental engineering, and civil engineering disciplines. It is divided into subsections on human health risk assessment (HHRA), ecological risk assessment (ERA), and toxicology.

Human Health Risk Assessment (HHRA)

HHRA been defined as "the characterization of the potential adverse health effects of human exposures to environmental hazards" (NRC, 1983). The determination of an adverse effect is a value judgment. It can be defined quantitatively as an hazard quotient (HQ) exceeding 1.0 or a risk factor of cancer occurring in 1 out of a million, to more difficult-to-measure concepts such as the quality of life or spiritual values.

As an emerging science, risk assessment has gained more acceptance by both the regulators and the public. The basic risk assessment process involves identifying hazards, such as the release or potential release of a toxic substance into the environment, and then using measurement, testing, and mathematical or statistical models to quantify the relationship between the event and the effect. Therefore, the HHRA can be discussed in terms of three major sections or phases: hazard identification, exposure assessment, and risk characterization.

Hazard Identification

Hazard identification is concerned with the presence of potentially hazardous substances, their potential toxicity, and the site situation. All available data specific to the location is examined and summarized. A clear understanding of the hazardous substances at the site, their concentration in the media present, and spatial distribution need to be developed. Hazardous substances can occur in groundwater, surface water, soil (both surface and subsurface), air, and food.

It is important to evaluate the site history, land use, and environmental characteristics. The description of the site should include location, cultural resources, and regulatory status. The current activities should be documented as well as the past history, particularly as it relates to potential contamination. Environmental characteristics of importance to the assessment may include physiography, topography, meterology, geology, and hydrology. Initially, potential contamination associated with the facility's operations is identified by historical knowledge and then characterized for risk assessment by sampling. The contaminants should be broadly characterized, for example, as organics, metals, and radionuclides.

A few contaminants and exposure routes usually dominate total risk, and minimal effort should be spent in detailed evaluation of minor contaminants and routes of exposure. Therefore, after concentrations by media type have been determined, it is common to screen chemicals and radionuclides, to focus on those substances that are present at higher concentrations in the environment, are more toxic, are more persistent, or mobile. These contaminant-specific screenings include statistical comparisons between site-related and background samples, special handling of undetected contaminants, evaluation of detection frequency, and comparison with applicable regulatory guidance and requirements.

Two approved approaches to additionally eliminate substances of less concern are either a scoring or ranking process for both the contaminants and routes of exposure or the use of a risk-based concentration screen (USEPA, 1989). Appropriately used, these processes can dramatically reduce the effort of risk assessment, while not significantly changing the results.

Screening can be performed against risk-based concentrations (RBCs) and preliminary remediation goals (PRGs). The U.S. Environmental Protection Agency (USEPA) Region 9 developed PRGs as tools for evaluating and cleaning up contaminated sites. The PRGs contained in the Region 9 PRG Table were calculated using generic standardized equations, combining exposure information assumptions and EPA toxicity data. They are calculated without site-specific information. These PRGs are useful for site "screening" and as initial clean-up goals, if applicable. This Website is located at: http://www.epa.gov/region09/waste/sfund/prg/index.htm. USEPA Region 3 has developed RBCs for use for risk assessment purposes calculated using genetic exposure models from USEPA (1989). This Web site is located at: http://www.epa.gov/reg3hwmd/risk/riskmenu.htm

Exposure Assessment

Exposure assessment is a key phase in the risk assessment process, because without an exposure, even the most toxic substance does not present a threat. Exposure assessment includes three steps:

1. Characterization of the exposure setting
2. Identification of complete exposure pathways
3. Quantification of the exposure

To characterize the exposure setting, it is important to identify both the exposed populations (general public or selected groups) and the exposure scenario (residential, worker, trespasser, recreation, or construction).

Potentially exposed populations are determined based on the surrounding land use and documented sources of demographic information. Populations that may be exposed as the result of contaminants that migrate from the site are also considered. A site visit is important to verify patterns of human activity associated with various land uses. Potentially exposed populations include:

- Present populations in the vicinity
- Future populations in the vicinity
- Subpopulations of special concern (e.g., infants, elderly, pregnant women, and those with chronic illness)
- Potential on-site workers (e.g., during remediation)

The development of exposure scenarios characterizes the conditions under which the populations may be potentially exposed. This consists of an evaluation of both current and reasonable future uses of the site. After scenarios have been determined, then the specific parameters needed to assess exposure (exposure frequency, duration, and intake rate) can be selected. Commonly used exposure scenarios include current and future daily worker, a construction worker, recreational use, current and future residential use, and trespassers.

Once potentially exposed populations have been identified and characterized, exposure pathways can be traced from the site to the exposed populations. Each exposure pathway describes a mechanism by which a population or individual might be exposed to contaminants. The exposure pathway is the environmental route that substances from the site can reach receptors. A pathway consists of the following: a source, a release and transport mechanism, an exposure point, a receptor, and an exposure route.

Exposure routes are the pathways by which contaminants gain entry into the body. There are three exposure routes by which environmental contaminants may enter the body: (1) inhalation (respiratory tract), (2) ingestion (gastrointestinal tract), and (3) dermal contact (skin). For radionuclides, there is a fourth exposure route, external exposure.

The result of this analysis yields a conceptual site model, which is an overview of the actual movement of the contamination through the system, the exposure routes and the receptors. An example is shown in Figure 9.2.1.

Actual measurements of exposures are not commonly available. Exposure models are frequently used to develop exposure point concentrations. For example, in air quality studies, chemical emission and air dispersion models are used to predict the air concentrations to downwind populations. Residential drinking water wells downgradient from a site may not currently show signs of contamination, but may become contaminated in the future as contaminants in the groundwater migrate to the well site. In these situations, groundwater transport models can estimate when contaminants of potential concern will reach the wells.

Pollutants can be transported away from the source. They can be physically, chemically, or biologically transformed. They can also accumulate in various media. Assessment of the contaminate fate requires knowledge of many factors, including organic carbon and water partitioning at equilibrium (K_{oc}), chemical partitioning between soil and water (K_d) partitioning between air and water (i.e., Henry's law constant), solubility constants vapor pressures, partitioning coefficients between water and octanol (K_{ow}), and bioconcentration factors (BCFs).

Risk Characterization

This final stage in the risk assessment process involves prediction of the frequency and severity of effects in exposed populations. Conclusions reached concerning hazard identification and exposure assessment are integrated to yield probabilities of effects likely to occur in humans exposed under similar conditions.

Because most risk assessments include major uncertainties, it is important that biological, analytical, and statistical uncertainties are described in the risk characterization. The assessment should identify which components of the risk assessment process involve the greatest degree of uncertainty.

Potential human carcinogenic risks associated with chemical exposure are expressed in terms of an increased probability of developing cancer during a person's lifetime. For example, a 10^{-6} increased cancer risk represents an increased lifetime risk of 1 in 1 million for developing cancer. For carcinogenicity, the probability of an individual developing cancer over a lifetime is estimated by multiplying the cancer slope factor (in units of mg/kg/day) for the substance by the chronic (assumed to be a 70-year average) daily intake (in units of mg/kg-day).

For non-carcinogenic effects, the exposure level for each potential contaminant is compared to a chemical-specific Acceptable Daily Intake (ADI) or Reference Dose (RfD) derived for similar exposure periods. Three exposure durations are considered: acute, intermediate, or chronic. For humans, acute effects are considered those that arise within days to a few weeks; intermediate effects are those evident in weeks to a year; and chronic effects are those that become manifest in a year or more.

Risk assessments at mixed waste sites are additionally complex, due to:

- Exposure to multiple substances, both radioactive and nonradioactive, with the potential for numerous chemical and biological interactions
- Exposures to multiple media and pathways (e.g., via water, air, and soil)
- Exposure to multiple organisms with differing susceptibilities (e.g., infants, elders).

The assumption of dose additivity is most acceptable when substances induce the same toxic effect by the same mechanism. When available, information on mechanisms of action and chemical interactions are considered and are useful in deriving more scientific risk assessments.

Individuals are often exposed to substances by more than one exposure pathway (e.g., drinking of contaminated water, inhaling contaminated dust). In such situations, the total exposure will usually equal the sum of the exposures by all pathways.

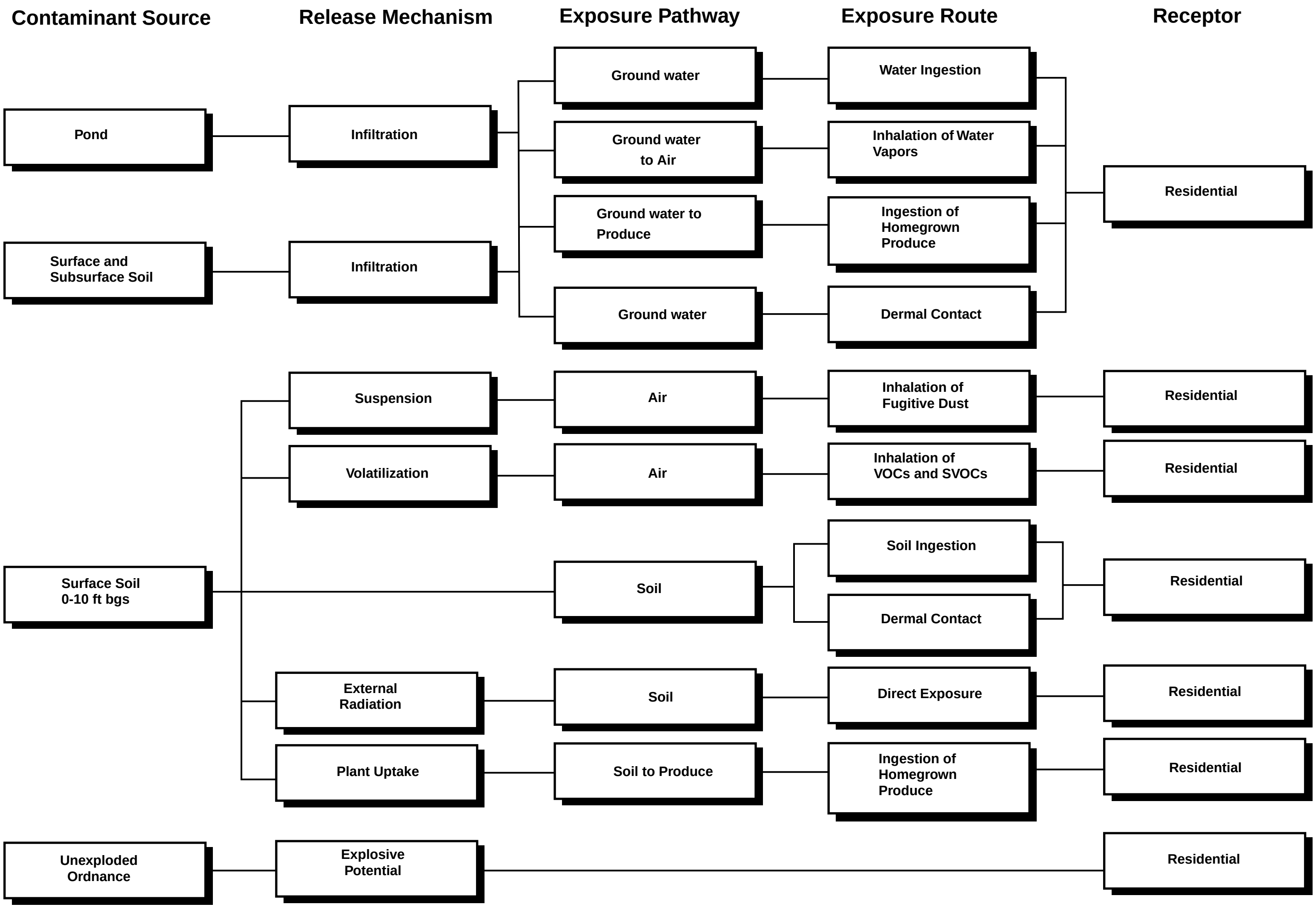

FIGURE 9.2.1 Residential exposure scenario conceptual site model (CSM).

In conclusion, whether the risk description is simply a brief presentation (particularly true when risks are below project-specific targets), or a long discussion of complex results, they must be usable to the risk manager. The EPA guidelines (USEPA, 1998) reiterates that to facilitate mutual understanding, it is critical that the risk assessment results are prepared in a manner that is clear, transparent, reasonable, and consistent with other risk characterizations of similar scope.

Ecological Risk Assessment (ERA)

Ecological risk assessment (ERA) is the evaluation of the likelihood that undesirable ecological effects will occur or are occurring as a result of exposure to one or more stressors. A stressor refers to any physical, chemical, or biological entity that can induce an adverse effect (USEPA, 1992). An ERA at a site can be indicated because it has been shown that protecting human health does not always result in protecting ecosystem integrity (Hegner, 1994).

Background and Guidance

Ecological risk assessment (ERA) was identified during the late 1980s as part of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) process, and for the last 20 years, the EPA responded by providing guidance to performing ERA. These references are located at http://www.epa.gov/superfund/programs/risk/rabasics.htm. Sorensen and Margolin (1998) have summarized the ERA assessment guidance available and provide a valuable resource. Since this paper was published, an additional guidance has come out in draft related to the evaluation of mixed waste issues related to incineration. This is the Screening Level Ecological Risk Assessment Protocol for Hazardous Waste Combustion Facilities (USEPA, 1999).

ERA Process Overview

The USEPA (1992 and 1998) presented a three-step approach to ecological risk that includes (1) problem formulation, (2) analysis, and (3) risk characterization. The following subsections discuss the application of this stepped approach and the type of information that should be included to support the assessment.

Problem Formulation

Problem formulation begins the ERA process by defining the site(s) of concern, contaminants of concern (or stressors), and receptors in an organized method. The goals of the ERAs are defined upfront as part of the planning process between the regulators, site officials, and risk assessors at this time. The USEPA has established biological technical assistance groups (BTAGs) to assist in scoping large ERAs and to provide technical support and review as necessary.

The general description and characterization of the site and the contaminant source and migration from the area of concern are identified. Combined with an evaluation of receptors, the exposure pathways of the identified contaminants are qualitatively modeled, and the potentially affected components of the ecosystem are identified. The relationship between the contaminants, exposure pathways, and ecosystem(s) at risk is then assimilated into the conceptual site model (CSM). Assessment and measurement endpoints are then defined and summarized.

Description of Site and Hazard Identification

At most facilities, previous investigations are directed primarily at defining stressors (generally contaminants) and areas of concern based on human health issues. Activities at the problem formulation stage of the ERA will be similar to the human health hazard identification, and should be performed in a similar time frame. ERAs have differing concerns from human health risk assessments due to multiple receptors and the possibility of greater toxicity from certain substances.

Existing data on potential contamination to the media associated with the area can be used to support the definition of the problem and support further evaluations based on ecological receptors. This includes the compilation of any relevant ecological investigations in the area of concern. The purpose of reviewing previous ecological and contaminant studies is to identify and locate data that can be used to support the ERA.

A wide range of properties should be considered during the ecosystem characterization portion of problem formulation. These properties include ecosystem structure (i.e., type and abundance of flora and fauna species), trophic-level relationships of flora and fauna species, ecosystem function (i.e., energy source and pathways of utilization, and nutrient processing), as well as abiotic components such as climate, topography, and soil. "Knowledge of the ecosystem potentially at risk can help identify ecological components that may be affected and stressor–ecosystem interactions relevant to developing exposure scenarios" (USEPA, 1992).

Receptor Identification

Identification of the biotic components (flora and fauna) is one of the initial steps of the risk assessment. This information may be available from past surveys or other local sources of information. A biological survey of the area of concern surrounding the facility may have been performed to develop vegetation and wildlife species lists. Potential risks to federally regulated threatened and endangered (T/E) species or other species of concern should be addressed in the risk assessment. Therefore, habitats critical to T/E species potentially present in the area should be identified and characterized. Other critical habitats (such as wetlands) that may be impacted by facility activities should be identified and characterized.

The development of a food web model for each ecosystem identifies the relationships between the flora and fauna found in the area of concern. The food web can also be incorporated into the CSM, depending on the simplicity of the assessment. Through the food web model, the trophic relationships within the ecosystem are identified so that the ecological risk assessor can define potential contamination pathways (Calabrese and Baldwin, 1993). This allows an estimation of contaminant transfer through each trophic level in the ecosystem and from the different sources via an abiotic medium (e.g., soil, sediment).

Because food web models are used to identify indirect effects of contaminant exposure to species that comprise upper trophic levels, they are important in producing the ERA pathways, as well as exposure and conceptual site models. Figure 9.2.2 depicts a simplified food web model developed for use at the Idaho National Engineering and Environmental Laboratory (INEEL) (VanHorn et al., 1995). This type of model is readily understood, but may be too simplistic. Other types of visual approaches that depict boxes and arrows may provide more information but can quickly become difficult to interpret.

Abiotic components such as topography, hydrology, geology, soil, and climatic conditions in the area may have significant impacts on transport, fate, and effects of environmental contaminants. A general characterization of the landscape should be provided as background for interpretation of potential effects identified in the analysis. Prominent landforms should be identified. Streams and wetlands should be mapped. If stream flow maps are available, they provide useful information. A characterization of soils present in the area should be included as part of this effort.

Pathways of Contaminant Migration and Exposure

Contaminant migration and pathways modeling are a major focus of ERA, incorporating source and receptor identification, contamination release mechanisms, and contaminant environmental transport. The models attempt to address direct exposure to terrestrial and aquatic species through the identification of exposure pathways, and indirect exposure (e.g., ingestion of contaminated prey) or direct contact with environmental media.

Typical exposure routes considered in ERAs include:

- Ingestion (soil, water, and biota)
- Inhalation
- Dermal contact
- External exposure for radionuclides

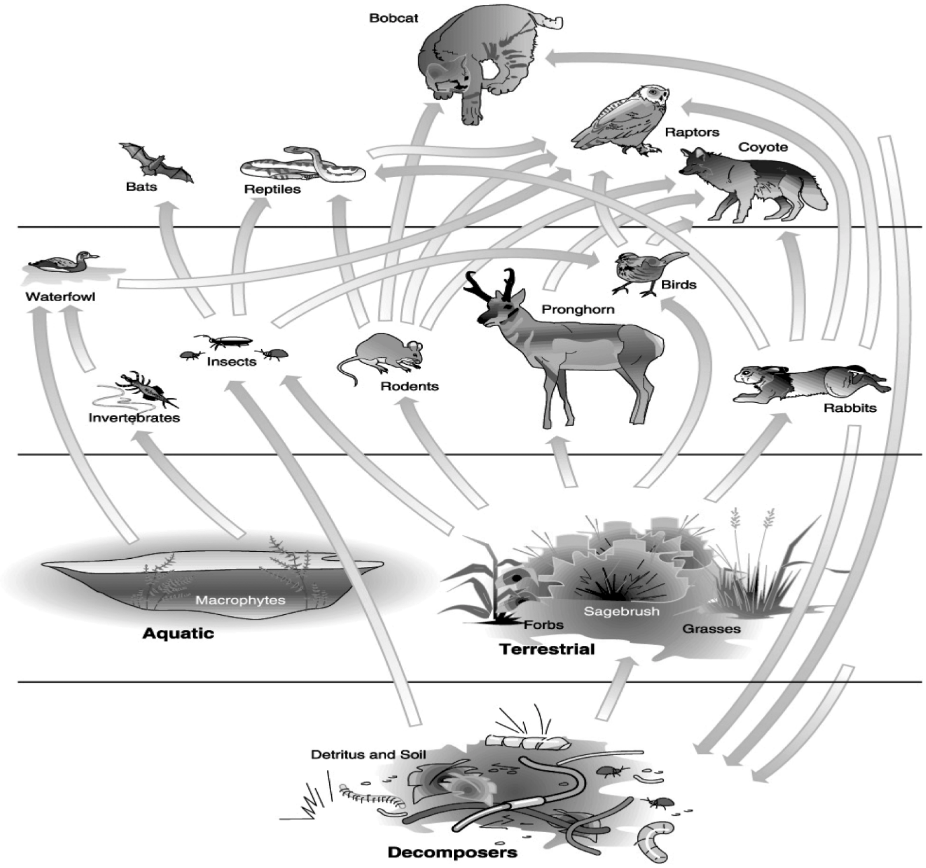

FIGURE 9.2.2 Simplified food web model. (From VanHorn, R.L., Hampton, N.L., and Morris, R.C., 1995. INEEL-95/0190, April.)

The Conceptual Site Model

Development of the conceptual site model is based on the food web and appropriate pathways/exposure models. Simplistically, the conceptual site model combines the ecological and contaminant characteristics of the ecosystem being analyzed to develop exposure scenarios for use in assessing the risk at the site. The model integrates all direct exposure pathway models identified with indirect exposure scenarios (i.e., prey consumption).

The basic components of the model are contaminant sources, pathways (including release mechanisms and environmental transport routes), and exposure scenarios (which link the receptors to the source). The conceptual model integrates receptors identified in the receptor characterization process with the pathway model to produce an overall summary of exposure for the ecosystem and serves as input to the analysis phase of the assessment (USEPA, 1992).

Conceptual site models can be presented in one of two formats:

An evaluation model is a flow chart analysis depicting the movement of contaminants from source to receptor (similar to the HHRA Figure 9.2.1). An illustrative model that depicts the site, source, affected media, and receptors with arrows indicating contaminant movement through the environment (see Figure 9.2.3).

Assessment and Measurement Endpoints

Assessment endpoints are "formal expressions of the actual environmental values that are to be protected" (Suter, 1989). For ERA, assessment endpoints are the focus for risk characterization and

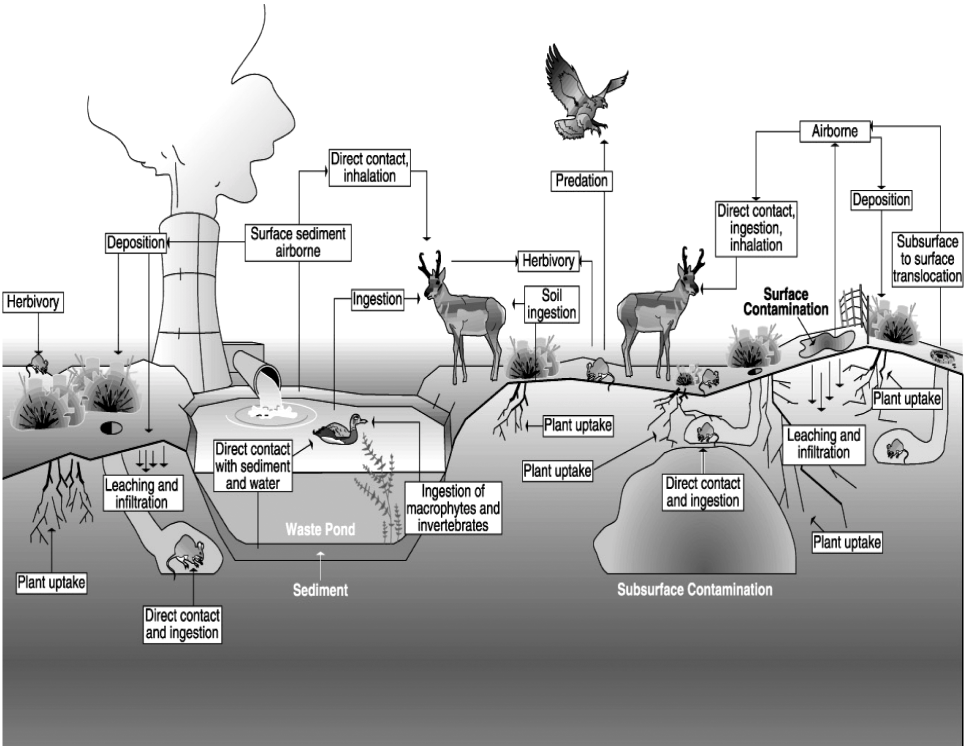

FIGURE 9.2.3 Conceptual site model. (From VanHorn et al., 1998.)

link the measurement endpoints to risk management goals (USEPA, 1992). Criteria for ERA assessment endpoints encompass biological relevancy policy goals and societal values, susceptibility to the contaminant, and consideration of measurability and predictability (USEPA, 1992; Suter, 1993). A measurement endpoint is "a quantitative expression of an observed or measured effect of the hazard; it is a measurable environmental characteristic that is related to the valued characteristic chosen as an assessment endpoint" (Suter, 1989).

Analysis

The information gathered during the problem formulation directs the analysis phase of the ERA and provides the basis for calculating an indication of risk. The analysis phase consists of exposure assessment and ecological effects analysis.

Exposure Assessment

The exposure assessment quantitatively determines the magnitude and routes of exposure, and contaminant fate and transport, as well as the ecosystem parameters, and an estimation of contaminant exposure point concentrations (EPCs) for receptors of concern.

Site-specific and literature-based information on the transport and fate in the environment for contaminants of potential concern are evaluated. As with human health risk assessment, it is common to model the exposure point concentration. This includes any available information on studies concerning the behavior of a contaminant in the biota (e.g., movement through the food web or accumulation in certain tissues). This information, combined with the ecological effects assessment, will provide an effective picture of the potential movement of the contaminant through the ecosystem and allow adequate characterization of the risk.

The ecosystem characterization that was performed for the problem formulation is the basis for the development of the ecosystem exposure parameters necessary to perform the analysis. The input parameters for the exposure assessment should be presented in this section of the assessment. Site-specific data should be used whenever available, and literature values related to the specific species used when site-specific data is lacking. Conservative assumptions are commonly necessary due to the lack of receptor-specific data. The EPA *Wildlife Factors Exposure Handbook* (USEPA, 1993) is an excellent source for this type of information. The ecosystem characterization presented in this section of the analysis phase should include a discussion of temporal and spatial characteristics, ingestion rates, body weight and diet, and food-chain exposure calculations.

Exposure Analysis

The exposure analysis section will summarize the information compiled during the problem formulation as the information relates to exposure pathways and conceptual site models. The characterization of the environmental media and contaminants is performed as part of the problem formulation phase of the ERA. This information can be presented as a review with a brief discussion. This review should include a discussion of the pathways identified, the species potentially exposed, and a review of the assumptions that will be made concerning the selection of endpoints and receptors.

For screening purposes, receptors are assumed to be exposed to stressors to the maximum extent, perhaps beyond what is actually expected (e.g., assuming that a raptor captures 100% of its prey from a contaminated site, and that all the prey are exposed to maximum contaminant concentrations). This is similar to the human risk assessment concept of the “maximally exposed individual,” a hypothetical individual who is assumed to live and grow his own food at a location of maximum exposure to a stressor. This conservative approach helps ensure that a potentially important contaminant will not be eliminated from future evaluations.

Exposure modeling is discussed in many of the available guidance documents (USEPA, 1993; 1998). The total exposure of each of the terrestrial and aquatic wildlife receptors to contaminants is calculated as the sum of the dietary, soil (or sediment), and drinking water (surface water) exposure estimates.

Effects Assessment

The purpose of the effects (or stressor-response) assessment is to characterize the toxicity of stressors to selected measurement endpoints (e.g., ecological receptors). In this section, effects of the contaminants on identified receptors will be quantified. This process relies on professional judgment, especially when minimal data is available or when choices among several sources of data are required. If the available data are inadequate, this will be identified as a data gap and will be addressed in the screening evaluation. The derivation of ecological toxicity reference values (TRVs) will often involve various extrapolations from literature reviews of laboratory studies and is discussed in greater detail below.

Risk Characterization

The final phase of risk assessment — risk characterization — involves the evaluation of the likelihood of adverse effects occurring as a result of exposure to stressors. Risk characterization includes two major steps: risk estimation and risk description. In the risk estimation, the contaminants that had an indication of potential risk based on the HQ approach are summarized. In the risk description, this potential risk is characterized and discussed. The risk description also presents and qualifies the uncertainty inherent in the assessment.

Risk Estimation

Risk is estimated by comparing the calculated dose to the TRV expressed as an HQ. Exposure parameters used to calculate dose have been discussed in the previous subsections. If the dose from the contaminant does not exceed its TRV (i.e., if the HQ is less than some target value, sometimes set at 1.0), adverse effects to ecological receptors from exposure to that contaminant are not expected and no further evaluation is required. Hence, as in human health risk assessment, the HQ is an indicator of potential risk. HQs are calculated using the following equation:

$$\text{HQ} = \text{Dose/TRV} \tag{9.2.1}$$

where

HQ = Hazard quotient (unitless)
Dose = Dose from all media (mg/kg/day)
TRV = Toxicity reference value (mg/kg/day)

Depending on the contaminants, receptors, and waste sites, HQs can be summed across the pathways by receptor. It is important to consider additive effects for all pathways and contaminants. This total is commonly called the hazard index (HI) and should be evaluated to determine if the sum is greater than 1.0. The HI is the summation of effects, the determination of relative risk from a suite of contaminants under consideration, and the propagation of higher risk contaminants through to more detailed risk assessment, while dropping those with low risk.

Risk Description, Uncertainty and Summary

For the risk manager to evaluate the full range of possibilities contained in the ERA, it is important at this stage to review the results based on the goals of the assessment developed during the problem formulation. The results of the risk estimation are discussed and interpreted. The uncertainties inherent in the assessment and how they relate to the results should also be brought forward into the uncertainty section.

As part of the ERA process, it is also important to consider the impact of any planned activities, such as a remediation, on the receptors at each site. An analysis of the planned response should be performed to determine if the solution is worse than the problem. In the evaluation of risk assessment performed at CERCLA sites, the determination may often be “no action.” The disturbance associated with remedial operations to ensure elimination of the contaminant may be more damaging to the environment and ecological receptors than the presence of the contaminant. For such sites, monitoring in lieu of active remediation can be conducted to ensure that changes are not occurring.

In conclusion, as with the HHRA, whether the risk description is simply a brief presentation (particularly true when risks are below targets) or a long discussion of complex results, they must be usable to the risk manager. When integrating the HHRA results with the ERA, it becomes more critical that the risk assessment results are prepared in a manner that is clear, transparent, reasonable, and consistent.

Toxicology

The dictionary definition of toxicology is “the study of the nature, effects, and detection of poisons and the treatment of poisoning.” A toxicologist is a scientist who determines the adverse effects of substances (chemicals) and the cellular, biochemical, and molecular mechanisms responsible for the effects. Toxicology is an extremely complex field. This subsection provides an overview of issues and terminology important to the performance of the risk assessment.

The risk to receptors as a result of the presence of substances in the environment is determined by the toxicity and the fate of the substance in the environment and in the receptor. The toxicologist uses a dose-response curve to determine toxicity. The EPA has provided systematic and in-depth toxicity evaluations for common contaminants of concern at hazardous waste sites for risk assessment purposes. Additional toxicity evaluations are performed only if specific issues arise during the assessment.

A basic understanding of the general routes of exposure, modes of toxicity, derivation of slope factors, and RfD, is important in performing a risk assessment. Most hazardous waste site risk assessments deal with multiple substances in the environment. The evaluation of the risk from the presence of these multiple substances with various exposure routes, modes of toxicity, possible interactions, as well as other considerations, introduces a large amount of uncertainty into the risk assessment process. Frequently, the risk assessment makes extensive simplifications during the analysis to address that lack of adequate data. An understanding of these issues allows the risk assessor to adequately address them during the analysis.

Exposure Routes

Toxic effects are evident only after absorption (the uptake by cells or organism). However, it is still important to know the route of entrance into the receptor. Except for those substances that have a direct harmful effect on the skin, the mucous membrane, the eye, or the inner lining of the lung, the crucial factor is not the external level of a substance but rather its concentration in the body or target organ(s). This concentration represents the internal exposure. When the absorption rate exceeds the rate of excretion and biotransformation, accumulation may take place, and the body burden will increase. Distribution over the body is dependent on the properties of the substance.

The media, the physical state, and the physiochemical properties of the substance determine the form of exposure. Exposure routes include inhalation (respiratory tract), ingestion (gastrointestinal tract), and dermal contact (skin). For radionuclides, there is a fourth exposure route: external exposure to radiation.

Categories of Toxin Effects

Toxic substances can be categorized as systemic toxins and organ toxins. A systemic toxin affects the entire body or many organs rather than a specific site. Organ or tissue toxicants affect only specific tissues or organs while not producing damage to the body as a whole. These specific sites are known as the target organs or target tissues. In some cases, the effect will occur at only one site or organ. This is referred to as the specific target organ. In other cases, toxic effects will occur at multiple sites or organs.

The types of systemic toxicity include:

1. *Acute toxicity* occurs within hours to days after exposure. An acute exposure is usually a single dose or a series of doses received within a 24-hr period.
2. *Subchronic toxicity* results from repeated exposure for several weeks or months.
3. *Chronic toxicity* represents cumulative damage to specific organ systems and takes many months or years to become a recognizable clinical disease.
4. *Carcinogenicity* is a complex multistage process of abnormal cell growth and differentiation, which can lead to cancer.
5. *Developmental toxicity* pertains to adverse toxic effects to the developing embryo or fetus.
6. *Genetic Toxicity* results from damage to DNA and altered genetic expression. This process is known as mutagenesis. The genetic change is referred to as a mutation and the agent causing the change as a mutagen.

Types of organ-specific toxic effects are:

1. *Blood and cardiovascular toxicity* results from chemicals acting directly on cells in circulating blood, bone marrow, and heart.
2. *Dermal toxicity* results from direct contact or internal distribution to the skin.
3. *Eye toxicity* resulting from direct contact or internal distribution to the eye.
4. *Hepatotoxicity* is toxicity to the liver, bile duct, and gall bladder. The liver is particularly susceptible due to a large blood supply and its role in metabolism.
5. *Immunotoxicity* is toxicity to the immune system
6. *Nephrotoxicity* is toxicity to the kidneys. A high volume of blood flows through them and they filter large amounts of toxins that can concentrate in the kidney tubules.
7. *Neurotoxicity* represents toxicant damage to cells of the central nervous system (brain and spinal cord) and the peripheral nervous system (nerves outside the central nervous system).
8. *Reproductive toxicity* involves toxicant damage to reproductive systems. This is one of the most critical effects evaluated for ecological receptors.
9. *Respiratory Toxicity* relates to effects on the upper respiratory system (nose, pharynx, larynx, and trachea) and the lower respiratory system (bronchi, bronchioles, and lung alveoli).

Factors Influencing Toxicity

The toxicity of a substance depends on form and innate chemical activity dosage, especially dose-time relationship, exposure route, species, age, sex, ability to be absorbed, distribution within the body, excretion, metabolism, and the presence of other chemicals. The form of a substance can have a profound impact on its toxicity, especially for metallic toxins. For example, the toxicity of mercury vapor differs greatly from that of methyl mercury. Another example is chromium. Cr^{3+} is relatively nontoxic whereas Cr^{6+} causes skin or nasal corrosion and lung cancer.

The dosage is the most important factor in determining if a substance will be an acute or chronic toxicant. Virtually all chemicals can be acute toxicants if sufficiently large doses are administered. Often the toxic mechanisms and target organs are different for acute and chronic toxicity.

Dose and Dose-Response

Dose, by definition, is the amount of a substance administered at one time. Exposure dose is the amount of substance encountered in the environment. The absorbed dose is the actual amount of the exposure dose that enters the receptor. The total dose is the sum of the individual doses.

The gram is the standard unit in toxicology for risk assessment. However, the milligram (mg) is also commonly used. The common dose measurement is milligram/kilogram (mg/kg), which stands for milligram of substance per kilogram of body weight.

Another important aspect is the time over which the exposure has occurred. This is especially important for chronic exposures. The commonly used time unit is one day and thus, the usual dosage unit is mg/kg/day, where body weight is implied.

The *dose-response* relationship is fundamental to and essential in evaluating the toxicity of a substance. Mathematical relationships between the dose and response have been established from theoretical models (e.g., the normal distribution as a statistical model). In general, the higher the dose, the more severe the response. This relationship is based on observed data from experimental animal, human clinical, or cell studies.

Knowledge of the dose-response relationship determines:

- Causality that the chemical has in fact induced the observed effects
- The lowest dose where an induced effect occurs — the threshold effect
- The slope for the dose response

The dose-response curve indicates the point at which toxicity first appears, or the threshold dose level. From that point, the curve increases with higher dose levels. A threshold for toxic effects occurs at the point where the body's ability to detoxify or repair toxic injury has been exceeded. The threshold concept is important in the regulatory context. It is often prudent to focus on the most sensitive members of the population; therefore, regulatory efforts are generally made to keep exposures below the population threshold, which is defined as the lowest of the thresholds of the individuals within a population.

Dose-Response Assessment

The dose-response assessment step determines the relationship between dose and incidence of effects. There are normally two major extrapolations required. The first is from high experimental doses to low environmental doses, and the second from animal to human doses. The procedures employed to extrapolate from high to low doses are different for assessment of carcinogenic effects and non-carcinogenic effects.

1. *Carcinogenic effects* are not considered to have a threshold, and mathematical models are generally used to provide estimates of carcinogenic risk at very low dose levels.
2. *Non-carcinogenic effects* (e.g., neurotoxicity) are considered to have dose thresholds. The lowest dose with an effect in animal or human studies is divided by safety or uncertainty factors to provide a margin of safety.

Cancer risk assessment. Assessing carcinogenic effects involves several steps. The substance's potential for human carcinogenicity is inferred from the available information relevant to the potential carcinogenicity of the chemical and from judgments as to the quality of the available studies. The EPA uses a weight-of-evidence approach to classify the likelihood that the substance is a human carcinogen. A three-stage process is followed. In Stage One, the evidence is characterized separately for human studies and for animal studies. In Stage Two, the human and animal evidence are combined into a presumptive overall classification. In Stage Three, the preliminary classification is adjusted upward or downward, based on analysis of available supporting evidence. The result is that each substance is placed into one of the following five categories:

Group	Category
A	Human carcinogen
B	Probable human carcinogen: B1 indicates limited human evidence B2 indicates sufficient evidence in animals and inadequate or no evidence in humans
C	Possible human carcinogen
D	Not classifiable as to human carcinogenicity
E	Evidence of non-carcinogenicity for humans

The key risk assessment parameter derived from the EPA carcinogen risk assessment is the cancer slope factor. This is a toxicity value that quantitatively defines the relationship between dose and response. The cancer slope factor is a plausible upper-bound estimate of the probability that an individual will develop cancer if exposed to a chemical for a lifetime of 70 years. The cancer slope factor is expressed as mg/kg/day.

Non-carcinogenic risk assessment. In the past, the Acceptable Daily Intake (ADI) procedure was used to determine permissible chronic exposure levels for humans based on non-carcinogenic effects. The ADI is the defined as the daily dose that a person can be exposed to for a long time (usually a lifetime) without suffering harmful effects. It is determined by applying safety factors (to account for the uncertainty in the data) to the highest dose in human or animal studies which has been demonstrated not to cause toxicity (No Observable Adverse Effect Level, or the highest exposure level at which there are no statistically or biologically significant increases in the frequency or severity of adverse effect between the exposed population and its appropriate control; some effects may be produced at this level, but they are not considered adverse, nor precursors to adverse effects. (NOAEL)).

The EPA has slightly modified the ADI approach and calculates a Reference Dose (RfD) as the acceptable safety level for chronic non-carcinogenic and developmental effects. The RfDs developed by the EPA are used extensively in the risk assessment process.

The EPA uses the following basic procedure for establishing an RfD:

1. Select the most sensitive species for which adequate studies are available.
2. Human data is always given priority for HHRA purposes.
3. Select the principal or critical studies using the appropriate route of exposure. RfDs are route specific.
4. Select supporting studies
5. Identify the NOAEL. When a NOAEL is not available, an LOAEL can be used to calculate the RfD. An additional safety factor is included if a lowest observed adverse effect level (LOAEL) is used. (The LOAEL is the lowest exposure level at which there are statistically or biologically significant increases in frequency or severity of adverse effects between the exposed population and its appropriate control group.)
6. The NOAEL for the most sensitive endpoint is adjusted downward by orders of magnitude to reflect uncertainty. The more uncertain or unreliable the data becomes, the higher will be the total uncertainty factor (UF) or modifying factor (MF) that is applied.

The RfD is determined using the following equation:

$$\text{RfD} = \text{NOAEL}/(\text{UF} \times \text{MF}) \tag{9.2.2}$$

In general, the RfD is an estimate (with uncertainty spanning perhaps an order of magnitude) of a daily exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime. The RfD is generally expressed in units of mg/kg/day.

The RfD is useful as a reference point from which to evaluate the potential effects of the contaminant at other doses. Doses less than the RfD are not likely to be associated with adverse health risks, and are less likely to be of regulatory concern. As the frequency and/or magnitude of the exposures exceeding the RfD increase, the probability of adverse effects in a human population increases. However, it should not be generally concluded that all doses below the RfD are risk-free and that all doses in excess of the RfD will result in adverse effects.

Reference doses for many contaminants are not available from EPA sources. Frequently only certain routes of exposure will have an EPA-developed RfD. In these cases, the risk assessment generally states this and discusses these issues qualitatively in the risk characterization or in the uncertainty sections. It is possible to study the relationships between physiochemical properties and biological activities. These techniques are known by the acronym QSAR (quantitative structure-activity relationships). If necessary, a toxicologist can use this approach or others to develop an RfD specifically for a contaminant of potential concern at a site.

Ecotoxicology

The derivation of ecological toxicity reference values (TRVs) will often involve various extrapolations from literature reviews of laboratory studies. Extrapolations commonly used include those between species, between responses from laboratory and field, and between responses from field to field. Differences in responses among taxa depend on many factors, including physiology, metabolism, resource utilization, and life history strategy. The relationship between responses also depends on many factors, including the mechanism of action and internal distribution of the stressor within the organism. When extrapolating between different laboratory and field settings, important considerations include differences in the physical environment and organism behavior that will alter exposure, interactions with other stressors, and interactions with other ecological components.

Depending on available data and endpoints, various adjustment factors are used to derive TRVs from experimental data to adjust HQs to account for uncertainty and extrapolation. Table 9.2.1 presents an example from Kester et al. (1998). This allows for a certain conservatism to be included in the assessment. There are various methods that are applicable to this task.

Guidance for developing TRVs can be found in Oak Ridge National Laboratory (Opresko et al., 1994) and INEEL (VanHorn et al., 1995) documents, as well as others. TRVs should be derived for each receptor species by selecting the most appropriate experimental study. The selection of appropriate toxicity information may require the expertise of a senior toxicologist.

Radiotoxicity

The EPA classifies all radionuclides as Group A carcinogens. Depending on the level of exposure, radiation can adversely affect individuals directly exposed as well as their descendants. Radiation can affect the cells of the body, increasing the risk of cancer or harmful genetic mutations that can be passed on to future generations; or, if the dosage is large enough to cause massive tissue damage, it may lead to death within a few weeks of exposure.

The EPA generally evaluates potential human health risks based on the radiotoxicity (i.e., adverse health effects caused by ionizing radiation), rather than on the chemical toxicity of each radionuclide present. However, in assessing the material, the chemical toxicity (e.g., uranium) may be also contribute to risk. Ionizing radiation has been shown to be carcinogenic, mutagenic, and teratogenic. Radiation can

TABLE 9.2.1 Adjustment Factor Values and Criteria for Use in Developing TRVs for INEEL (Kester et al., 1998)

Adjustment Factor	Qualitative Ranking	Value	Criteria
I	Low	1	Variability is low
	Medium	2	Variability is moderate or average
	High	3	Variability is high, or information on variability is inadequate
R	Low	1	Test organism and receptor (or all functional group members) are in same taxonomic order and trophic category
	Medium	2	Test organism and receptor (or all functional group members) are in same trophic category but in different taxonomic orders (at least one functional group member); or for bioaccumulative COPCs, if the test organism and the receptor (or functional group) are in different trophic categories and test organism is from a higher trophic category than the receptor (or functional group)
	High	3	Test organism and receptor (or all functional group members) are in different trophic categories, and the test organism is in a lower or equivalent trophic category than the receptor (or functional group)
Q_1	Low	0.1	Experimental endpoint is highly unlikely to occur in the field
	Medium	0.5	Experimental endpoint is moderately unlikely to occur in the field@@
	High	1	Experimental endpoint is likely to occur in the field
Q_2	Low	1	Study was of chronic duration
	Medium	2	Study was of subchronic duration
	High	3	Study was of acute duration
Q_3	Low	1	NOAEL
	Medium	2	LOAEL
	High	3	Adverse effect level or frank effect level
U	Low	1	High-quality studies
	Medium	2	Studies of reasonable quality
	High	3	Studies with flawed design or incomplete information

I = AF accounts for intratoxon variability

R = AF accounts for intertaxon variability

Q_1 = a data-quality AF reflecting the risk assessor's certainty that the COPC actually causes the critical effect in the receptor, and that it is an ecologically significant effect

Q_2 = a data-quality AF used when extrapolating across endpoint types to estimate an NOAEL

Q_3 = a data quality AF used when extrapolating across endpoint types to estimate an NOAEL

U = an AF to account for any residual uncertainty in the data evaluation process and estimation of other AFs based on data quality, study design, and/or known but otherwise unaccounted for extrapolation issues.

Modified from Ludwig et al., 1993.

induce cancers in nearly any tissue or organ in both humans and animals, and the risk of cancer increases with increasing dose. The assessment of dose from ionizing radiation is complex. This subsection discusses the general characteristics of concern and some of the concepts associated with management of radiation. An excellent source of detailed information is *Radiological Assessment: A Textbook on Environmental Dose Analysis* (Till and Meyer, 1983). If a facility is actively working with ionizing radiation, the special concerns (shielding and As Low As Reasonably Achievable [ALARA] practices) need to be addressed by a professional in this field.

Ionizing radiation is energy (particles or rays) emitted from radioactive atoms undergoing radioactive decay processes. The four basic types of ionizing radiation that are of primary concern for management of mixed waste are alpha particles, beta particles, gamma rays, and neutron particles.

1. *Alpha particles.* The alpha particle is a highly energetic helium nucleus that is emitted from the nucleus of the radioactive isotope (atom). It is a positively charged, massive particle, consisting of two protons and two neutrons. Because alpha particles are easily shielded and travel a short distance (2 in. in air), the primary exposure route of concern is internal ingestion or inhalation.
2. *BETA particles.* A beta particle is physically identical to an electron that is emitted from the nucleus of an atom, and is negatively charged. If ingested or inhaled, a beta emitter can be an internal

hazard due to it short range (typically 10 ft in air). Beta particles are easily shielded by plastic, glass, metal foil, or safety glasses; however, external exposure to beta particles is potentially hazardous to the skin and eyes.

3. *Gamma-rays/X-rays.* Gamma/X-ray radiation are electromagnetic waves or photons and have no electrical charge. Gamma/X-ray radiation requires shielding by very dense materials, such as concrete, lead, or steel. Because gamma/X-ray radiation has no charge and no mass, they are highly penetrating and have a large range (typically several hundred feet in air). Gamma/X-ray radiation can result in radiation exposure to the entire body.
4. *Neutron particles.* A neutron radiation consists of neutrons having zero charge that are ejected from the nucleus. Neutrons have a relatively high penetrating ability, large range (typically several hundred feet in air), and are difficult to stop. Materials with high hydrogen content, such as water or plastic, best shield neutron radiation. Neutrons are a whole-body hazard due to their high penetrating ability.

Units of Measure

The roentgen (R) it the unit that measures radiation as it travels through air. The roentgen unit is applicable only to gamma/X-rays and does not apply to particulate radiation (such as alpha, beta, neutron or high-speed ions) and it does not involve biological tissue. To account for the interaction with biological receptors, the concept of absorbed dose was introduced. The unit of absorbed dose is called a Rad (radiation absorbed dose); 1 rad is that quantity of ionizing radiation of any type that will deposit 100 ergs of energy in each gram of absorbing tissue.

The relationship between exposure and absorbed dose depends on the tissue involved. An X-ray exposure of 1 R will deliver a dose of very nearly 1 rad in soft tissue (e.g., muscle). In bone, an exposure of 1R corresponds to a dose of considerably more than 1 R. The units are not interchangeable. The difference in dose results from the fact that bones are opaque to X-rays, so they absorb most of the X-ray's energy, while flesh is transparent, allowing much of the X-ray energy to pass through without being absorbed. The rad has now been superceded by the Gray (Gy), where 1 Gy = 100 rad.

To account for differences in biological effectiveness between types of radiation, the unit of dose equivalence was introduced, called a rem (Roentgen Equivalent Man). The unit roughly indicates the relative degree of biological damage caused by a particular exposure to ionizing radiation.

The dose equivalent (in rems) is calculated by multiplying the absorbed dose (in rad) by a quality factor Q ($Q = 1$) for beta, gamma, or X-radiation, and twenty ($Q = 20$) for alpha particles or fast neutrons. Therefore, a dose of 1 rad of gamma-radiation delivers a dose equivalent of 1 rem; whereas a dose of 1 rad of alpha-radiation delivers a dose equivalent of 20 rem. It is possible to use experimentally derived quality factors to convert rads to rems, based on a careful measurement of Relative Biological Effectiveness (RBE). In general, the rem is an administrative unit used for regulatory purposes.

The rem is now superceded by the Sievert (Sv); 1 Sv = 100 rem. Thus, the dose equivalent in sieverts can be found by multiplying the absorbed dose in Grays by the same quality factor Q discussed above (because 1 Gy = 100 rad).

The dose is the amount of radiation received. The dose rate is the rate. Dose rate equals dose divided by time (e.g., rem/hr).

Radioactivity is measured in the number of disintegrations radioactive material undergoes in a certain period of time. The Curie (Ci) was the basic unit of activity. Originally defined as the activity of 1 g of pure radium, the Curie was later redefined as 37 billion disintegrations per second. The Curie has now been superceded by the Becquerel (Bq), which is one disintegration per second. Commonly, the measurement of radiation in the media of concern (e.g., ρCi/g) is used to assess risk to receptors.

Acute and Chronic Radiation Doses

Potential biological effects depend on how much and how fast a radiation dose is received. *Acute radiation dose* has an acute effect and is a physical reaction due to massive cell damage. An acute dose can occur to the whole body and to only part of the body. It takes a massive acute dose of radiation before any physical effect is seen (on the order of 500,000 mrem or larger). Acute effects include blood changes, hemopoietic (bone marrow) syndrome, gastrointestinal syndrome, and central nervous system syndrome.

Chronic radiation dose is typically a small amount of radiation received over a long period of time. The body is better equipped to tolerate a chronic dose. The body has time to repair damage because a smaller percentage of the cells need repair. Health effects in the exposed individual include somatic and genetic effects. A somatic effect is a mutation in a cell other those related to genetic information. Mutation in somatic cells can give rise to cancer. A genetic effect is passed on in the genetic material in the cell, possibly causing mutations in offspring. Delayed effects can include cancer, leukemia, bone cancer, lung cancer, life shortening, and cataracts.

Additional Radiation Dose Issues

Receptor populations are constantly being exposed to low levels of natural background radiation, including environmental sources, and at higher levels, occupational sources, medical therapy, and other human-mediated events. Risks to humans exposed to low levels of radiation are considered to be minimal and there is evidence that in many cases the effects may be beneficial. Available research has not yielded the type of information readily used to make risk assessments related to low exposures to radiation. As discussed, the severity of many effects is dose dependent. However, the severity of most delayed effects does not depend on the dose received. For example, there is no such thing as a “little bit” of cancer. This is also true in the case of a genetically-defective child. These effects could have resulted from either a large or a small dose of ionizing radiation. Effects of this nature are said to be stochastic.

- *Stochastic effects* are effects that occur on a random basis with the effect independent of the size of dose. The effect typically has no threshold and is based on probabilities, with the chances of seeing the effect increasing with dose
- *Non-stochastic effects* are effects that are related directly to the dose received. The effect is greater with a higher dose (i.e., the burn gets worse as dose increases). It typically has a threshold, below which the effect does not occur.

Radiation-Specific Risk Assessment Issues

Factors affecting biological damage due to exposure to radiation include total dose, dose rate, type of radiation, area of the body exposed, cell sensitivity, and individual sensitivity. These factors should be addressed in the risk assessment.

Another unique characteristic of radionuclides is that different isotopes disintegrate at different rates, and each isotope has its own characteristic decay rate. Radioactive decay is important for management of mixed wastes. Atoms in a radioactive substance decay in a random fashion but at a characteristic rate. The length of time this takes, the number of steps required, and the kinds of radiation released at each step are well known.

The half-life is the time taken for half of the atoms of a radioactive substance to decay. Half-lives can range from less than a millionth of a second to millions of years, depending on the element concerned. After one half-life, the level of radioactivity of a substance is halved; after two half-lives, it is reduced to one quarter; after three half-lives, to one-eighth; etc. This will generally reduce the risk accordingly. This decay, combined with the exposure scenario, needs to be considered during the evaluation. However, radioactive decay can also produce longer-lived radioactive daughter products. These may contribute significantly to the risk and will need to be taken into consideration as well.

Radiation dose limits are established for occupational workers. The organizations that have set standards include the International Commission of Radiological Protection (ICRP), the International Atomic Energy Agency (IAEA), and the National Committee on Radiation Protection and Measurements (NRCP), as well as others. These types of guidance should be consulted when evaluating exposures at each site.

Sources of RfDs and Slope Factors

- The Integrated Risk Information System (IRIS) at http://www.epa.gov/iris/ is the primary source of toxicity information for non-radioactive contaminants promulgated by the EPA. The information represents a consensus opinion of EPA health scientists representing the Program Offices and the Office of Research and Development. The consensus process involves interpreting the scientific literature applicable to health effects of a chemical, and using established methodologies to develop values for oral reference doses, inhalation reference concentrations, carcinogenic slope factors and unit risks. The products of this process, summarized in IRIS and elaborated in chemical-specific support documents, have been subject to the EPA's peer review policy since its issuance in 1994. As new scientific information becomes available, the EPA will review it, as appropriate, and revise IRIS files accordingly.
- Heath Effects Assessment Summary Tables (HEAST) located at http://www.epa.gov/radiation/heast/index.html#index is the primary source of toxicity information for radionuclides compiled by the U.S. EPA's Office of Radiation and Indoor Air Radiation Protection Division focusing on radiation and dose risk modeling. HEAST lists ingestion, inhalation and external exposure cancer slope factors for radionuclides. Ingestion and inhalation, slope factors are central estimates in a linear model of the age-averaged, lifetime attributable, radioactive cancer incidence (fatal and nonfatal cancer) risk per unit of activity inhaled, or ingested expressed as risk/pCi. External exposure slope factors are also central estimates of lifetime attributable radiation cancer incidence risk for each year of exposure to external radiation from photon-emitting radionuclides (e.g., gamma) distributed uniformly in a thick layer of soil and are expressed as risk/year per pCi/gram soil.
- U.S. Agency for Toxic Substances and Disease Registry (ATSDR) toxicity profiles found at http://www.atsdr.cdc.gov/ provide excellent supporting information and detailed evaluations of substances that have been analyzed.

TOXNET is cluster of databases on toxicology, hazardous chemicals, and related areas. A valuable source of available toxicity databases is available at http://toxnet.nlm.nih.gov/.

Additional Resources

Various individual Department of Energy (DOE) facilities have produced risk assessment guidance. The DOE Oak Ridge National Laboratory (ORNL) has produced extensive guidance, benchmark documents, and general support. Their Web site (http:\ornl.gov) provides a listing of the documents available that can also be downloaded from this location.

The DOE Biota Dose Assessment Committee (BDAC) Web site is located at http://homer.ornl.gov/oepa/public/bdac/. BDAC has assisted DOE in developing a DOE Technical Standard "A Graded Approach for Evaluating Radiation Doses to Aquatic and Terrestrial Biota," that provides a graded approach for evaluating radiation doses to aquatic and terrestrial biota. The DOE Technical Standard can also be used for assessing ecological effects of radiological impact when conducting ERAs.

The EPA Superfund Web site at http://www.epa.gov/superfund/ provides access to EPA information and guidance. It also provides links to other sites of interest. The EPA also has a Web site called tools of the trade; this site has access to guidance, policy, and technical tools for Superfund risk assessment. Information on both human health and ecological risk assessment is included, and most of the resources referenced can be downloaded. This site is located at http://www.epa.gov/superfund/programs/risk/tooltrad.htm#dbsw.

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Chapter Ten

10

Planned Life-Cycle Cost Estimates

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Introduction

Selection and design of systems and technologies for treatment of mixed low-level waste (MLLW) requires knowledge and understanding of the expected costs, schedules, risks, performance, and reliability of the total engineered system. These factors are all related. For example, cost is a function of:

- *Schedule.* The longer the schedule required to treat a given quantity of waste, the greater the operating and maintenance cost.
- *Reliability.* The greater the system reliability, the lower the maintenance cost, the greater the system availability, and therefore the shorter the schedule. However, increased reliability may increase capital cost for more reliable equipment. A system with low reliability will increase operational and economic risk associated with increased probability of equipment failure, increased maintenance and a drawn-out schedule.
- *Risk.* Additional costs are required to mitigate environmental safety and health (ES&H) risks associated with handling and treating mixed waste. The design requirements for risk mitigation will depend on the waste content and the technologies used in the treatment process.
- *Performance.* A system that performs poorly in terms of meeting treatment goals and regulatory requirements may require post-treatment, re-treatment, or system modifications, all of which will increase cost and schedule.

The purpose of this section is to provide the reader with insight into factors involved in determining the cost of a mixed waste treatment system, the relative cost of various treatment concepts, and the trade-offs that should be considered when developing an economic system design.

This section is based on the results of an integrated process analysis project (Feizollahi et al., 1994; Feizollahi and Quapp, 1996; Biagi et al., 1997) commissioned by the Department of Energy (DOE), Office of Science and Technology (OST), to evaluate thermal and non-thermal treatment systems for DOE mixed low-level waste (MLLW). The purpose was to evaluate and compare the performance and cost of various treatment technologies in the context of a complete treatment system capable of treating the wide variety of mixed waste in the DOE complex. Subsequent to these initial studies, additional analyses were performed to obtain greater insight into the cost sensitivities and trade-offs associated with operating parameters that differed from those used in the initial studies.

These studies did not include the time value of money, escalation for expenditures occurring at different times, or salvage value of the facility. Many textbooks on engineering economy and cost engineering are available that provide methods for taking these factors into account for commercial operations.

Thus, costs identified in subsequent subsections are for specific systems designed to treat specific DOE waste streams for the integrated process analysis project. These costs should not be taken to represent the costs of different treatment systems designed to process other combinations of waste streams. Rather, the relative costs, their trends with respect to system parameters and waste characteristics, and the implications of these factors on life-cycle cost are the important factors to consider in evaluating the life-cycle cost of a mixed waste treatment facility.

Standard Cost Factors

Total life-cycle cost of a mixed waste treatment system is a function of six major work breakdown structure (WBS) components. Contingency should be included in all costs and generally should be higher for systems using less-developed technologies to reflect operational uncertainties. However, increased contingency cost for less-developed technologies is one factor that makes such technologies and associated systems less economically desirable than more mature technologies (Harvego and Schafer, 1997). The six cost components of the WBS are (Feizollahi et al, 1994; Feizollahi and Quapp, 1996):

1. *Studies and bench-scale tests and demonstration*. Costs for treatability studies and bench-scale testing include research personnel, equipment, facilities, and project management before Title I design. Demonstration costs include personnel, design and inspection, construction and equipment including construction management, project management, waste disposal, and decontamination and decommissioning.
2. *Facility capital costs*. This cost element consists of five subcomponents described below that involve design, equipment costs, and building costs. Design, inspection, management, and indirect costs are dependent costs that are calculated as a fraction of the purchase costs for the building structure and equipment.
   a. *Design*: preliminary and detailed designs
   b. *Inspection*: this includes engineering support during construction
   c. *Project management*: management costs incurred by site management and the contractor
   d. *Construction*: Facility construction costs are developed from the preconceptual design package and include site development, construction of buildings and structures for alpha and non-alpha waste, processing and material handling equipment, installation, and indirect costs such as subcontractor overhead and fees
   e. *Construction management*: this includes material and services procurement and control activities, allowances for project scope change, management reserve, and contingency reserves to reduce the impact of missed cost or schedule objectives
3. *Operations budget funded activities*. These are preconstruction and preoperational activities. This cost element includes conceptual design, safety assurance, National Environmental Policy Act (NEPA) compliance efforts for government projects, permitting, preparation for operations, and project management. Conceptual designs may consist of process functional diagrams, facility layouts, equipment lists, personnel requirements, and material mass balances.
4. *Operating and maintenance costs*. This cost element includes operating labor, utilities, consumable materials, maintenance (parts, equipment and labor), and transportation. Transportation costs include transportation of wastes to the treatment facility and transportation of treated waste to a disposal site. Allowances for management reserve and contingencies should be included.
5. *Decontamination and decommissioning costs*. These costs include decontaminating the facility, removing the structures and equipment, and decontaminating the site.
6. *Disposal*. This cost includes the price charged by the disposal facility. This is usually a one-time cost based on the volume of waste to be disposed. However, the per-unit volume cost may vary, depending on the type and quantity of hazardous species and radionuclides remaining in the waste.

Facility Design Issues

Facilities handling MLLW are placed in Seismic Category 1 and are classified as moderate-hazard facilities (Kennedy et al., 1992). A major area of concern for ES&H and a major cost driver is the design for alpha containment. All systems and critical operations related to handling alpha-contaminated MLLW are classified according to safety. They should have high-quality, low-maintenance features to keep personnel exposure as low as reasonably achievable. Operations with alpha-MLLW should be confined, to the greatest extent practical, to remote cubicles.

All process steps with potential for generating airborne alpha contamination should have a tertiary containment system. Thus, equipment used to process alpha-MLLW should be placed in triple confinement, airtight cells with personnel access through airlock doors. Such cells should operate at slightly negative pressure to avoid releasing contamination outside the units. Only two levels of containment are required for other processes involving materials with a limited potential for becoming airborne. However, this requirement should be carefully assessed to avoid potential worker inhalation risks. Personnel entering alpha cells must wear Level A protective equipment, including self-contained breathing equipment.

The facility should be designed and equipment selected to minimize maintenance requirements and minimize the personnel exposure time while performing maintenance operations. Large corridors may be required next to each cell for equipment removal and maintenance. In this corridor, equipment may be disassembled, decontaminated (if required), and sent to the maintenance shop for further repair. There are two maintenance issues to be considered. The first issue is the basic maintenance costs (e.g., labor, equipment, parts and material, and lost production due to downtime, which can be minimized with a just-in-time supplier or an inventory of spare parts or replacement equipment). The second issue is the need to have sufficient staff to prevent any single individual from exceeding his/her daily or annual radiation exposure limits while performing maintenance functions.

Facility concepts and confinement levels require detailed analysis and refinement when processing alpha-MLLW to determine the most cost-effective design that meets ES&H requirements. The risk of cost overruns may be high when the system is applied to alpha-MLLW because most system components must be further developed to allow ease of decontamination and maintenance for application in an alpha cell environment and to prevent the inadvertent release from processing systems. Of particular concern are high temperature processes and the entrainment of actinides in the off-gas.

Facility Subsystems

MLLW consists of organic and inorganic solids and liquids comprising a wide variety of materials contaminated with hazardous organics, toxic metals, and radionuclides. Such waste matrices may include any of those shown in Table 10.1 (Huebner et al,. 1994).

Treatment of such a wide variety of waste streams requires a complex treatment system consisting of many subsystems to handle separate waste matrices and, in some cases, specific contaminants. The types of subsystems that may be required are as follows.

1. *Front-end handling*. Waste is received and characterized. Instrumentation can include real-time radiography (RTR), gamma-spectroscopy, and passive/active neutron (PAN) assay. The waste is removed from the incoming drums, sorted, separated, size reduced, and transferred to the next process. Contaminated empty drums can be decontaminated for reuse, melted for metal recovery, or compacted for disposition, depending on the waste content and residual contamination.
2. *Primary treatment*. For thermal systems, primary treatment generally consists of a single process to destroy the organic waste components, and in some cases to vitrify the inorganic components (incinerator, plasma furnace, steam reformer, etc.), although some variations may exist. For non-thermal systems, the primary treatment consists of a treatment train such as a separation process (thermal desorption or washing) to remove organics from inorganic waste matrices and a chemical oxidation process to destroy organic waste.

TABLE 10.1 Mixed Waste Matrices and Contaminants

Aqueous Liquids and Slurries
- Acidic wastewaters and aqueous slurries
- Basic wastewaters and aqueous slurries
- Cyanide wastewaters

Organic Liquids
- Aqueous/halogenated or nonhalogenated organic liquids
- Pure halogenated or nonhalogenated organic liquids
- PCBs

Solid Process Residues
- Inorganic particulates
- Ash
- Sand blasting media
- Absorbed aqueous or organic liquids
- Ion exchange media
- Calcined solids
- Inorganic sludges
- Wastewater treatment sludges
- Plating waste sludges
- Paint waste-liquids/sludges, chips/solids
- RCRA metal salt wastes
- Activated carbon (halogenated or nonhalogenated)
- Organic resins (halogenated or nonhalogenated)
- Organic absorbents (halogenated or nonhalogenated)
- Organic sludges (halogenated or nonhalogenated)
- Organic particulates (halogenated or nonhalogenated)
- Biological materials
- Organic Chemicals (halogenated or nonhalogenated)

Soils
- Organic contaminated soils (halogenated or nonhalogenated)
- RCRA metal contaminated soils
- Soils with debris

Debris Waste
- Metal debris
- Concrete
- Glass
- Ceramic/brick
- Asbestos
- Combustibles (plastic/rubber, wood, paper/cloth/trash)
- Graphite
- Biological
- Composite filters
- Asphalt

Special Waste
- Reactive metals
- Components (contaminated with reactive metals)
- Pyrophoric fines
- Explosives/propellants
- Compressed gases/aerosols

Inherently Hazardous Waste
- Elemental mercury
- Elemental lead
- Beryllium
- Batters – Cd/Pb/Hg
- Batters – Cd/Pb/Hg
- Cadmium metal/alloys

3. *Aqueous waste.* All aqueous waste, including secondary waste generated internally (e.g., from washing or decontamination processes or from off-gas scrubbers, etc.), will require treatment.
4. *Air Pollution Control (APC).* APC systems may be required for various subsystems such as the primary treatment unit, stabilization process, metal melter, or decontamination system. Details and size of the air pollution control system depend on the specific process and contaminants in question. The components of thermal and non-thermal APC systems are similar and perform similar functions. However, because approximately an order of magnitude more non-toxic gases are emitted from thermal systems than from non-thermal systems, more fume, particulates, and contaminants can be carried over with the off-gas from the thermal systems. Thermal systems are also more likely to generate specific hazardous compounds and volatile off-gas constituents (e.g., dioxins/furans, NO_x, Cd, Pb, Hg, etc.). Thus, the off-gas from thermal systems requires more complex treatment and the APC system must be much larger and more effective than that for non-thermal systems to achieve the same level of performance.
5. *Metal recovery.* Melters can be used to produce ingots from ferrous metal wastes that cannot be decontaminated for subsequent recycle or disposal. Metal and lead decontamination can use an abrasive water jet or CO_2 pellets to decontaminate the metals. Mercury can be removed from inorganic wastes with a retort or by a leaching process.

6. *Stabilization.* Several stabilization options are available as indicated in previous portions of this Handbook. Stabilization is generally required to meet Resource Conservation and Recovery Act (RCRA) Land Disposal Restriction (LDR) requirements.
7. *Certification and shipping.* The physical and radiological properties of the packaged waste are certified in accordance with transportation, storage, and disposal requirements. The containers of packaged waste are weighed, examined with an RTR to ensure that the matrix is homogeneous and contains no free liquid, and beta and gamma radioactivity is assayed.
8. *Administration and support.* This includes all technical and administrative functions required to manage the operation of a waste management facility. These functions include security, access control including personnel decontamination, maintenance of uncontaminated areas and equipment, health physics and radiation badges, sanitary facilities, work control and personnel support, public relations communications, emergency response provisions, analytical laboratory, environmental field sampling, environmental regulatory reporting, and records management.

Treatment systems that accept fewer types of waste matrices, contaminants, or wastes with low levels of contamination will naturally require fewer subsystems. However, most treatment systems will require some form of sorting and segregation of the waste to prevent accidents, inadvertent releases or equipment damage. Many waste treatment technologies have limits on feedstream chemical content, physical composition, and particle size. Systems using a rotary kiln or plasma furnace for primary thermal treatment require the least feed preparation. In contrast, fixed-hearth controlled-air incinerators, indirectly fired pyrolizers, and non-thermal systems require a well-sorted feed.

In general, it is undesirable for materials such as bulk lead and mercury to enter a thermal treatment unit because they are particularly hazardous volatile materials that are difficult to collect in the off-gas system. If these materials can be found using RTR performed on containers of intact waste, the containers should be emptied and the prohibited items removed and treated separately. Similarly, if RTR detects other bulk metals (e.g., steel, and aluminum), these metals should also be removed to minimize challenges to the shredder and physical damage to the thermal treatment unit's refractory.

These constraints, coupled with the nature of the waste, dictate at least some degree of feed material sorting and separation and, if there is a limitation on particle size, some level of shredding may be required. The extent to which waste feed must be sorted and shredded to produce an acceptable feedstock has a significant impact on system cost. Manual sorting is labor intensive, and automated sorting requires highly sophisticated and costly instrumentation and involves high programmatic risk.

Trade-offs between manual sorting by direct contact, or using telerobotics and automated sorting, will depend on several factors, including labor costs, costs associated with sufficient personnel on staff to meet daily exposure limits, and the cost of personnel protective equipment. These costs can be compared to the labor costs of operating telerobotic or automated equipment, the reliability of identifying waste items to be sorted, capital cost and maintenance cost of the equipment, and equipment reliability and availability.

Excessive shredding is mechanically demanding and significantly increases maintenance cost. Low-speed shredders have been identified as the best candidates because they can tolerate the widest variation in waste feedstreams, are the least costly, and are least prone to operational problems (Soelberg and Reimann, 1994). However, commercial low-speed shredders reduce waste to 1 to 12 in. in size — too large for many potential MLLW treatment technologies. The reaction rate for most non-thermal processes is surface-area limited; thus, such processes require particle sizes of 0.5 in. or less. The maximum feed size for molten salt oxidation and supercritical water oxidation is approximately 0.125 in. To achieve these small particle sizes requires low-speed shredding followed by high-speed sizing, typically a hammer mill. It has been estimated that separating and shredding combustible waste to a size range of 1 to 12 in. at a rate of 1 ton/hour would cost \$700/ton. Reducing the maximum particle size to 0.125 in. would raise the cost to \$1600/ton with the incremental cost attributable to the hammer mill, its inert gas system, additional separation equipment and maintenance requirements. Reducing the particle size to less than 0.004 in. would increase the pretreatment costs to approximately $2100/ton due to additional screening and recycling of waste through the hammer mill, and higher hammer mill operating and maintenance costs. The processing rate also affects sizing costs; reducing the processing rate by a factor of 10 increases the pretreatment unit costs by a factor of 4 to 5 because most of the equipment is the same so fixed capital costs are spread over less waste.

Other required subsystems include primary treatment to destroy the hazardous organic components in accordance with EPA requirements, and the nonhazardous organics to decrease the volume of waste to be disposed. Under EPA regulations, residues and secondary wastes will require treatment and/or stabilization before disposal if leachability standards are not met. Variations of the stabilization process include vitrification, polymers, and cement or grout. Thus, operations are needed to stabilize the treatment residues, unregulated organics that have not been destroyed, inorganic materials, and radionuclides prior to disposal in a MLLW disposal facility.

In general, systems that require complex mechanical, thermal or chemical processes, or precise control of these processes, are difficult to operate and subject to frequent failures resulting in low operating efficiency, low availability and reliability, and high maintenance. Cost confidence is achieved using proven technologies. Conversely, technologies based on innovative or untested concepts pose a high risk of overruns. Other factors contributing to system economics are availability of construction materials, system size, and the use of commercial equipment. Volume reduction is also a principal cost consideration due to the costs associated with packaging, shipping, and disposing of secondary wastes. However, the cost of achieving significant volume reduction can exceed the savings depending on the complexity of the system and its reliability and availability.

Cost Comparisons

Systems conceptualized in the integrated process analysis project consisted of all facilities, subsystems, equipment, and methods needed to treat and dispose of the MLLW stored in the DOE complex, including waste receiving, characterization, sizing, organic destruction, air pollution control, metal recovery, and secondary waste residue processing for eventual disposal. A generalized configuration is shown in Figure 10.1.

Various technologies were assembled into 30 different conceptual systems: 20 thermal systems (Feizollahi et al., 1994; Feizollahi and Quapp, 1996), 5 non-thermal systems (Biagi et al., 1997), and 5 enhanced non-thermal systems (Biagi, Schwinkendorf, and Teheranian, 1997). The thermal systems used incineration or other thermal processes for organic destruction, and vitrification, grout, or polymer for stabilization. The non-thermal systems used wet oxidation processes operating at less than 350°C, such as acid digestion for organic destruction, and grout, phosphate bonded ceramic, or polymer for stabilization. The enhanced non-thermal systems included non-thermal organic destruction and vitrification for stabilization.

These systems were compared to understand risks, cost and performance (Schwinkendorf, 1996). Material mass balances were prepared using the Aspen Plus© computer code (Aspen Technology, Inc., 1994) to analyze preconceptual system designs. The resulting equipment sizes, the “space footprint,” and associated operating and maintenance staff requirements were estimated to develop the total life-cycle cost (TLCC) that covered everything from current storage through final disposal and release of effluents in accordance with expected regulations. A comparable basis among the various systems was made possible by maintaining the following assumptions throughout all of the studies.

1. The same waste characteristics and distribution of constituents were used for all analyses.
2. A single, centralized government-owned and contractor-operated (GOCO) facility capable of treating all DOE MLLW was assumed.
3. About 70% of the current DOE MLLW inventory, or 236 million pounds (107 million kilograms), of waste was treated over the system lifetime of 20 years.

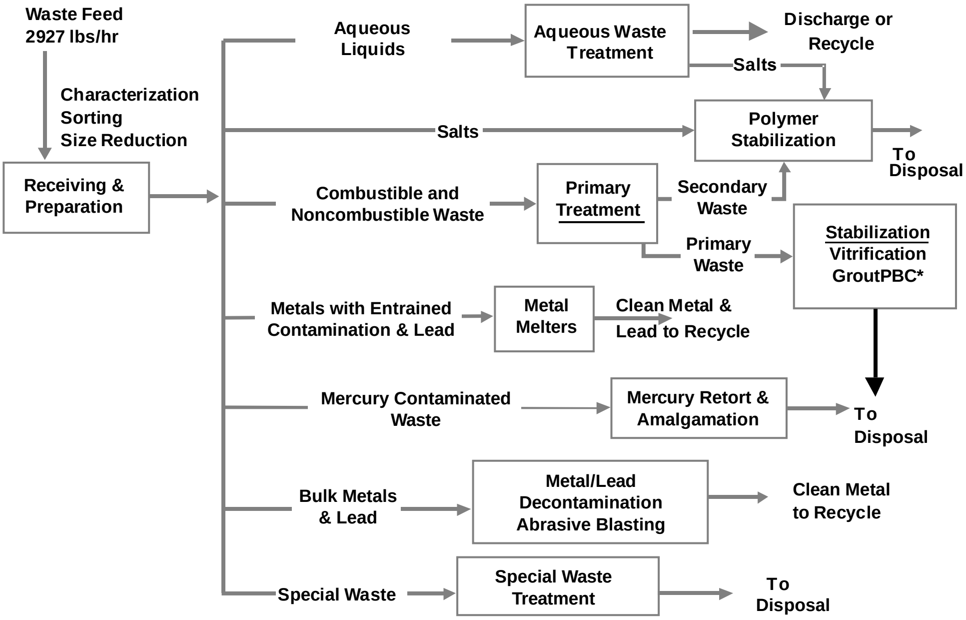

FIGURE 10.1 Generalized MLLW treatment system (*PBC = phosphate bonded ceramic).

4. Waste was treated at a rate of 2930 lb/hr (1330 kg/hr) with 46% online availability (4030 hr/yr of operation out of 8760 hr) due to uncertain equipment life and maintenance requirements with radioactive operations.
5. Because the treatment systems are used for alpha and non-alpha waste, a tertiary containment system was used for all process steps from waste sorting through stabilization.
6. Except where a Joule-heated melter is explicitly identified, all vitrification is performed in a high-temperature plasma furnace that produces a slag.
7. Waste loadings (i.e., mass of treated waste incorporated into the final waste form divided by the mass of the final waste form) of 67 wt% in high-temperature slag, 50 wt% in polyethylene, and 33 wt% in grout were assumed.
8. Disposal was in an RCRA engineered on-site disposal facility meeting land disposal restrictions with a disposal cost of \$240/ft^3 (\$8480/m^3).

One of the primary products of these studies was the total life-cycle cost of these systems. It should be recognized that the actual costs of real systems will depend on the waste to be treated, the processes and technologies used, and the marketplace. However, the cost estimates developed in these studies are appropriate for system comparisons, identification of major cost elements, and identification of potential cost savings.

Differences in the TLCC among systems of thermal technologies are minor. Likewise, only small differences were found among systems using non-thermal technologies. However, the cost of non-thermal systems was about 50% more than thermal systems. This difference appears significant because the studies should be within ±30% owing to the comparative bases used.

TLCC costs were estimated to be approximately \$2.1 billion for a thermal metal melting system vs. \$3.9 billion for a non-thermal acid digestion system. The unit costs for treatment (without disposal) vary between ~\$8/lb (\$17.60/kg) for thermal systems and \$13/lb (\$28.70/kg) for non-thermal systems. Table 10.2 illustrates a typical distribution of subsystem costs for a rotary kiln system with vitrification and a non-thermal process with grout stabilization. Table 10.3 illustrates typical WBS cost components for the same systems.

TABLE 10.2 Subsystem Cost Distribution for Thermal and Non-thermal Systems

Thermal Subsystems		Non-Thermal Subsystems	
Subsystem	% Total Life-Cycle Cost	Subsystem	% Total Life-Cycle Cost
Front-end handling	27	Front-end handling	24
Stabilization	15	Stabilization	12
Primary treatment	7	Primary treatment	17
Disposal	11	Disposal	19
Administration	10	Administration	7
Air pollution control and aqueous waste treatment	11	Air pollution control and aqueous waste treatment	6
Certification and shipping	8	Certification and shipping	11
Metal recovery	10	Metal recovery	3
Special waste	1	Special waste	1

TABLE 10.3 Distribution of Cost Components for Thermal and Non-Thermal Systems

Thermal Cost Components		Non-Thermal Cost Components	
Cost Component	% Total Life-Cycle Cost	Cost Component	% Total Life-Cycle Cost
Operating and maintenance	56	Operating and maintenance	53
Capital (facility and equipment)	23	Capital (facility and equipment)	17
Disposal	11	Disposal	19
Pre-operational	4	Pre-operational	4
Test and demonstration	4	Test and demonstration	5
Decontamination and decommissioning	2	Decontamination and decommissioning	2

The non-thermal system costs are more than thermal systems because the operations and maintenance (O&M) costs are estimated to be 50% higher due to more waste sorting and preparation, and more unit operations requiring more personnel, equipment, and facilities. This is because non-thermal systems are limited to the types of waste and waste matrices that can be treated, require greater size reduction, and generate more secondary waste than thermal systems. Non-thermal systems, using grout for stabilization vs. vitrification used with thermal systems, produced more final waste form volume with the associated higher certification, packaging, and shipping cost and higher disposal costs.

Non-thermal waste treatment technologies (e.g., alternative oxidation technologies such as acid digestion) are also immature technologies that have not been fully demonstrated and implemented in a variety of waste treatment applications. In contrast, incineration is a mature and proven technology that has generally been the primary choice of industry for destroying hazardous waste. The technical risks are low and the costs are well established. However, public opposition to incineration is well established and growing.

Thus, there may be niche applications or site-specific applications where non-thermal technologies could be used economically or are necessary for treatment. Such applications might include difficult-to-treat wastes, orphan wastes that exist in small quantities and that cannot be transported to a centralized facility, or wastes that cannot be treated by incineration either due to safety or permitting issues or public opposition.

O&M costs are the highest percentage (50 to 60%) of TLCC, followed by capital cost (23% of TLCC, most of which is facility cost), and then by disposal costs for systems that vitrify waste (11% of TLCC). Systems that use a non-thermal waste form (e.g., grout) have a significantly higher disposal cost — approximately 20% of the TLCC. Because costs are only modestly affected by the choice of treatment technologies or equipment (i.e., equipment purchase costs less than 5% of TLCC), reliability, performance, and safety are the most important considerations in selecting equipment for treatment of MLLW. It is these equipment characteristics that will affect operating and maintenance costs.

In all cases, energy costs are less than 1%of the treatment costs (i.e., TLCC without disposal costs). The hourly costs ranged from $80 to $200, with thermal treatment systems using electrical energy (metal melting and plasma systems) having the highest energy costs. Transportation costs were also found to be only 1% or less of the TLCC.

Sensitivity Analysis

Sensitivity studies were performed to determine the effects of varying the assumptions used in comparing treatment system costs. The sensitivity of system life-cycle costs was determined relative to changes in subsystem costs and WBS component cost, facility capacity, operating life, stabilization options and system availability.

Effects of Changes in WBS Component Costs

For all systems, the most cost-sensitive component is O&M. Because this is a major cost contributor to TLCC, a decrease in cost in these areas can have a significant impact on total system cost. When annual operating, utility, material, and maintenance costs are reduced by 50%, the treatment costs (costs without disposal) decrease by an average of 32% and total life-cycle costs (costs with disposal) decrease by 27%. This may amount to as much as $680 million over 20 years for a rotary kiln system with vitrification treating DOE's legacy MLLW.

The second most cost-sensitive component is capital costs; a 50% decrease will result in a 12% decrease in treatment costs and a 10% decrease in total life-cycle cost. In this analysis, all dependent costs were changed; for example, design, inspection, and management costs are a percentage of building and equipment purchase costs. If these costs change, the dependent costs increase or decrease by the same percentage. As seen later, equipment reliability and system availability have a significant impact on TLCC as well as the choice of stabilization technology. Thus, an increase in equipment cost due to the purchase of higher reliability equipment should only have a marginal effect on dependent costs but significantly decrease O&M and total life-cycle costs.

Effects of Changes in Subsystem Costs

Front-end handling is the highest cost subsystem; thus, a decrease in cost in this area can also have a significant impact on total system cost. This subsystem has cranes and forklifts to unload waste containers from incoming vehicles, and various instruments to characterize the physical state of the contained waste. Computer software and barcode scanning record and track the waste. Containers not requiring sorting are moved directly to the appropriate treatment subsystem. If sorting is required, the container is opened and emptied onto a sorting table where the waste is segregated into treatment types. If required, the waste is size reduced.

Opportunity exists for reducing front-end handling costs by reducing labor costs, the major O&M cost driver. For example, the integrated process analysis studies defined labor requirements for the receiving and inspection process to be three 28-person shifts per day to process approximately 150 55-gal drums of waste per day. In this case, each person processes 1.8 drums per day at 4.4 hr per drum. If improved technology allowed each person to process 5.4 drums per day at 1.5 hours per drum, then only one 28-person shift or three 7-person shifts would be required, for a savings of $235 million over 20 years (Harvego and Schafer, 1997). This indicates that time and motion studies on labor-intensive subsystems to identify rate-limiting steps can be an important tool to identify areas for process improvements and cost savings.

Operating Efficiency

Significant cost savings are possible by increasing the operating efficiency or system availability. However, management's ability to affect significant life-cycle cost savings with relatively small investments in capital or other resources diminishes exponentially as the project evolves beyond the conceptual design phase and into development, construction, and operation. Typically, 40 to 70% of the life-cycle cost of high-technology systems have been locked in by the end of the conceptual design phase (Michaels and Wood, 1989) whereas only 3% of the project funds have been spent. As indicated in Figure 10.2, there is an optimal period when timely management action can provide significant savings.

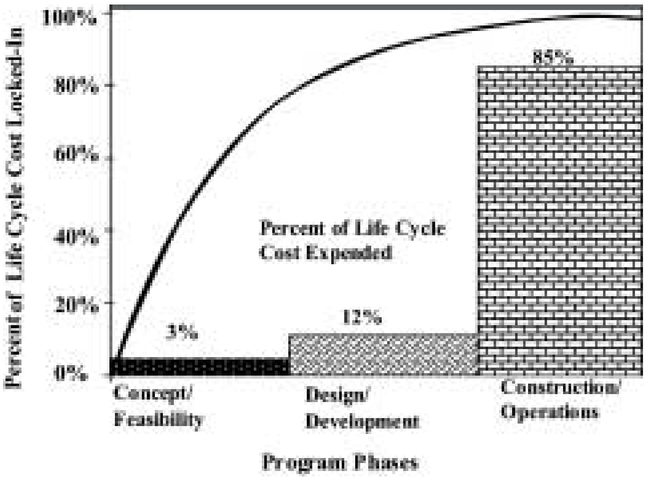

FIGURE 10.2 Percent of total life-cycle costs vs. locked-in costs. (Adapted from Arsenault and Roberts, *Reliability and Maintainability of Electronic Systems*, Computer Science Press, Potomac, MD, 1980.)

The optimum reliability (or mean time between failure) is indicated by the minimum in the curve for acquisition cost plus operational cost, as shown in Figure 10.3. (Lamb, 1995). Improving reliability — and therefore system availability — reduces the time required to treat a given quantity of waste as well as maintenance and operational costs. However, acquisition costs must generally increase to achieve higher reliability. Thus, the objective is to find the optimum balance between investing in improved reliability during system conceptual design and development and reducing operations and maintenance costs so that life-cycle cost is minimized.

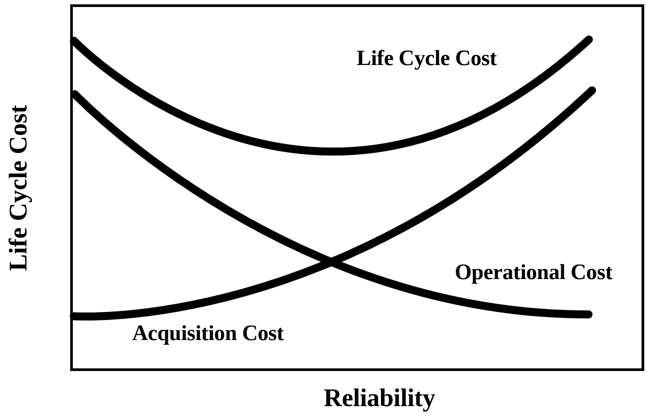

FIGURE 10.3 Reliability optimization to minimize life-cycle cost.

Operational availability is defined as the fraction of time that the plant or its subsystems are physically able to perform their intended function as defined in Equation (10.1). It is the mean time between maintenance (MTBM) divided by the sum of the MTBM and the mean maintenance downtime (MMDT). MTBM includes the mean time between failure, which is a measure of system reliability (or the probability of successful operation for a specified time interval), and the time between planned or preventive maintenance. MMDT is also a probability distribution, providing a measure of the time required for a failed or shutdown subsystem or piece of equipment to be restored to service.

$$A = \frac{MTBM}{MTBM + MMDT} \tag{10.1}$$

Thus, availability is characterized as a probability distribution associated with the plant operating conditions. The plant does not need to be shut down to experience reduced availability. For example, a failure might result in a reduced production level in which availability at the desired production level is lost although the plant continues to produce. Thus, additional costs are incurred due to lost productivity and increased time required to process a given quantity of waste.

Alternatively, when a plant has two pieces of equipment with one as a spare, when one fails the other is placed into service. Although the plant's real production level is not reduced, the probability of maintaining that production level is significantly reduced during the time that the first item is being repaired and until the first item becomes available for service. Other than the presence of the failed item, the reduction in availability is not visible in plant performance. However, the expectation of meeting plant production levels is now lower (Lamb, 1995).

Various methods exist for improving system availability including increased component and system reliability through improved design or redundancy, or decreased maintenance time — all of which have an associated cost. Thus, it is important to understand the costs incurred vs. the cost savings realized by improving the system availability. Reliability, availability, and maintainability (RAM) analysis early in the design phase can significantly increase the probability of success of any waste treatment system and/or innovative technology, and provide significant cost savings over the lifetime of a treatment system through increased availability.

Using the systems analyzed in the integrated process analysis project, the effect of improved system availability is shown in Figure 10.4 (Schwinkendorf and Cooley, 1998). In this case, treatment costs are compared for rotary kiln systems that differ only in the type of final waste form produced: vitrified waste, grouted waste, or waste stabilized in phosphate bonded ceramic (PBC). For equal availability, there is little difference in the treatment costs for these systems. The major cost differences would be in disposal costs due to differences in final waste-form volume. However, there is a significant decrease in cost for all processes as system availability is increased.

The results of improving system availability for a rotary kiln system from 46 to 67% are also seen in Figure 10.5 (Cooley, Schwinkendorf, and Bechtold, 1997). Increasing the availability increases the operating hours of the plant from 4032 to 5850 hr/yr with a decrease in total years of operation from 20 to 14. Increasing the availability produces savings of $380 million for a rotary kiln with vitrification and $415 million for a rotary kiln with grout. Thus, designs should be developed for maximum improved equipment reliability. However, the estimated operating efficiency and the cost of increased reliability must be determined from actual operating experience, detailed component RAM analysis, or extrapolation from similar systems.

As mentioned previously and discussed in detail later, as long as the operating efficiency is comparable among technology systems, there are significant incentives for vitrification. This is due to typically high waste loading, high density, and the resultant significant waste volume reduction associated with the slag waste form. However, referring to Figures 10.4 and 10.5, if the operating efficiency of a system using vitrification is less than a system producing grout, the cost advantages of vitrification can be decreased significantly.

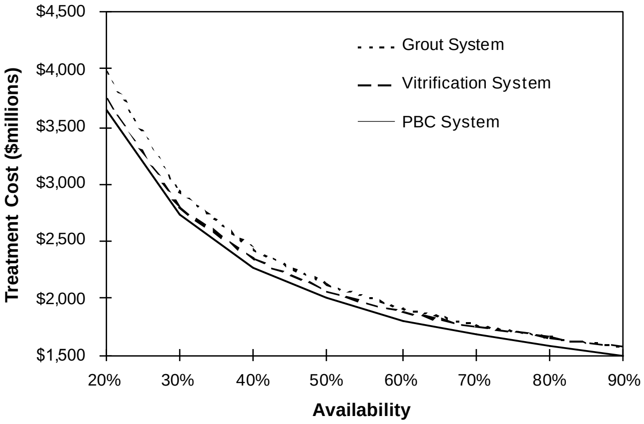

FIGURE 10.4 Treatment cost as a function of system availability source. (From Schwinkendorf, W.E. and Cooley, C.R. 1998. Costs of mixed low-level waste stabilization options. Waste Management '98 Conference Proceedings. WM Symposia, Inc., Tucson, AZ.

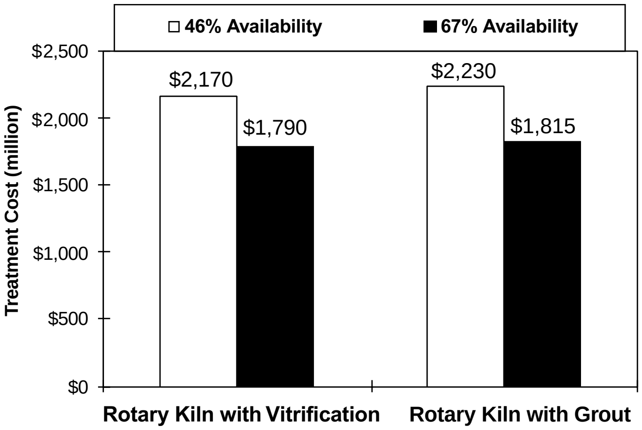

FIGURE 10.5 System availability is an important factor in system cost. (Reprinted from *The Journal of the Franklin Institute*, 334A(2-6), C.R. Cooley, W.E. Schwinkendorf, and T.E. Bechtold, Integrated process analysis of treatment systems for mixed low level waste, 303-325, Copyright 1997. (With permission from Elsevier Science.)

The effects of differences in system availability on TLCC are shown in Figure 10.6. At equal availability of 46%, the treatment cost of a rotary kiln system with grout is about $60 million greater than the treatment cost of a rotary kiln system with vitrification, primarily due to the higher final volume of grouted waste and the associated cost of certifying and shipping this waste for disposal. The treatment cost is shown on the ordinate at zero disposal cost. The TLCC of the two systems diverges with increased unit disposal cost. However, if the grout system availability is greater than the availability of the vitrification system, the relationship between TLCC changes.

If the grout system availability is increased from 46 to 60%, the treatment cost decreases from $2.2 billion to $1.9 billion, as shown by the intercept for zero unit disposal cost in Figure 10.6. The TLCC for the grout system (with 60% availability) remains less than that for the vitrification system (with a 46% availability) until the unit disposal costs reach $6700/m^3 ($190/ft^3), at which point the economic advantage of volume reduction become greater than the advantage of greater availability. If the grout system availability can be increased to 70%, it retains an economic advantage over a vitrification system with 46% availability until the disposal cost reaches $10,600/m^3. This illustrates the importance of process

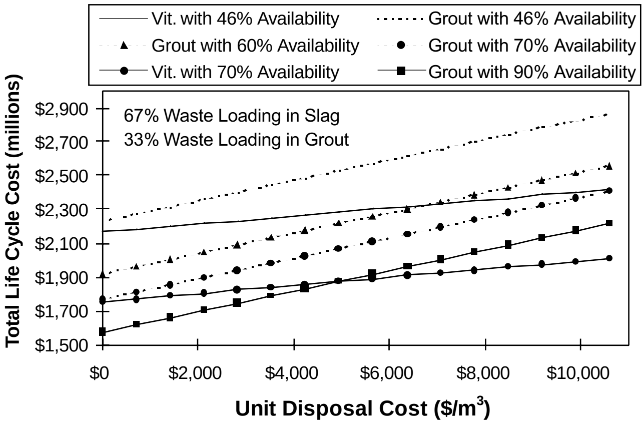

FIGURE 10.6 Improved operating availability decreases treatment cost and total life-cycle cost.

reliability and system availability (Cooley, Schwinkendorf, and Bechtold, 1997). Thus, the objective of any system design should be to achieve the optimum operating efficiency as illustrated in Figure 10.3.

Facility Capacity and Treatment Schedule

The effect on cost of treating the 236 million pounds of DOE MLLW in 10 years rather than 20 years was evaluated using scaling factors to estimate the costs of a facility with twice the capacity. The system availability was assumed to be the same in both cases and only throughput or system capacity is increased. The effect on cost as a result of increasing capacity depends on the scaling factor used in the exponential scaling relation in Equation (10.2), where C_1 is the cost of a treatment facility of capacity q_1; and the cost of a similar treatment facility of capacity q_2 is given by C_2, where n is the scaling factor (Perry and Green, 1984). A scaling factor between 0.6 and 0.7 is typically used in industry for a processing plant.

$$C_2 = C_1\left(\frac{q_1}{q_2}\right)^n \tag{10.2}$$

The results of this scaling of capacity are shown in Figure 10.7 for a rotary kiln system with vitrification using a scaling factor of 0.6 (Cooley et al., 1997). In this case, costs were scaled uniformly. However, it may be appropriate to vary the scaling factor for each individual cost component. For example, although partially dependent on the size of the equipment, the operating and maintenance costs likely do not scale to the same magnitude as the equipment costs. Further, the calculated treatment cost is a significant function of the scaling factor, which must be chosen carefully for less developed technologies and equipment used in mixed waste treatment.

For the example in Figure 10.7, where the system capacity is doubled, increased equipment costs offset decreased operating costs; thus, there was little difference in treatment cost for the same operating time per year for this scaling factor. In this case, a scaling factor of 0.58 is the break-even point where the treatment cost for operating for 10 years is the same as the baseline system operating for 20 years. If costs were scaled using a factor less than 0.58, then the 10-year treatment cost would be less than the baseline system treatment cost operating for 20 years (Harvego and Schafer, 1997). Although the shorter processing time does not affect treatment cost significantly, it appears attractive to minimize storage costs, either prior to or during treatment. This assumes that the logistical and transportation problems are manageable over this shorter operating period.

A cost for storage is incurred until the stored waste is completely treated, as shown in Figure 10.7. Treatment of 236 million pounds of waste in 20 years incurs a treatment cost of $2167 million and a cost of $216 million to store the waste as it is being treated, assuming a storage cost of $207/m³/yr

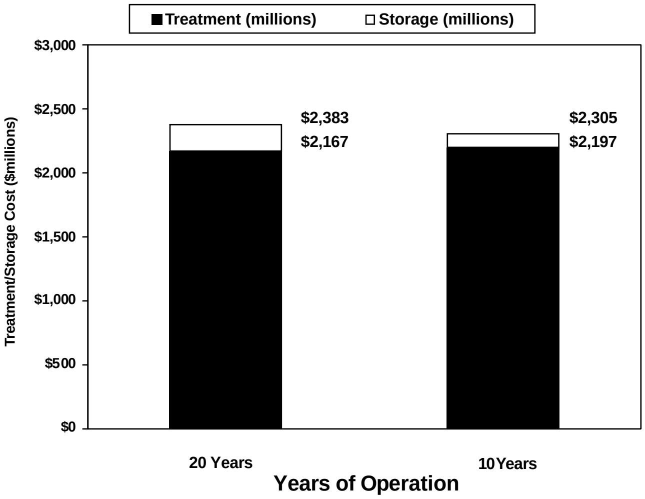

FIGURE 10.7 Cost of waste treatment and storage during treatment. (Reprinted from Cooley, C.R., Schwinkendorf, W.E., and Bechtold, T.E. 1997. Integrated Process Analysis of Treatment Systems for Mixed Low Level Waste. *The Journal of the Franklin Institute.* 334A(2-6):303-325. (With permission from Elsevier Science.)

(Shropshire et al., 1995). Decreasing the time required for treatment to 10 years increases the cost of treatment slightly to $2197 million, but the storage cost decreases to $108 million. Thus, treatment of waste in 10 years as opposed to 20 years could save approximately $78 million. However, shortening the schedule may have significant repercussions on the supporting infrastructure that must be considered.

This shortened operating period required to treat the baseline stored waste allows scheduling of the facility to process additional future waste through the same facility. Additional wastes arise from processes that generate new waste, including clean-up operations such as site remediation and the decontamination and dismantling of facilities. Doubling the capacity and operating for 20 years to treat twice the total waste (e.g., 472 million pounds) increases the treatment cost but decreases the unit cost from the baseline of $9.18/lb ($20.24/kg) to $6.85/lb ($15.10/kg).

Scaling of capacity can also be used to evaluate the effect of multiple facilities to treat the same quantity of waste. In the integrated process analysis project, a single facility was assumed. As illustrated in Table 10.4, constructing and operating two facilities to treat 236 million pounds of waste over 20 years results in a 38% increase in treatment cost. Five regional facilities incur a 113% increase in treatment cost (Harvego and Schafer, 1997).

Although transportation costs will be less for shipping waste to multiple facilities, the transportation of waste to a single large facility is small — less than 1% of the baseline life-cycle cost. Thus, transportation cost provides little incentive for selecting one versus multiple facilities. However, non-economic factors such as the ability to transport across state boundaries may favor multiple facility locations.

Effect of Present Value Analysis

Up to this point, the discussion has been based on a summation of costs over the life of a treatment facility. The time value of money is taken into account by calculating the present value of costs in order to compensate for differing cash outlays or expenses at different times during the system life time. That is, the value of a given sum of money depends on when it is received or expended. The economic worth, or purchasing power, of money changes over time, with the preference being to receive dollars today rather than some time in the future or, conversely, to spend the dollars later rather than earlier. This preference is due to the cost of forgoing the opportunity to earn interest, or a return, on investments if funds are spent today rather than later.

TABLE 10.4 Waste Distribution and Total Treatment Costs for Multiple Facilities (0.5 scaling factor)

System	Capacity (%)	Capacity (million pounds)	Total Treatment Cost ($Millions)	Unit Treatment Costs ($/lb)
Baseline	100	236	$2167	$9.18
		Two Regional Facilities		
Eastern Facility	66	156	$1781	$11.42
Western Facility	34	80	$1208	$15.10
Total Cost			$2989	$12.66[a]
		Five Regional Facilities		
Oak Ridge	60	141	$1703	$12.00
INEEL	20	47	$1028	$21.80
Rocky Flats	10	24	$758	$32.10
Hanford	5	12	$568	$47.30
Savannah River	5	12	$568	$47.30
Total Cost			$4625	$19.60[a]

[a] Weighted average unit cost

The result of performing a present value analysis on the systems analyzed in the integrated process analysis project is that the present value of the cost for completing the earlier phases of the treatment is a greater percentage of the TLCC, whereas the present value of the costs for completing the later phases is a smaller percentage of the TLCC. When compared to simply adding the life-cycle costs over time, the present value comparison shows that construction costs increase as a percentage of TLCC, whereas the operating costs decrease as a percentage of TLCC (Harvego and Schafer, 1997).

Although present value analysis demonstrates that cash outlays in the later phases of the life-cycle of a treatment system are more economically favorable than cash outlays in the earlier phases, it does not change any previous conclusions regarding relative costs or trends between projects assuming the timing of expenses is similar.

The time value of money is also important in evaluating the cost benefit of early completion of a treatment project; for example, doubling the capacity and treating a given quantity of waste in 10 years versus 20 years, or increasing capital expenditures to increase system availability and decrease the time required for treatment. For a GOCO facility, there is no direct revenue to counterbalance the costs of construction and operation. Thus, the preference, from a present value perspective, may be to postpone the expenditure as long as possible to maintain the earning power of the dollars. However, storage costs being incurred immediately may tip the scales in the other direction, indicating a present value benefit to early treatment. Penalties for non-compliance with regulations or agreements with federal or state regulators may also impact the present value cost/benefit evaluation.

Effect of Stabilization Processes and Final Waste Form Volume

Assuming equal system availability, the use of a high-temperature vitrifier rather than grout stabilization can provide significant savings in disposal costs and certification and shipping costs. Disposal costs constitute about 20% of the TLCC for non-thermal waste forms and about 11% for thermal waste forms. A volume reduction factor (input volume divided by output volume) of 3.4 was generally predicted for all of the waste being treated and stabilized in a high-temperature vitrified waste form (slag) with an assumed waste loading of 67 wt%. However, the volume reduction for the rotary kiln with grout was zero to 1.5, assuming a 33 wt% waste loading. The effect of final waste form volume on disposal cost and the cost of handling the final waste form through certification and shipping are shown in Table 10.5 (Cooley et al., 1997).

TABLE 10.5 Waste Form Volume Affects Disposal and Certification & Shipping Costs

System	Total Disposal Volume[a]	Disposal Cost ($Million) @ $243/ft^3 ($8590/m^3)	Certification & Shipping Cost ($Million)	Disposal + Certification & Shipping Cost ($Million)
Rotary kiln with Vitrification; volume reduction = 3.4	1,096,700 ft^3 (31,040 m^3)	270	210	480
Rotary kiln with Grout; volume reduction = 1.5	2,507,900 ft^3 (70,970 m^3)	610	370	980

[a] Disposal volume of stabilized waste includes the volume of special waste and polymer stabilized waste, which are approximately the same for these two systems. Slag waste loading is assumed to be 67 wt% and grout waste loading is assumed to be 33 wt%.

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The difference between the total disposal cost of grout and high-temperature vitrified waste as a function of the unit disposal cost is shown in Figure 10.8. A significant cost saving of $330 million is achieved using vitrification rather than grout if the disposal cost is $240/ft^3 ($8480/m^3) and all other operating parameters are kept the same. These savings assume a centralized facility treating 236 millions pounds of waste and equal system availability (46%).

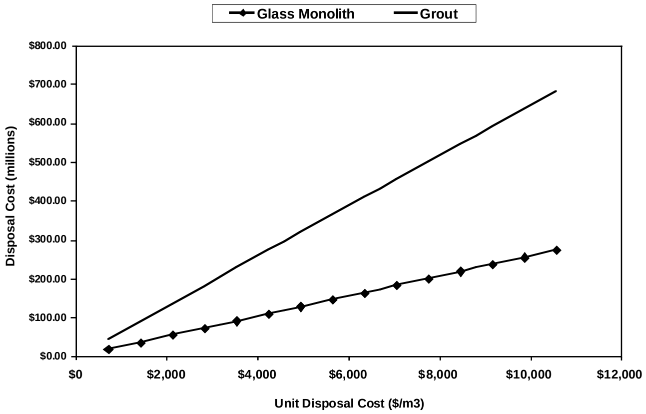

FIGURE 10.8 Vitrification can save disposal costs over grout stabilization for the same system availability. (Assumes a total of 236 million lbs treated with a grout waste loading of 33 wt% and a slag waste loading of 67 wt%.)

Use of contaminated soil as an additive to achieve vitrification can also provide a significant savings (up to $120M in the integrated process analysis project) by avoiding the cost of separate soil treatment, assuming that soil treatment costs $350/ton ($386/tonne) (DuTeaux, 1996). The use of soil also provides a greater net waste loading and displaces additives thereby reducing the overall waste volume. The use of contaminated soil as a glass former will likely require high-temperature melters (e.g., plasma or electric arc furnaces) and would preclude the use of Joule-heated melters. However, high-temperature melters are expected to have more volatile metals released from the melt, a higher volume of secondary waste from the off-gas system associated with metal capture, and an increased uncertainty in the life of refractory liners.

As shown in Figure 10.9, volume reduction can be achieved through increased waste loading in a final waste form, or by stabilizing waste in a high-density waste form. This illustrates a variety of waste forms available for stabilization of treated waste, including:

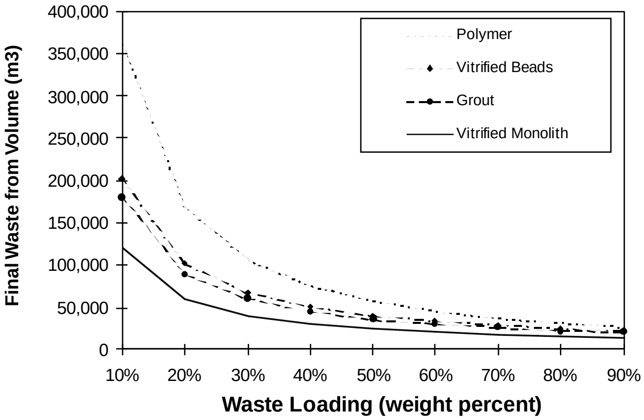

FIGURE 10.9 Disposal volume for various waste forms.

- Slag monoliths produced by high-temperature vitrification, with a density of about 188 lb/ft^3 and an estimated waste loading between 50 and 70%.
- Glass monoliths produced by low-temperature vitrification, with a density of about 188 lb/ft^3 and an estimated waste loading between 30 and 50%.
- Slag or glass marbles with 60% packing fraction and an overall *effective* density of about 113 lb/ft^3. Production of marbles limits the filling of the final volume of a container to about 60% of the total available volume of the container (Cumberland and Crawford, 1987) thereby increasing the total disposal volume from that of a vitrified monolith.
- Phosphate bonded ceramic produced by equipment similar to that used for cement mixing, with a density of about 127 lb/ft^3, and an estimated waste loading of 50 to 70%.
- Grout produced by equipment similar to that used for cement mixing, with a density of about 127 lb/ft^3, and an estimated waste loading of 30 to 40%.

For vitrified waste, thick-walled steel containers may be required if the casting process involves pouring molten glass directly into the waste container. It is assumed that these containers can be qualified to meet Department of Transportation (DOT) and TRUPACT II criteria or equivalent. However, if these containers are degraded by the molten glass such that DOT requirements are not met, then an overpack will be required at least for shipment and possibly disposal. If this is the case, then the packing fraction will be approximately 60% and the disposal volume of a vitrified monolith will be the same as vitrified marbles.

Achievable waste loading depends on the contaminant in the waste, the ability to pass the EPA's toxicity characteristic leaching procedure (TLCP) test, the disposal facilities waste acceptance criteria (WAC), or the radionuclide content. Disposal cost is then determined by the volume of the final waste form and the unit disposal cost (cost per unit volume of waste). Disposal costs for several waste forms, waste loadings and unit disposal costs are shown in Table 10.6 (Cooley et al., 1997), along with the cost associated with waste handling for certification and shipping. As expected, waste form loading and volume reduction also affect costs for certification and shipping of the final waste form. Decreasing the volume of the final waste form will decrease the amount of waste that requires handling, certification, and shipping at the end of the treatment process.

This indicates that low-temperature vitrification that produces a glass waste form is expected to have a higher disposal volume than high-temperature slag, and possibly higher than phosphate bonded ceramic. This would be especially true if the waste form were produced in the form of glass marbles or beads. Thus, for the specified waste loadings in Table 10.6, the lowest disposal cost waste form is the slag monolith followed by phosphate bonded ceramic, and the highest disposal cost waste form is glass beads. However, potential volume reduction is not the only factor to consider in determining cost-effectiveness.

TABLE 10.6 Disposal Cost of Various Waste Forms for 236 Million Pounds of Original Waste

				Unit Disposal Cost		
Waste Form	Waste Loading	Waste Form Volume	Certification & Shipping Cost ($millions)	$\$20/\text{ft}^3$ ($\$707/\text{m}^3$)	$\$100/\text{ft}^3$ ($3534/\text{m}^3$)	$\$240/\text{ft}^3$ ($\$8480/\text{m}^3$)
				Total Disposal Cost ($millions)		
High-temperature slag monolith	67%	640,000 ft^3 (18,100 m^3)	$169	$12.80	$64.00	$153.60
Slag beads	67%	1,067,000 ft^3 (30,200 m^3)	$202	$21.30	$106.70	$256.00
Phosphate bonded ceramic	67%	948,000 ft^3 (26,800 m^3)	$192	$19.00	$94.80	$227.50
Low-temperature glass monolith	33%	1,299,000 ft^3 (36,800 m^3)	$223	$26.00	$130.00	$311.90
Glass beads	33%	2,166,000 ft^3 (61,300 m^3)	$322	$43.30	$216.60	$519.80
Grou	33%	1,924,000 ft^3 (54,400 m^3)	$290	$38.50	$192.40	$461.90

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Effects of Radionuclide Concentration

Changes in pricing for shipping and disposal may be such that the cost of shipping and disposal is based not only on volume, but also on curie or hazardous material content or concentration because a particular site may be limited in the amount or concentration of radionuclides or hazardous material it can accept. Limitations may be imposed by regulators or safety professionals to limit the radiation at the surface of the waste container for worker protection, or may be recognized through performance assessments that predict the effects of migration from the disposal site. Thus, there may be step changes in the shipping and disposal costs as the radionuclide content changes from Category A through Category C low level waste, to alpha-contaminated waste, to transuranic waste, or the waste concentration causes the contact radiation level to exceed 200 millirem/hour.

If volume reduction causes the contaminant concentration in the final waste form to increase beyond the waste acceptance criteria for a disposal site, disposal may be more difficult and costly although the waste volume has been decreased (Cooley, et al., 1997). Thus, the relationship between volume reduction, contaminant concentration, waste loading, and disposal cost needs to be determined on a case-by-case basis.

Using radionuclide concentration as an example, for an initial radionuclide concentration in the waste of 350 Ci/m^3, a 50% volume reduction during treatment leaves 700 Ci/m^3 in the residue prior to stabilization. Assuming a residue density of 1280 kg/m^3 (80 lb/ft^3), the concentration in the final waste form increases linearly with waste loading as shown in Figure 10.10. For vitrified waste, the initial residue concentration occurs at a waste loading of about 40 to 50wt%, whereas for grout or phosphate bonded ceramic the initial residue concentration is reached at a waste loading of 60 to 70wt%. Thus, a higher waste loading can be achieved in a grout or phosphate bonded ceramic before some critical concentration is reached that may cause an increase in disposal cost.

The effect on waste disposal cost by consolidating radionuclides can be seen in Figure 10.11 where the unit disposal cost is assumed to increase by an order-of-magnitude [from $\$20/\text{ft}^3$ ($\$707/\text{m}^3$) to $\$200/\text{ft}^3$ ($\$7070/\text{m}^3$)] when the radionuclide concentration increases above 700 Ci/m^3. Although high waste loadings and high-density materials decrease the volume of waste to be disposed (see Figure 10.9), for this example (where the initial waste volume was assumed to be 10,000 m^3), the disposal cost for high-temperature slag (with a waste loading between 42 and 62 wt%) is significantly higher than the disposal cost for grout or a cementitous type waste that can accept a high waste loading (e.g., phosphate bonded ceramic).

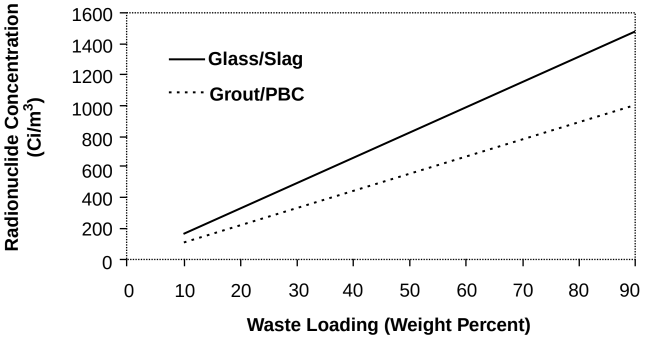

FIGURE 10.10 Radionuclide Concentration in the Final Waste Form Increases with Waste Loading and Volume Reduction. Assumed initial waste loading of 350 Ci/m^3 with a 50% volume reduction leaving 700 Ci/m^3 in the residue prior to stabilization. Assumed residue density = 1280 kg/m^3 (80 lbs/ft^3).

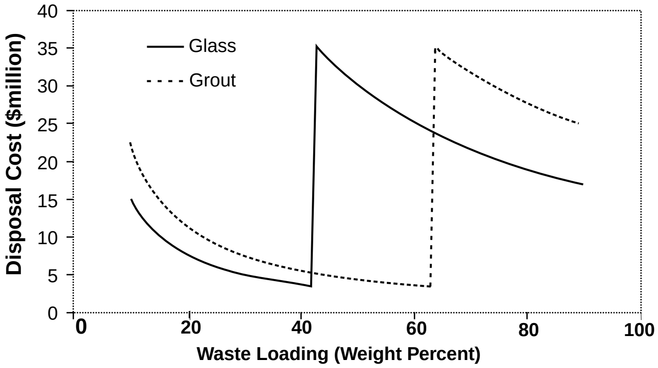

FIGURE 10.11 Disposal Cost Varies as a Function of Radionuclide Concentration in the Final Waste Form. Unit disposal costs are assumed to be \$20/ft^3 (\$707/m^3) for radionuclide concentrations less than 700 Ci/m^3, and \$200/ft^3 (\$7070/m^3) for concentrations greater than 700 Ci/m^3.

Waste Container Size

The size of the container used for collection, transportation and disposal of MLLW can impact the post-treatment cost of certification and shipping. Increasing the size of the container from a 55-gal drum to a 6 × 4 × 4 (1.8 × 1.2 × 1.2 m) box will decrease the certification and shipping cost by about 90% due to the decrease in the number of containers handled and associated decrease in labor. This assumes that equipment costs for handling the larger boxes are the same as the costs for handling 55-gal drums throughout the certification and shipping area, and the assay equipment (RTR, gamma and PAN) can be designed to inspect the larger boxes at the same costs per container.

In the integrated process analyses, transportation costs alone were generally less than 1% of TLCC, or \$24 million, and the cost of transporting 55-gal drums should be about the same as transporting the larger containers because the total volume and mass will be about the same. However, in addition to the potential for decreased certification and shipping labor costs, several other potential advantages of large containers include: capability to dispose large bulky waste in a large container and surround the waste with other stable, solidified waste such as grout; the capability to include compacted empty drums for disposal; economy in the number of post-treatment final characterizations required; and potential economy in shipment and disposal operations due to the smaller number of containers that require handling. Standardization of waste containers for all types of waste could provide significant cost savings by decreasing the type and quantity of handling equipment and operations required.

Container Disposal vs. Decontamination and Reuse

The integrated process analyses indicates that 25,200 55-gal drums per year containing 11.8 million pounds of waste are delivered to a centralized treatment facility. Of these drums, it was assumed that 50% are undamaged and can be decontaminated for recycle or reuse at a cost of up to $72/drum or the equivalent of $1.20/lb ($2.65/kg) of surface-contaminated metal (Kluk et al., 1996). The remaining drums are assumed degraded to the point that they must be disposed or melted into ingots. Several options can be considered for the 12,600 drums that are reusable. They can be decontaminated for reuse at an annual cost of $900,000, or compacted and disposed. Assuming a 90% volume reduction of compacted drums, and an 80% fill factor of compacted drums in 6 × 4 × 4 ft boxes, then 1086 large boxes will be required to dispose of 12,600 compacted drums. The final package and disposal costs, including the cost of the large boxes at $700/box, the cost of certification and shipping, and the cost of compaction, are shown in Figure 10.12 as a function of unit disposal cost. This indicates that the disposal cost is greater than the decontamination cost and that compaction costs have a negligible effect on treating and disposing of drums.

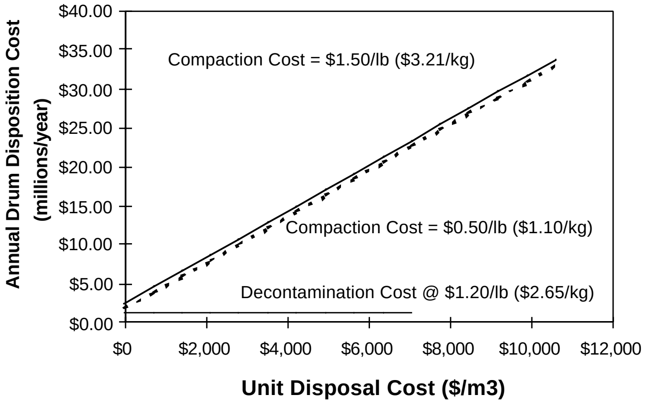

FIGURE 10.12 Cost of compacting and disposing of drums. Total cost of drum disposal includes compaction, certification & shipping, and disposal in a 6 × 4 × 4 ft Type A box. No decontamination is required. From Cooley, C.R.: Schwinkendorf, W.E.; and Bechtold, T.E. 1997. Integrated Process Analysis of Treatment Systems for Mixed Low Level Waste. *The Journal of the Franklin Institute*. 334A(2-6):303-325. (With permission from Elsevier Science.)

Summary

This section has illustrated the relationships between costs, schedules, risks, performance, and reliability of mixed waste treatment systems. Several conclusions can be drawn from the studies referenced in this section:

1. Operations and maintenance (O&M) is the major cost element associated with a system designed to treat MLLW.
2. Capital costs are the second highest cost element. However, the purchase cost of equipment is small relative to facility and dependent costs. The cost associated with purchasing equipment with high reliability and ease of maintenance is small relative to the savings achieved through lower O&M costs.
3. The highest cost subsystem is front-end handling, which is associated with waste characterization, sorting, segregating, and size reduction.
4. The life-cycle cost of non-thermal treatment systems is generally greater than that for thermal treatment systems, even when a low-volume final waste form (e.g., vitrification or phosphate-bonded ceramic) is used. This is due to the immaturity of such processes, and the need for extensive

waste sorting and size reduction. However, there are some waste streams that are difficult to treat thermally (e.g., wastes with mercury or plutonium contamination); and there is increasing difficulty in permitting thermal processes, making, non-thermal processes attractive in certain situations.

5. Reliability, performance, and safety are the most important considerations in selecting equipment for treatment of MLLW. These are also factors that have a major influence on system cost. Depending on unit disposal cost, poor system availability can overcome the cost benefits associated with low disposal volumes. System designs should optimize efficiency and availability, usually through redundancy, readily available spare parts, or improved equipment reliability.
6. High-temperature vitrification can provide significant savings in certification and shipping costs and disposal costs relative to grout due to the lower volume of the final waste form.
7. Disposal costs are affected by a variety of factors, including final waste form volume, final waste form type and performance, packaging and transport limitations, waste acceptance criteria, and radionuclide concentration.

Defining Terms

Alpha-MLLW: Mixed low-level waste containing greater than 10 nanocuries per gram (nCi/g) but less than 100 nCi/g of alpha-emitting radionuclides.

Availability: As used in this section, the term “availability” refers to operational availability, which is the probability that a system or equipment, when used under specified conditions in an operational environment, will operate in a satisfactory manner when called upon.

Leachability standards: Concentration-based extraction test performed in accordance with the EPA’s toxic characteristic leaching procedure (TCLP).

Level A protective equipment: Fully encapsulating chemical protective suit: positive-pressure, full facepiece, self-contained breathing apparatus; inner and outer chemical resistant gloves; chemical resistant boots with steel toe and shank.

Low-level waste (LLW): LLW includes all radioactive waste other than uranium mill tailings, transuranic waste, high-level waste, and spent nuclear fuel. While most low-level waste is relatively short-lived and has low levels of radioactivity, some present a significant radiation hazard and require special treatment and disposal. LLWs are classified as class A, B, or C, according to the concentration and the radionuclides contained in the waste. These classifications determine the requirements for handling, packaging, shipping, and disposing of LLW.

Maintainability: A characteristic of system design and installation expressed in terms of probabilities of maintenance frequency, maintenance time (i.e., elapsed times and labor hours), and maintenance cost.

Reliability: The probability that a system will perform in a satisfactory manner for a given period of time when used under specified operating conditions.

Total life-cycle costs (TLCC): All costs associated with treating waste over the lifetime of a treatment system, *including* disposal costs.

Transuranic Waste: Waste contaminated with alpha-emitting radionuclides of atomic number greater than 92 and half-lives greater than 20 years in concentrations greater than 100 nCi/g.

Treatment Costs: All costs associated with treating waste over the lifetime of a treatment system, excluding disposal costs.

Triple confinement: Operating areas with independent, fully contained ventilation system surrounded by a second independent, fully contained system surrounded by a third containment system where pressures are controlled so any leakage will be inward toward the more highly contained system.

Waste loading: The percentage of waste, on a weight basis, contained in a stabilized waste form ready for disposal. Equal to the weight of the treated waste incorporated into the final waste form divided by the weight of the final waste form.

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