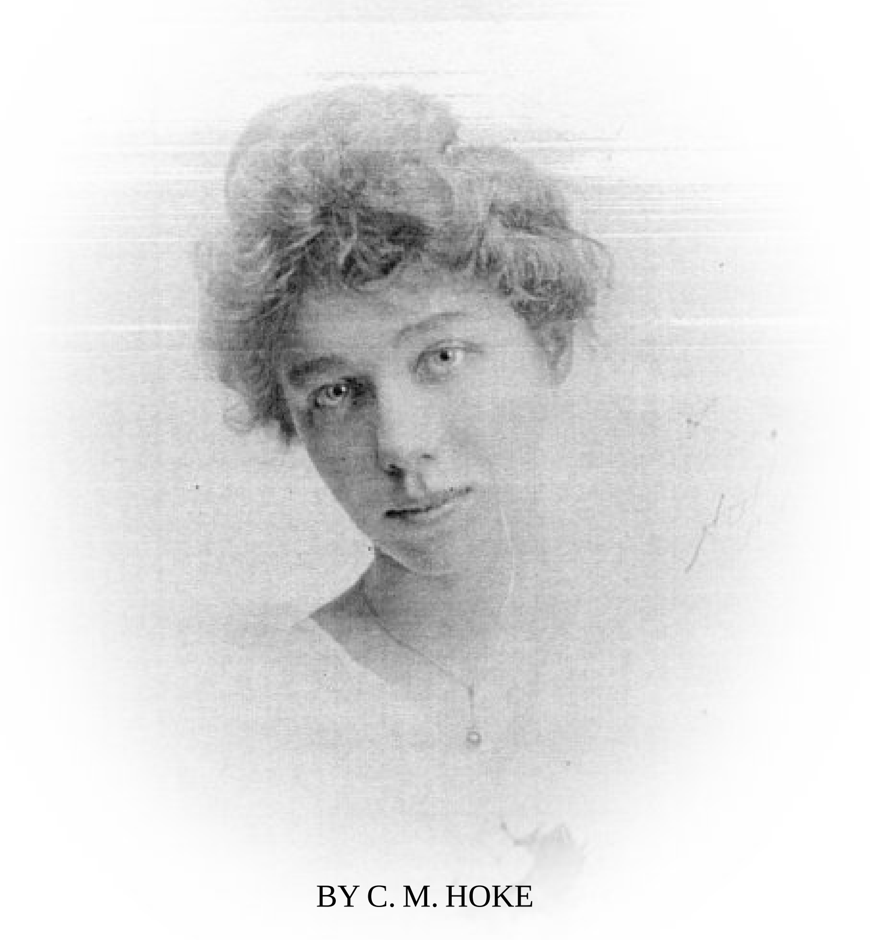
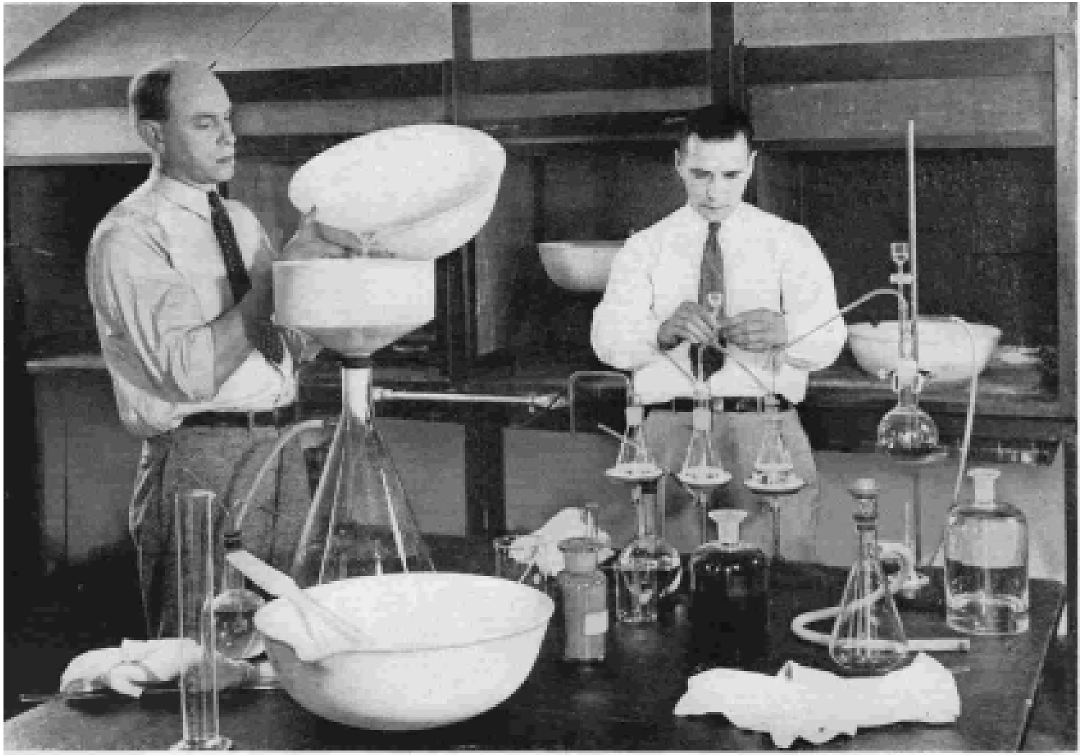
REFINING PRECIOUS METAL WASTES

Gold — Silver — Platinum Metals

A Handbook for the Jeweler,
Dentist and Small Refiner



BY C. M. HOKE



Purifying the platinum metals.

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PRECIOUS METAL WASTES

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A Handbook for the Jeweler, Dentist and Small Refiner

BY C. M. HOKE

Consulting Chemist, Jewelers Technical Advice Co. Member: American Institute of Mining and Metallurgical Engineers, American Chemical Society. Fellow: American Association for the Advancement of Science, American Institute of Chemists.

METALLURGICAL PUBLISHING CO.
123 WILLIAM STREET
NEW YORK
1940

PRINTED IN THE UNITED STATES OF AMERICA

PRESS OF
BRAUNWORTH & CO., INC.
BUILDERS OF BOOKS
BRIDGEPORT, CONN.

DEDICATED TO
THOMAS ROBERT McDEARMAN

Calm Morrison Hoke
1887 — 1952

ACKNOWLEDGMENT

The list of friends and co-workers who have helped in the preparation of this book is so long that space is lacking to give each the individual thanks that he deserves. I must, however, express my gratitude to T. R. McDearman, Margaret Stockford, Stanislaus Skowronski, Adolph Bregman, Edward Wichers, and the late Philip E. Browning, for especial courtesies. I wish to thank again the many authors and publishers who have granted permission for the use of their writings, and the several business organizations that have placed illustrations at my disposal. In particular I wish to mention the frontispiece, copyrighted by the National Geographic Society, and reproduced from the National Geographic Magazine with special permission; and to thank Drs. Wichers and Gilchrist for their permission to use it here.

C. M. HOKE

PALISADE, NEW JERSEY.
January, 1940.

INTRODUCTION

Calm Morrison Hoke's book was published in 1940. Many things have changed since that time, especially in our knowledge of the health consequences and recognition of the ecological impact of our processes. For example, while it was common practice in that time to pour untreated wastes down the drain, such practices are no longer acceptable, and in most places they are illegal. In other cases, better methods have been developed which can replace those explained in the book. The purpose of this introduction is to point out these minor concerns in an otherwise outstanding work.

The information is provided in three categories, depending on the importance/hazard level of the information and how it is treated in the book.

INACCURATE INFORMATION - This is information that should NEVER be followed. These passages will remain in the book for historical integrity, but will be modified with the strikethrough attribute. They are significant enough to address them individually here as well as where they appear in the book.

Home Refining - On page 9, Hoke writes that home refining has been found profitable and is advised for most high grade wastes. She goes on to say, "the work might well be done at his residence; there are many excellent basement and roof refineries." While refining "at home" is fine, refining "in your home" is not. NEVER refine in your residence, especially your basement! At the least, the fumes will consume any metal they contact. At worst, someone will die.

Explosive Materials - On page 31, in a discussion of fume hoods, she states “The refining processes do not produce explosive materials.” When all processes are done correctly, she is right. However, there are numerous cases where, if a process is not done as specified, explosive compounds can indeed be created. The reader is cautioned not to rely too heavily on this overly broad statement.

Evaporation - Hoke discusses reducing the volume of solutions in various chapters throughout the book. This process is known as evaporation. In other areas, she writes about boiling solutions for various reasons. It is important to understand the difference. Boiling is used in processes like dissolution and washing. When a solution containing values is being boiled, the vessel should be covered with a watch glass or be otherwise similarly contained. Boiling creates tiny eruptions at the surface of the solutution as bubbles pop, and can propel values out of the vessel. The watch glass captures these minute droplets and causes them to drop back into the vessel. When evaporating a solution to reduce its volume, the solution must be kept below the boiling point to avoid any bubbling which could cause a loss of values, as the vessel is not covered during evaporation. Do not boil when evaporating. (page 44, 57)

Mercury and Mercury Compounds - Mercury has been found to be a very toxic element. While its use was common at the turn of the last century, and continued for decades after, it is now considered to be among the most hazardous elements commonly available. While mercury and its compounds are still in use, its use in recovery and refining is discouraged as there are much safer alternatives.

Bichloride of Mercury - This chemical is mentioned in a description of melting fine gold on page 48. While the reader is advised in the book not to inhale the fumes, it is better to avoid the chemical entirely. Mercury is highly toxic. Mercury and its compounds have no place in refining.

Mercuric Cyanide - This is another mercury compound that should NEVER be used. It is mentioned as an alternate testing method for palladium on page 99. Of the mercury compounds, mercuric cyanide is particulary dangerous, able to enter the body by inhalation, ingestion, or by absorption through the skin and carries the added hazard of potential cyanide poisoning. Do NOT use this chemical.

Incineration - Incineration is an important technique in recovery and refining. Although it is suggested several times in the book, no one should ever "pour on gasoline" when incinerating! NEVER! (page 49, 214, 216)

Tasting Wash Waters - On page 71 Hoke describes washing metal scrap after a hydrochloric acid treatment "till the washings have no more sour taste, or fail to turn blue litmus paper red." NEVER taste your wash solutions. NEVER! Use litmus paper.

Fumes - Many of the fumes produced in these processes are extremely hazardous. While the dangers weren't well known in 1940, we are more aware of the cumulative damage they can cause now. In discussions of dealing with fumes on page 25 and the need for a "gas mask" on page 328, the advice provided is unsound. Shutting oneself up in a small room, opening the windows, and *hoping* the fumes will drift out is extremely hazardous. A wet handkerchief draped over the face is no substitute for a proper chemical respirator, and most respirators do not protect against the fumes of nitric acid.

EXTRAORDINARY HAZARDS - While all recovery and refining operations are dangerous, certain procedures described in the book can be extremely hazardous. If performed correctly, the hazards can be minimized, but anyone using them is advised to study the individual procedure IN DEPTH before attempting them. These topics are mentioned in this introduction to bring to the attention of the reader the elevated hazard involved.

Alcohol and other Organic Compounds - Organic compounds can form dangerous combinations when added to the solutions we produce. Add organic compounds to your solutions only if you fully understand the risks and methods to minimize them.

Ammonia - Like alcohol, ammonia is a useful tool to the refiner, but it can also form dangerous compounds. In addition, it can form complexes with metals in solution, e.g., the PGMs, making them harder to recover. Use ammonia only when you understand its proper use and how to avoid the potential risks and problems.

Osmium and Ruthenium - These two metals form volatile and very poisonous oxides when heated. These metals are best handled by the professional refiner.

Hydrofluoric Acid - This acid is mentioned a number of times. The reader is cautioned that hydrofluoric acid is among the most dangerous compounds discussed in the book. An accidental splash covering only 25 square inches of skin can be fatal! The reader is advised to use this acid only if they have the experience and sufficient safety measures in place, including a supply of calcium gluconate or other hydrofluoric acid specific treatment.

Cyanide - Cyanide became very popular around the turn of the twentieth century as a cost effective leach for gold ores and other recovery processes. Unfortunately, it is also extremely poisonous. With the heightened concern in our modern world to such agents, cyanide is no longer easily obtained in most parts of the world.

Asbestos - This was a wonder material in its time, but was also found to be a carcinogen. It was often used in the lab as a center on wire gauze pads to evenly spread the heat of a flame as well as in other applications. The reader is advised to search out modern alternatives whenever asbestos is mentioned.

OUTDATED INFORMATION / BETTER METHODS / MINOR OMMISIONS / CLARIFICATIONS - While most of the processes used today haven’t changed much since 1940, there have been some improvements. This category includes some areas where better methods have been developed than those provided by Hoke, as well as several cases where additional information may be helpful to prevent loss of values or to minimize risks.

Throwing the Liquid Away / Pouring it Down the Drain - The reader is told throughout the book to throw away or otherwise dispose of various waste, in some cases being told to dump them down the drain. All waste generated in the process of recovering and refining precious metals should be treated to render it as harmless as possible before proper disposal.

Filtering Precipitated Gold Powder - In Chapter V, Ms. Hoke provides a nine step process for refining common scrap. Step 7, Washing the Fine Gold, provides a method for washing the gold that includes pouring the final wash through a filter to collect the gold powder. A better alternative is to dry the gold powder in the vessel in which it was precipitated, thus eliminating any possibility of losses in the filter paper.

Recovering Silver as Silver Chloride - In the same chapter, step 9 provides a method for recovering silver from a nitric acid leach in a previous step. The AgCl conversion is a valid method and has its place in refining, but most refiners prefer to cement silver out of a nitrate solution with metallic copper as it produces much less waste.

Reducing Silver Chloride the Dry Way - Reducing silver chloride “the Dry Way” as outlined in the book will likely result in loss of values unless the refiner is set up to capture the silver that volatilizes in the process.

Do Not Dry Silver Chloride - Hoke mentions preparing silver chloride for sale to a refiner by drying it. While a refiner can deal with dry silver chloride, the reader is advised that allowing silver chloride to dry can complicate the recovery and refining process. If the reader intends to convert the silver chloride to metallic silver, it is best to keep the material wet at all times prior to the conversion. On page 49 she does recommend keeping AgCl moist.

The Stock Pot - While Hoke mentions that some workers wait until they have accumulated several gallons of solution, this practice can quickly get out of hand. A better practice is to handle waste solutions on a regular basis, cycling solutions through the stock pot on the same frequency at which they are produced.

Premixing Aqua Regia - In Hoke’s day it was common to premix aqua regia in a fixed ratio, then to combine it with the metal. While others have developed similar techniques, GoldSilverPro has championed the cause of adding nitric acid in increments. It is far better to add only the amount of nitric needed to perform the task than to add too much and have to deNOx after the metals have been dissolved.

Using a Gold Button to Eliminate Excess HNO_3 - While the suggestion above recommends adding only enough nitric acid to complete digestion, in practice it is common to end up with a small amount of excess. While several options are available to eliminate this excess, including evaporating the solution to a syrup and adding HCl, using sulfamic acid, etc., the most elegant solution, taught to us by Harold_V, is to add a weighed button of refined gold to the solution and drive the reaction to completion with heat. Once the reaction is complete, the button can be retrieved and reweighed for accountability purposes.

SMB for Precipitating Gold - Hoke discusses the use of sulfur dioxide gas, but she does not mention sodium metabisulphite (SMB). SMB is available as a dry crystal. When added to an acidic solution, SO_2 gas is produced which acts to reduce gold to a metal just as the gas obtained in steel cylinders.

Cover Solutions when Boiling to Prevent Losses - The difference between boiling and evaporating is discussed above. When boiling a solution containing values, it is recommended that a watch glass, funnel, reflux condenser, or similar device be used to prevent the losses associated with boiling liquids.

Incinerate Between HCl and HNO_3 to Avoid Losses - In some cases the worker may want to use hydrochloric acid followed by nitric acid, or nitric followed by hydrochloric. It is important to remember that the combination of these two acids forms aqua regia acid which can put gold into solution. No amount of washing can eliminate all chlorides or nitrates from a precipitate as they can remain as insoluble salts. Whenever switching from hydrochloric to nitric acid, or nitric to hydrochloric, unless you intend to put the gold into solution it is advisable to incinerate the solids to remove all remaining chlorides or nitrates before adding the second acid.

Chemical Burns also Affected by Temperature - In Chapter B - Hazards, it is mentioned that the severity of a chemical burn depends upon (1) the concentration of the chemical, and (2) the duration of the contact. Temperature should be considered as a third factor. Sulfuric acid is dangerous. Boiling sulfuric acid is extraordinarily dangerous.

Melting Platinum Without a Flue - Hoke mentions on page 295 that “Since the melting of clean platinum produces no unpleasant fumes no flue is needed.” The statement is technically accurate, with 2 cautions for the reader. While “clean” platinum may produce no fumes, impurities in the metal definitely can. For example, if zinc has been used to reduce the platinum , the zinc will create dangerous vapors when heated. The choice of melting dish is also important as silica based dishes will volatilize and can be inhaled. The safest practice would be to perform all melting with proper ventilation.

Smelting vs. Melting - The term smelting is often misused. In very general terms, smelting is a process that employs both heat and a chemical reaction to drive off impurities and concentrate the precious metals from an ore, low quality scrap, etc. Melting is the appropriate term when one is applying heat alone to cause solid metal particles to become liquid and flow together into a button or be ready to pour into an ingot or other form.

Recovery vs. Refining - High quality scrap like jewelers' bench filings can go directly to refining processes. Many readers may not have access to such high quality scrap, and may start with low quality material, e.g., ores, ewaste, etc. In these situations, the process should be viewed in two steps - recovery and refining. Recovery methods, e.g., the Acid/Peroxide (A/P) method for ewaste or one of a number of leaches for ores are used to separate the gold bearing materials from the majority of the waste material/ gangue. The concentrated material still contains a significant amount of waste, but it is concentrated enough to move to refining processes. Refining processes convert high quality waste and concentrates to refined metals.

DISCLAIMER

Every procedure described in this book carries some degree of risk. This introduction is intended to point out certain specific hazards. The absence of a procedure in this list does not indicate that it is without risk. Unless you understand these hazards, take steps to minimize the risks, and have a plan to deal with the situation if something goes wrong, you could endanger yourself, your family and your neighbors.

For much more detailed information, join us at goldrefiningforum.com.

FrugalRefiner
December, 2013

With Special Thanks to 4metals, butcher, freechemist, goldsilverpro, Harold_V, lazersteve, and Lou. Without their contributions, this introduction would not have been possible.

PREFACE

This book is based on twenty-four years of experience in teaching jewelers and others how to refine their precious metal wastes.

In many cases, especially at first, the instructions were given in person, at the jewelry factory or dental laboratory. Mostly, however, the instructions were given by mail, in the form of typed direction sheets, supplemented by replies to such questions as came to the student's mind. These instructions were prepared to meet the individual requirements of the user, and were adapted to the type of jewelry he made, the size of his shop, his own background of education or experience, and the kind of waste he happened to have on hand at the moment.

This book is based on these oral and written instructions, and differs from them mainly in that it hopes to meet, in one volume, the needs of many workers handling many different problems. It assumes complete inexperience on the part of the reader.

For many centuries—from the days of the Egyptians up to about 1900 A.D.—the metals used in jewelry were gold and silver. Copper and zinc were added to cheapen and to strengthen them. The processes of melting and refining were simple, well known, and adequately described in the literature. A young man wishing to learn the art or trade could do so either through the printed word, or by apprenticing himself to some older artisan.

But at about the beginning of the 20th century, platinum entered the fields of jewelry-making and dentistry. By the time we entered the first World War, it had burst like a nova into first magnitude in the jewelry firmament. Its sister metals, palladium and iridium especially, came with it. Immediately the problems of refining, separating, and remelting the scrap metal became problems indeed.

At first, say up to about 1915, comparatively few jewelry shops in the whole world were equipped to melt their platinum scrap, and the task of separating the platinum from the gold scrap was equally beyond their powers; a handful of professional refiners handled the entire output. Reasons for this were several; preoccupation with war was only one. The habit of secrecy among many workers was a potent reason; the institution of apprenticeship was dying out; the literature of platinum was scanty and so highly technical as to discourage the average reader. Platinum was so valuable that in many shops the proprietor did all the melting and refining himself—such as it was—and excluded all workmen from the room where he worked, thus increasing the superstitions and misinformation that collected around the whole subject.

(A practical reason was the fact that the melting point of platinum is much higher than that of silver or gold; so high, in fact, that an oxygen flame is required for melting it. That is, a gold-melting furnace, using gas or coke with compressed air, is not hot enough to melt platinum. The fuel must be combined with oxygen—oxygen such as is now provided in steel cylinders—in order to attain the necessary high temperature. The lack of compressed oxygen was a major factor in the non-use of platinum; its introduction at low prices was a major factor in its popularization.)

Nor were these the only complications that beset the precious-metal worker of the early Nineteen Hundreds. New gold alloys appeared—white golds and green golds—which made refining more difficult. Electroplating became commoner, adding its cyanide solutions to the duties of the harassed refiners. Chromium and rhodium plating did their bit to complicate matters. Stamping laws that insisted upon definite percentages of metal and alloy added further to his legal, as well as his ethical responsibilities.

Indeed it has been said, with truth, that there have been more changes in precious metal technology during the last thirty years, than during the previous thirty centuries.

Hence this book.

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APPENDIX

Notice Concerning Safety, First Aid, and Pollution Control

Due to the enormous changes in these fields over the past fifty years, you should not rely on the information presented in this book but should consult current sources on these subjects.

REFINING PRECIOUS METAL WASTES

CHAPTER I

THE PURPOSE OF THE BOOK

What the book does. What it does not do. Is a knowledge of chemistry essential? How to use the book.

* * * *

When a jeweler makes a piece of jewelry, he starts with a sheet of metal and he hammers and carves it and drills holes in it, and files off the rough edges; possibly he engraves it; and finally he polishes it. He winds up with a piece of jewelry that weighs one-half or maybe only one-tenth as much as the original sheet. The rest is now in the form of clippings, scrap, filings and the minute particles that are now mixed with the polishing materials—all contaminated with more or less dirt.

When a dentist makes a denture he does much the same thing; he starts with gold or some other metal, usually of high intrinsic value, and when he is done, a good part of the original metal is now in the form of scrap, grindings, and the like.

These precious metal wastes are useless until refined. In most cases, especially when the proportion of dirt is small, the task is easy. In some cases the mixture is of such a nature as to make it wise for him to sell the stuff to a professional refiner. In a few cases the proportion of dirt is so high that the owner might as well throw the thing away.

The purpose of this book is to teach the jeweler or dental technician how to handle all these kinds of waste. The equipment needed will be described, the processes will be explained, and he will be told how to decide whether a given type of waste is too complex for him to refine or not.

This book does not cover the refining of virgin ore or crude metal, nor any phase of mining engineering.

It does not cover assaying—which is the analysis of a small weighed sample, made to learn its ingredients and their proportions.

It concerns itself only with secondary refining—that is, the refining of precious metals that have already been in use and are now waiting to be returned to further employment in art, science, or industry.

And while the book does describe fully the processes used by such huge plants as the United States Mints and others who handle gold by the ton and platinum by the hundredweight, its main concern is with the small plant—the jewelry factory of from one to a hundred men, and the average dental laboratory—and it covers the recovery of gold, silver, and the platinum-group metals from the wastes that such plants produce.

IS A KNOWLEDGE OF CHEMISTRY ESSENTIAL?

For the task that we have set ourselves, the answer is no. Many excellent refiners have no formal chemical training. Of course by the time they learn to refine they have acquired a knowledge of the behavior of several metals and acids, and the worker with a knowledge of chemistry can progress more rapidly and with greater assurance. However, this book is written for the man without a knowledge of chemistry.

It is pertinent to digress here and recall the origin of chemistry. . . . It began with man's dream of making gold out of base metals. In the pursuit of this dream he experimented with every substance he could lay hands on, combining them, heating them, cooling them, crushing them, cursing them and blessing them, and learning a great deal about them. Chemistry of today is an outgrowth of these efforts. The student of this book will have some of the same mental adventures that were enjoyed by the Alchemists, but, it is hoped, with a greater monetary reward.

HOW TO USE THE BOOK

We shall begin with easy tasks—tasks that are easy to perform and easy to understand. The assumption is that the reader has never even seen the processes of refining precious metals. It is taken for granted that he hopes to learn how to handle even the more complex mixtures normally found in the jewelry shop or dental laboratory; therefore we shall go step by step to the more complex cases. Finally it is assumed that he has eyes with normal color-perceptions, a fairly steady hand, and will perform *in order* the various “acquaintance” tests, without too great impatience to reach the more interesting chapters in the back of the book. He must of course obtain the required equipment and chemicals.

Precautions against the hazard of fumes, acids, poisons, etc., will be brought to his attention.

After performing the acquaintance tests, the reader will take small quantities of filings, clippings, etc., and will read about the first procedure in the instructions, and perform it. Then he will read about the next step, and perform it. Soon he will have clean metal, ready to melt up and use again, or to be sold.

The process of learning can be carried out best with small quantities of material. Later, after the process and its reasons are familiar, the reader will handle larger and larger quantities of material at a time; this means larger vessels, and sometimes different ones, all of which are described in their place.

* * * *

There are three agencies used in refining: acids and other chemicals; heat; and the electric current. Most refining is done with acids—the so-called wet way—which will occupy a large part of this book. The dry way, which means heating the metal sufficiently to melt it, and then removing impurities by means of fluxes, has fewer applications today than it had a generation ago. Electrolytic refining may be the method of the future, and is now an accepted method for handling large quantities of materials. All three of these will be described, so that the reader may choose the agency best suited to his needs.

* * * *

“No matter how a text is written, one reader will yearn for more details while another will be bored by the tedious explicitness.” These words of truth can be found in the Introduction to J. Harry Howard’s *Handbook for the Amateur Lapidary,* and they seem so applicable that we must here echo his request that the reader take this into account when tempted to criticise the book. The author has purposely gone into every small detail necessary to instruct the newcomer who knows nothing of chemistry or laboratory technique. From the chemist, who may skip these elementary instructions, we ask patience with the beginners.

CHAPTER II

MATERIALS TO BE DISCUSSED

Jeweler's wastes. Dental wastes. Photographer's wastes. Base metals present in precious metal wastes. Non-metallic admixtures. Old electroplating and stripping solutions. Economics of refining the various kinds of wastes.

* * * *

The simplest and cleanest kinds of precious metal waste are old jewelry, the metal parts of old dentures, and the clean scrap metal that is produced in the manufacture of jewelry or dentures. The refining of this material is easy because there is little or no dirt to be removed, and the job is profitable for the same reason.

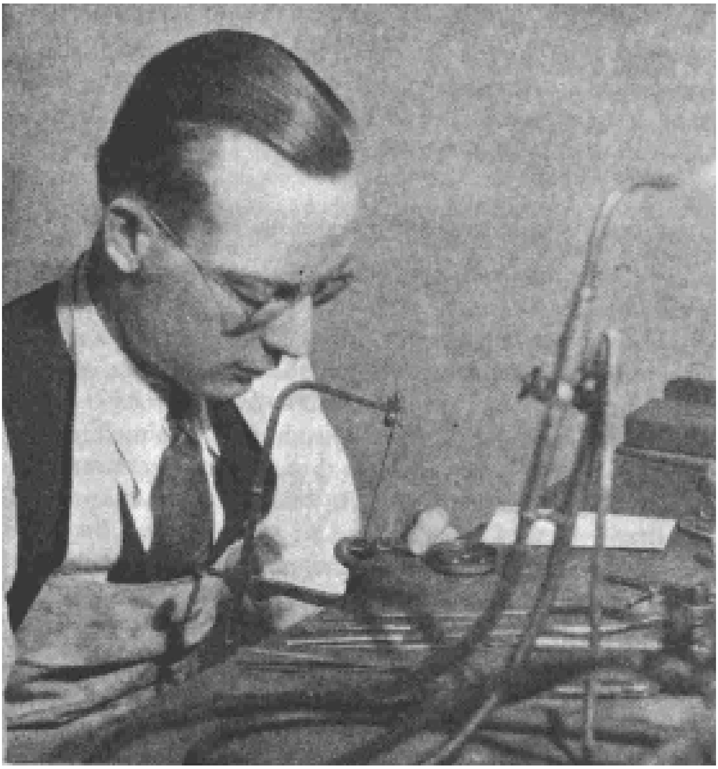
Old jewelry may be made of Sterling silver, or of base metal plated with silver; or of karat gold—in which pure gold is alloyed with more or less of other metals; or of base metal plated with gold; or of platinum, which also is alloyed with other metals. Dental restorations such as bridge work, plates, fillings, etc., are often made of high quality gold; sometimes of platinum; sometimes of alloys in which gold, platinum, silver, copper, and other metals are combined; sometimes of metals as inexpensive as stainless steel.

Non-metallic substances are often found in conjunction with these precious materials: the crystal of the watch-case; the porcelain tooth in the denture; the sapphire in the ring.

In the jewelry factory and the dental laboratory we find metal-bearing wastes generated in the processes of manufacture, and it is with these that we shall concern ourselves most, partly because they are the stuff on which the refiner spends most of his time, and partly because the processes involved are more complex.

These wastes are sometimes of quite high intrinsic value, as in the case of the sprues chipped from castings, or the little shavings produced by the engraver's tools, or the clippings that fall on the jeweler's bench. The neater the workman, the higher the value per ounce; that is, the less trash, the fewer match ends, bits of paper, cigarette ashes, etc., that have to be removed.

In other cases these wastes contain much dirt. For example, when jewelry is polished, the dust and the used polishing materials are collected (usually by an exhaust system) and saved for refining. The particles of precious metal are too small, as well as too dirty, to be distinguished by the unaided eye, but they are large enough to be worth recovery in most cases. Then we have old plating baths, for example the solutions used in gilding or silver plating.



Jeweler at work. Small particles of platinum, mixed with bits of steel from the saw, are being produced.

Courtesy of Byard A. Brogan.

Photographic wastes are not legitimate parts of the jeweler's problem, but now and then are brought to the small refinery, and are therefore discussed here briefly.

Some shops handle only gold and silver. Some handle only platinum. Most jewelry shops and dental laboratories handle all three, as well as palladium and iridium. In a few instances we find osmium and rhodium and ruthenium—rare and expensive metals of the platinum group—in addition.

Finally we have very low grade wastes, including the stuff swept up from the floor, the deposit scraped out of the flue over the melting furnace, the discarded crucibles in which metal has been melted, and the settlings from the water in which the workmen wash their hands.

All of these are treated for the recovery of their values in the well-ordered jewelry factory and dental laboratory. All of these—and more—will be discussed in this book.

BASE METALS PRESENT IN PRECIOUS METAL WASTES

So much for the precious metals. The other metals that will be covered in this book are:

(a) Copper, which is a component of most gold alloys, serving to harden and cheapen them. It serves the same purpose in Sterling silver, and also is found in most dental alloys.

(b) Iron or steel. This is present as the fine wire used in holding the parts of jewelry together while they are being soldered; also as particles from the files or saws, old watch-springs, etc.

(c) Brass, an alloy of copper and zinc, is also found in the form of binding wire. Rolled-gold articles, or filled gold, or cheap electroplated novelties, may be composed largely of brass, the outer coating being in some cases extremely thin.

(d) Nickel is a component of many white gold alloys. It is also a component of German silver (or nickel silver), which is not silver at all, but an alloy of copper, zinc and nickel. German silver is often used as the basis of rolled or filled articles, and in table silver.

(e) Zinc is found in many gold alloys and in some solders.

(f) Tin and lead, melted together, constitute soft solder, which is used in fastening the parts of cheap jewelry together, and in the manufacture of rolled and filled gold stock. Tin is a component of some dental alloys. Lead sometimes gets into jeweler’s filings from the lead blocks that are used by the lapidaries, and from other sources.

(g) Mercury is normally to be found in dental scrap, and occasionally in jeweler’s wastes. Sometimes it is present in sufficient quantity to justify its recovery.

(h) Cadmium a metal closely related to zinc in many of its properties is sometimes found as a component of gold solders.

* * * *

Crude gold ore sometimes contains arsenic, selenium, tellurium, and other of the less common elements. These do not come within the scope of this book, and materials containing them should not be refined according to the methods here given.

NON-METALLIC ADMIXTURES

(a) Those that will burn are numerous and varied: dust, paper, match ends, scraps of tobacco, charcoal, the wax used by dental mechanics, shellac, the strings and cloth used in polishing, wood rubbed from the bench or peg, and, if we are truthful, we must include nail parings, hair, and bits of food, from the filings swept up from the worker's bench.

(b) Those that will not burn include an occasional precious stone, bits of glass, sand from the sand-blasting machine, emery from the files, carborundum, plaster of paris, dentists' investment compounds, vulcanite, fragments of porcelain teeth, rouge and other polishing materials, pieces of crucible, and grit from city dust.

Floor sweeps are not unlike bench sweeps in composition, except that the proportion of dirt is higher. The settlings from wash-barrel wastes contain much soap and soap scum.

Polishings contain the lint from the buffs, the rouge, pumice and other materials used in polishing, atmospheric dust, and rather small quantities of precious metals.

OLD ELECTROPLATING AND STRIPPING SOLUTIONS

Solutions for pickling, stripping or plating gold and silver are common in most jewelry shops, including many retail stores and repair shops. Sometimes platinum, palladium, and rhodium baths are used. When these solutions become foul or exhausted, they must be treated for the recovery of their valuable content.

* * * *

ECONOMICS OF REFINING THE VARIOUS KINDS OF WASTES

Precious metal wastes may be divided into high grade and low grade. They may also be divided into (a) wastes whose only precious metals are those of the platinum group; (b) those whose precious elements are gold and silver only; and (c) those that contain both gold and platinum-group metals.

Up to the time when the United States went off the gold standard, most shops sold their high grade wastes of group (b)—those containing gold and silver—to the United States Assay Offices or Mints, that being the best way to dispose of lots sufficiently high grade to meet the Treasury Department's requirements.

Since the United States went off the gold standard, the regulations have been drastically modified. The reader is advised to apply frequently for current rulings, which are subject to change from time to time; these are obtainable from any Federal Reserve Bank, or from the Mint or Assay Office of his district.

At present it pays most shops to refine all their high grade wastes of whatever composition.

Wastes of groups (a) and (c), in which platinum is present, cannot be sold profitably to the Government, which is not authorized by Congress to buy platinum or its group. It can accept them, as constituents of gold or silver shipments, but cannot pay for them. In fact the refining charges are increased when these unwanted metals are present. In spite of this fact much platinum is turned in, mostly in shipments where it is a minor constituent, in sufficient quantity to net the Government many thousands of dollars a year.

The owner of platinum-bearing wastes, therefore, must decide whether to refine them himself or sell them to a professional refiner. Group (a), containing platinum but no gold, is so simple to refine, as will shortly be seen, that it is rarely shipped out. Group (c), however, calls for special knowledge and some little equipment—knowledge that this book will give, and equipment that this book will describe. It also represents the most profitable branch of the refiner's art.

Let us compare the expense of selling a lot of high grade material to a refiner, and doing it yourself. Suppose you have $1000 worth of filings, old dentures, jewelry, or the like. If you sell it to a refiner you must consider several costs:

(I) The interest on the cost of the metal while it is idle. Two months at 5% per annum would be $8.34.

(2) An assay should be made, which will cost the same for a small lot as for a large one. If platinum group metals are present, the cost will be considerably more than for gold and silver alone.

(3) Cost of packing, shipping, and insurance during transit.

(4) The refiner's legitimate fee, and his profit.

Some refiners buy dirty filings at so much per ounce, then sell clean metal at a higher rate per ounce. The difference in the case of platinum-group metals is apt to be considerable, this sum being in effect the refining charge per ounce. Sometimes the refiner simply returns a certain sum, without information as to what it represents.

Now, if you refine this $1000 worth of metal yourself, in your own shop, you (I) cut down its period of idleness; (2) cut out the assay entirely; (3) cut out the shipping expense and chance of loss during shipment. And your expense for acids and labor is generally less than the refiner's charge plus his legitimate profit.

In a well-managed shop, the total expense is much less. Even when the metal is in the form of dirty mixed filings, the cost of refining is generally less than the cost of a good assay. And the factor of idleness is important—a shop can do business with a smaller capital investment when it can promptly return its scrap to usable condition.

There are reasons why the small shop, in particular, should do its own refining. A shop that has only small amounts of filings, etc., is apt to wait a long time before sending them away; this means a relatively high loss through idleness. Then it has to pay just as much for an assay as a big shop; or maybe it makes the mistake of selling them without an assay, which is a false economy if there ever was one. The expense of shipping is nearly the same as for a large lot, the insurance only a little less. And if the refiner charges a flat fee, this means that the expense *per ounce* on a small lot is much more than for a large one.

So far we have talked of high grade wastes, clean scrap, bench filings, old dentures, etc. Home refining for these has been found profitable in such a large proportion of cases that it is advised for all except a few very oddly situated establishments. Thus a jeweler in an office building with no gas, no suitable sink, and no way to dispose of fumes, may not afford to rent extra space elsewhere simply for refining. On the other hand the work might well be done at his residence; ~~there are many excellent basement and roof refineries~~.

But when we come to low grade wastes such as polishings, floor sweeps, and old crucibles, then we begin to question seriously the economics of refining. In general it has been found that even the smallest shop should take certain measures to dress and reduce the bulk of such materials before shipping them to a professional refiner. And even the largest plant, that always burns, sieves, grinds and samples these materials, will need to question the economics of the actual ultimate refining of the final low-grade dust. (This will be discussed again in Chapter XVIII.)

In general, the larger the shop the more economically it can operate. However, there are limits to economy even when there are no limits on the supply of material. To explain: It has long been known that there is gold in sea water. Some years ago the Dow Chemical Company built an enormous plant to extract bromine (used in the manufacture of ethyl gasoline) from sea water. Sea water contains about 61 grams (almost 2 Troy ounces) of bromine per ton of water, but they manage to extract over 15,000 pounds of it every day, at a good profit. Naturally these chemists considered the recovery of the gold in the sea water, since they can extract it with the same operation as that used for bromine simply by adding one or two more steps. There was no question as to the presence of the gold, which is there to the extent of about 0.002 gram per ton of water. So they worked for some weeks, handled 12 tons of sea water, spent the value of many ounces of gold, and recovered a tiny scrap of metal weighing about 1/10,000 of a gram. They labored over a mountain and brought forth much less than a mouse.

* * * *

The first time you refine, handle a small quantity of material, and keep your attention centered upon the *process*. The third or fourth time, however, that you carry through a given procedure, make written note of the following things: the exact weight of the material you start with; the amount of time and chemicals you consume; and the weight of pure metals recovered. The apparent loss will be made up of the following; base metal and trash; metal tied up in old filter papers or in solutions laid aside for later treatment; and actual true loss.

As time goes on, you will find that the time and chemicals consumed will become less—much less. The proportion of immediate recovery will become higher and higher, and the actual loss and the proportion of metal tied up will become lower; the process therefore will be more and more profitable as your skill increases.

* * * *

The purpose of this book is to tell the precious metal worker not only how to refine, but also what to refine and when to refine it.

CHAPTER III

THE SIMPLEST CASE—PLATINUM FILINGS THAT CONTAIN NO GOLD

Equipment and chemicals. "Acquaintance experiments." Beginning work; sieve; magnet; caustic; heat. The nitric acid treatment. How to fold a filter paper. Summary. Questions and answers.

* * * *

This type of waste consists primarily of bits of platinum or iridio-platinum produced by the file or saw, and larger pieces that were clipped or sawed out. It is found in shops that make only high grade platinum jewelry. It is rarely found in dental laboratories. Now and then we find a jewelry shop making both gold and platinum articles, in which a given workman may handle only one kind of goods, and the man who works on platinum only will assume that his filings are truly free from gold.

Now and then he is right, especially if his bench is in a separate room. But usually his filings will contain a little gold carried in by the tools, or by his hands in their contact with door-knobs and faucets that are handled by the gold workers. Moreover, most platinum solders contain gold, and filings normally contain bits of solder. Accordingly this type of filings is rather rare. However, it is so obviously the simplest case and the most logical to begin with, that we shall describe it fully.

Mixed with the bits of platinum there will be steel particles also, from the files and saws; brass or steel binding wire; the usual organic dirt such as paper, tobacco, hair, emery, etc.; and possibly other kinds of dust. One unexpected contamination that sometimes occurs is nickel—in the form of filings put in by a dishonest workman as a substitute for platinum, with the purpose of cheating his employer. Shellac from the diamond-setter's bench is often present.

If your material contains pure palladium, or alloys containing as much as 40% palladium, do not use the methods of this chapter; save it for refining by the methods described in Chapter XII.

The student is advised to read this chapter to the end, without attempting to remember the steps, and without any great effort to understand them. He should then return to this point, and provide himself with the necessary articles; then read one paragraph at a time, do what it says; then read the next paragraph, do what *it* says; and so on. Points that seem obscure at the first reading will clear up when put into operation.

EQUIPMENT AND CHEMICALS USED

These are obtainable at almost any chemical supply house; nothing of an unusual nature is needed. For purpose of identification we shall give the catalogue numbers used by Eimer and Amend, of New York City. Prices are subject to change, and are F.O.B. New York City; higher prices prevail throughout the West and South. Other dealers all over the world have access to this catalogue, and can provide you with similar articles if you mention these numbers as being taken from Eimer and Amend's 85th Anniversary Catalogue of Laboratory Apparatus and Supplies.

Apparatus:

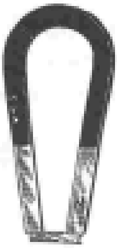
A porcelain casserole, such as the one illustrated, will serve many purposes. Eimer and Amend Catalogue No. 19656, the 6½ inch size, costs $2.20. A second and smaller casserole, for example the 3½ inch size at 6o¢, will be used in making tests and handling small samples. You may need additional casseroles later, especially if you refine more than one batch of material at a time.

Casserole; stirring rod; thin asbestos disc; one type of heater.

A magnet; No. 25746, 6 inches, costs 35¢.

Wash bottle No. 18952, size 1000 cc, 70¢.

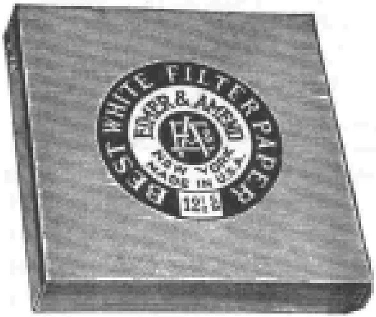
A glass funnel; No. 23632, size 5 inches, costs 25¢ Filter paper to fit it is necessary. E. & A. Nos. 23150 and 23180 are good kinds, and the 25 cm. size fits the 5 inch funnel; 100 sheets cost 55¢ (Later



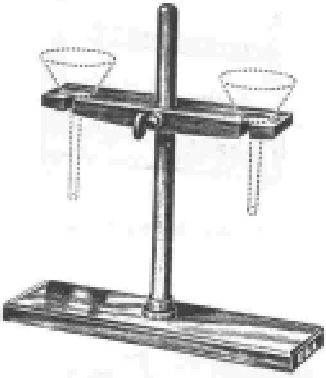
Magnet

Wash bottle

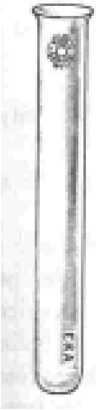
Funnel



One kind of filter paper



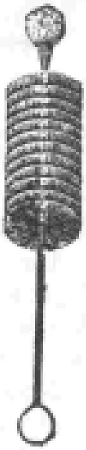
One kind of funnel support



Test
tube

Test tube
clamp

Spoon-
spatula



Test tube
brush

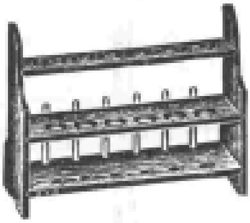
you will want additional and larger funnels, with filter paper to fit each size funnel.)

A funnel support; No. 31937 holds two funnels and costs 90¢ Home-made supports are good if made to slide up and down, and if so built that even when the funnel is full of liquid they will not tip over.

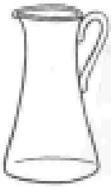
A dozen glass test tubes, size 6 inches by ¾ inch or smaller, No. 32124; about 60¢ the dozen.

Test tube support No. 31989 at 60¢.

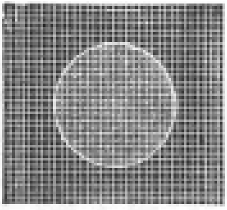
Test tube clamp No. 20260 or equivalent, about 15¢.



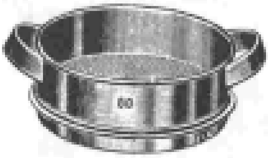
Support for test tubes.



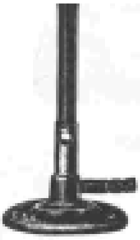
Pitcher.



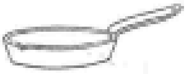
Wire gauze with asbestos center.



Sieve.



One type of burner.



Frying pan.

Test tube brush No. 19058 or equivalent, about 10¢.

Glass stirring rod No. 24562; a 6 inch or 8 inch length costs only a few cents. You will need several, of assorted lengths.

A useful tool for stirring, taking samples, making tests, etc., is a porcelain spoon-spatula; No. 31280, 16½ cm. long, 50¢.

Paper towels to wipe your hands and mop up spilled solutions.

A sieve. Many shops already have a series of sieves with different meshes, such as No. 30920 to No. 30960. If not, buy a rice strainer at a department store. Also a frying pan, and two or three plain glass pitchers of the kind used for ice-water. Those straight across the top are best, because a funnel can be rested on them. The two-quart size is useful.

You will need a stove or heater such as the one in the first sketch, with one or two burners. A piece of thin asbestos to go between the dish and the flame is helpful, or better, a square of wire gauze with asbestos center, such as No. 33090, 6 inches, at 15¢.

A Bunsen or Meker burner is useful for many purposes; No. 19240 at 30¢ to 50¢ according to the type of gas you use—when ordering be sure to specify.

CHEMICALS: Nitric acid, chemically pure. A 7 lb. bottle costs about $2.00, and an allowance will be made for the empty container. Large shops save money by buying acids in carboys.

You will use considerable ordinary tap water.

If your material contains much shellac or grease, you will need some caustic soda, in sticks, lumps, or flakes. (Caustic lye, also called potash, serves the same purpose.) It need not be chemically pure; the ordinary household kind at 10¢ a can is excellent.

"ACQUAINTANCE EXPERIMENTS"

Let us become acquainted with our materials through exposing them, in turn, to the reagents that are used in refining. We cannot too strongly urge the reader to make every one of these tests, himself, working in a good light and noting down in writing the effects that he observes.

To describe these effects in words is easy, but for the man who seriously wants to learn the nature of these metals, wordy descriptions are a waste of time. He must see for himself what happens. Half an hour spent making these tests with his own hands will tell him more than a thousand words in print.

(1) Platinum. Place some clean platinum scrap in a casserole or test tube and cover it with C.P. nitric acid, full strength. . . Nothing happens. . . Warm the vessel gently. . . Nothing happens to the platinum; the acid simply boils away. You are safe to use your best platinum ring for this test, if its stones will not be injured by acid and if it is truly platinum. (Iridio-platinum, the alloy generally used in good jewelry, behaves so much like pure platinum, that in most of this book we shall make no distinction between the two.) You will find that diluting the acid produces no unexpected change in its action.

(2) Copper. Repeat with copper scrap. Note the speed with which the acid goes to work, even when cold, giving off a brown gas of extremely unpleasant nature. Thin wire will disappear within a few seconds. Notice the effect of heating the acid. Diluting the acid slows matters up, but produces no other conspicuous change. The resulting liquid is green—of a color that we associate with copper compounds—and contains copper nitrate.

(3) Nickel. Repeat with a piece of pure nickel. (The 5¢ coin known as a nickel is not suitable; it is mostly copper, alloyed with enough nickel to make it white.) Nickel, like copper, dissolves readily in nitric acid, either concentrated or dilute, giving off the same brown fumes. The liquid remaining is again green, and contains nickel nitrate.

(4) Similar tests with brass, gold, silver and zinc, will suggest themselves and will be instructive. Now is the time, also, to begin to read the trade publications, Government reports, books, and other literature, some of it obtainable without charge, that are mentioned in Chapter X and Chapter E of the Appendix.

BEGINNING WORK: SIEVE; MAGNET; CAUSTIC; HEAT

Let us start with a small quantity of filings or scraps. A few pennyweight will be enough; do not use more than five ounces. To many workers this will seem a ridiculously small quantity, because they expect to refine many ounces of such goods every day. It would be a small quantity to refine, perhaps, but it is an excellent quantity to learn on.

Begin by sieving the filings. This will remove bits of paper, match ends, etc. Some large pieces of clean metal, and perhaps a stone or two, may appear and can be returned to their proper places.

Next, spread the filings out on hard-surfaced paper, or in a flat dish, and pass a magnet through them, back and forth, to collect iron and steel. Brush the steel particles into a separate vessel, and you will note that some platinum has been carried along with them. You can remedy this by a second treatment of the steel particles, spreading them out thinly and again letting the magnet pick them up. Return the platinum particles to the main dish.

It is not possible to get rid of all steel by this treatment, partly because some kinds of steel are not attracted to the magnet, but we shall remove any remaining steel in a subsequent treatment.

By this time you have observed the nature of the dirt that is present, and its character will determine your next step.

If the filings contain much shellac or grease, place them in a casserole, cover well with water, and add about a half ounce of lye or caustic. Use care; heat is generated when caustic and water combine, and there may be some spattering. Bring the solution to a boil, and stir with a glass rod.

(This caustic is bad for the skin, so do not get it on your hands. If you should spill it on your hands, wash them at once with plenty of water and they will not be hurt.)

The porcelain used in chemical ware will, if properly treated, resist heat amazingly well. Place a piece of thin asbestos or wire gauze between it and the flame; do not use thick asbestos because it wastes time and heat. Have your dish perfectly clean and dry on the outside, and it will not crack. Get into the habit of wiping the outside of the dish every time you put it on the fire.

Stir the material frequently with a glass rod or porcelain spoon.

After the solution has boiled a few minutes, remove it from the fire, fill the dish with water, let the filings settle, and pour off the liquid into a pitcher, leaving the filings in the casserole. Let this liquid settle well, and save any metal that you may have poured over; then throw the liquid away.

Fill the casserole again with hot water, to wash the filings. Stir well, then pour off this wash-water. Repeat until the filings no longer feel slippery. Let the wash waters settle before you throw them away, to be sure that you do not throw away any metal.

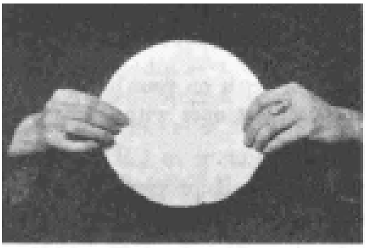
If your filings contain only a little shellac or grease, they will not need to be boiled in caustic. In that case, simply burn out the wood, paper, etc., by heating them to redness in a frying pan.

Do not use both the caustic and the frying pan. Use one or the other, according to the kind of dirt present.

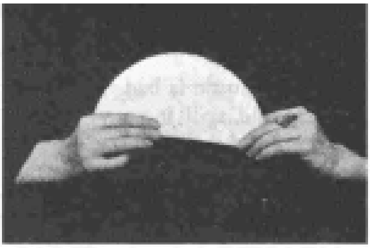
THE NITRIC ACID TREATMENT

Next, dissolve base metals, such as brass, nickel, etc., by boiling the filings in nitric acid, chemically pure. The filings should be in the casserole. Pour on enough nitric acid to cover them and add a little water. Heavy brown fumes will appear, which are poisonous and very disagreeable, and will damage your machinery, so do this work outdoors, or near a good flue. Or have an exhaust fan in your window, and let the fumes go out the window. Ways of disposing of fumes are discussed fully in the next chapter.

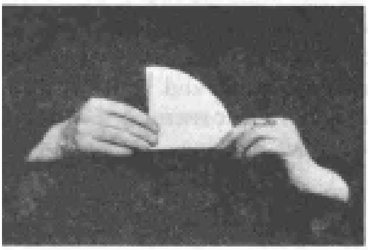
HOW TO FOLD A FILTER PAPER



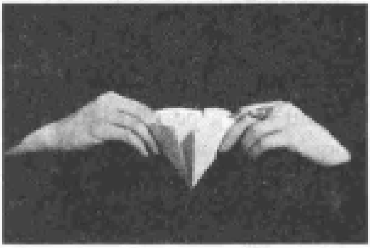
Use a paper of the right size.



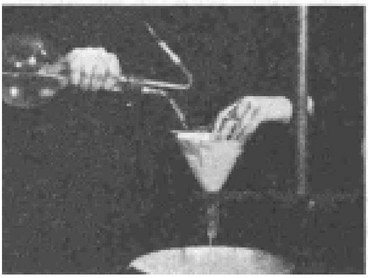
Fold it in half.



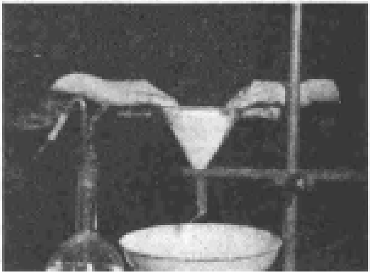
Fold again in right angles; this gives you a pie-shaped piece of four thicknesses.



Open it up, with three thicknesses on one side and one on the other side.



Fit it into the DRY funnel, and then wet it with water. (This shows one way of using the wash-bottle. Hold your thumb against the stopper.)



Press the paper in with your two hands, pressing it down smoothly so that the liquid will run through rapidly. It pays to use paper of proper thickness.

Add the acid slowly, or it might boil over. If there is much base metal, there will be heavy fumes. If there is very little base metal, there will be only light fumes. Stir well with the glass rod.

This may stand overnight, or longer. But if you are in a hurry, heat the acid to boiling, and the base metals will all dissolve in a few minutes. Stir often, so that the acid may reach all parts of the filings.

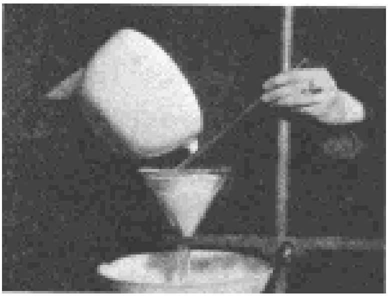
While the acid is acting, let us learn how to fold a filter paper, following the illustrations on page 18.

It pays to work with a filter till it fits, by folding wider or narrower pie-shaped pieces, even if you waste several papers. If it does not fit the liquid will run through very slowly.

Large filters are apt to break at the point. So fold a second small filter, and fit it as a cap over the point of the big one, with the three-thickness side of one covering the single thickness of the other.

Use filter paper of the right size. It should not reach the top of the funnel. If so big that it sticks up beyond the funnel, it is impossible to wash it down properly, so trim it off with scissors.

Let the acid work all it will, then dilute it, pour it off, and either filter it through the filter paper, or let it settle. It is best to use the filter paper and funnel; you may pour over some filings, and the filter paper will catch them. Let the paper dry and put it away in a jar or box, which we shall call your "paper storage." Eventually you will refine this and recover the metal that it contains.



When pouring, hold the glass rod or porcelain spoon against the lip of the dish, and pour down it. In that way you avoid splashing acid and staining the outside of your dish.

Pour against the side of the filter. Do not let the liquid fall heavily against the thin point of your filter paper.

Throw the acid away. Leave the filings in the dish. Add fresh acid, heat, and see if it changes color and gives off fumes; if ,so, that means that there are still base metals for the acid to work on. Stir well.

Continue this treatment until there is no more action between the acid and the metal; that is, continue until all base metals are dissolved.

Wash off the acid from the filings carefully, with plenty of hot water. Wash several times. Then let the filings dry. In most cases they are now ready to be remelted, for use in making up new jewelry. Methods of melting are discussed in the Appendix.

Sometimes it is plain that sand or emery still remains, mixed with the filings. If the quantity is small, it will do no harm, but will flow to one side when the metal is molten. If the quantity is large, it may become troublesome; this will be discussed later, in Chapter XVI.

* * * *

SUMMARY

To repeat—the procedure, in one sentence, is the *removal of unwanted materials* from the platinum, which itself remains unchanged. Thus we sieve out paper or trash, remove iron with a magnet, remove shellac and grease with caustic (or burn it out in a frying pan), and remove base metals with nitric acid. Then we wash, dry, and melt the clean platinum.

* * * *

QUESTIONS AND ANSWERS ON CHAPTER III

The following are questions that have been asked on this chapter, with replies.

Q. You tell us to filter the nitric acid solution, but you did not tell us to filter the caustic solution.

A. Acid solutions, unless very concentrated, are easy to filter. Caustic solutions are difficult to filter; if concentrated they destroy the filter paper; if somewhat diluted they toughen it and make it almost impervious. Only when very dilute are they filtered with ease. Usually you save time by setting any kind of a solution aside to settle, then pouring off the top part, and filtering only the last portion. This is especially true with caustic solutions.

* * * *

Q. Why not use aqua regia instead of simple nitric acid ?

A. Because aqua regia (a mixture of nitric and hydrochloric acids) dissolves platinum. The action is slow, especially if cold, but none the less it does dissolve platinum. Some old-fashioned workers do not realize this, but you can easily prove it by trying it on some clean filings; notice how the color of the acid darkens.

As you will learn later, if your filings contain gold, you would use aqua regia to remove it. But that is a different story.

* * * *

Q. I have read somewhere that steel, especially stainless steel, will not dissolve in nitric acid. Yet here we are told to get rid of it with nitric acid.

A. An excellent question, and one that can be answered best by a simple acquaintance experiment. Take a piece of clean steel, either stainless steel or ordinary steel. Place it in a clean dry dish, and pour a little full strength nitric acid over it. In most cases nothing will happen, at least for a while. Stainless steel, especially, will remain unaffected—in what is called the "passive" state—for some time. But if you sprinkle a few platinum filings over the steel, or if you touch it with the sharp edge of a piece of platinum scrap, the acid will go to work at once, evolving brown fumes and dissolving the steel speedily. Sometimes a mere touch with a glass rod will start it. Dilute acids also will go to work at once. Chromium is another metal that will lie passive in strong acid, but will dissolve in dilute acid, or will be galvanized into action by the touch of a piece of platinum.

* * * *

Q. What are those brown fumes?

A. Mostly oxides of nitrogen—products of the interaction of nitric acid with the base metals. These same fumes will be seen again and again when nitric acid is interacting with other substances.

* * * *

Q. Is there any other acid that would do this work as well as nitric?

A. You could use hydrochloric acid in some cases. It dissolves iron and steel readily, also tin. But it does not dissolve copper or nickel, both of which are rather apt to be present. Sulphuric acid is another possibility, but nitric acid is best.

* * * *

Q. Would it not be easier simply to melt the platinum filings and let the flame burn out the impurities? When gold filings are melted into a button, the dirt is burned out or goes into the flux. Certainly the oxygen flame is hot enough to burn out most impurities.

A. Actual experiments many times repeated show that it is much easier to remove the dirt with magnet and acid than to try to burn it out with the oxygen flame. Even small amounts of impurities make platinum brittle, apparently by forming compounds such as platinum carbide. This point will be discussed again in Chapter A of the Appendix.

* * * *

Q. You say for me to boil the filings in nitric acid, to which a little water may be added. How much water is advised?

A. Diluted acid is more efficient per unit of acid in the sense that it wastes less of the brown gas which is an active part of the reaction. But it works less rapidly. However, the matter is not as simple as it appears, because as soon as the acid starts to work it begins to dilute itself. Since the concentration changes every second, it seems idle to be too dogmatic about the exact concentration at the start.

The concentrated acid sometimes works so rapidly that it boils over; this tendency may be reduced by adding water. Frankly it is hard to say how much water to add, because this tendency to boil over is dependent upon the size of the pieces of metal as well as upon the number of them, and these factors change with every batch.

If you use much water you increase your acid efficiency but decrease the speed of operation, and you have more liquid to filter and store. Some workers use ten parts of water to one of acid; others use ten parts acid to one part water. The results are the same in the end. We ourselves use about equal quantities of water and acid.

* * * *

Q. You say that it is impossible to remove all the steel and iron with the magnet—that the remainder is removed by the acid. Then, why bother to use the magnet—why not let the acid take care of all the steel ?

A. When you make your acquaintance experiments with copper and nickel, you observe that the acid will dissolve all of the copper, and all of the nickel. If you make the same experiment with steel, you will find that nitric acid will, under certain circumstances, dissolve steel, but that it always leaves a small black residue, undissolved, behind it. This residue is carbon, a constituent of all kinds of steel, appearing as a fine powder when steel is dissolved. When you remove your steel by the magnet, you remove both iron and carbon; whatever steel is acted on by acid, leaves a residue of carbon mixed with the platinum filings. This residue, if small, does no harm; but if copious it might cause trouble.

* * * *

Q. Why are we told to use chemically pure acid? Why wouldn't ordinary commercial acid be good enough?

A. This will be answered later, in the chapter on gold scrap. In general it may be said that the chemically pure ("C.P.") acids are more concentrated than the others, therefore go further and cost less in the end. But there are other reasons as well which will be discussed in Chapter V.

* * * *

Q. Should I use distilled water in this work?

A. No. Ordinary tap water is satisfactory in all the processes described in this book. It contains impurities, but these do no harm.

* * * *

Q. Why is it they use oxygen when melting platinum? Isn't it the same as compressed air, only in a tank? What is the advantage?

A. No, the oxygen in the tank is not just the same as compressed air. Air, ordinary air that we breathe, is a mixture of one part oxygen to about four parts of nitrogen, plus small amounts of other gases. That one part of oxygen—about 20 percent of the whole—is the only part that produces heat or sustains life—the other 80 percent simply dilutes the oxygen.

As a result, when you compress air you compress 20 percent useful oxygen and 80 percent useless nitrogen. It is as though you bought coal in which one-fifth of the lumps were coal, and the other four-fifths slate. The slate (similar to nitrogen) is useless in itself, and also tends to cool the fire through taking up heat itself.

The stuff in the oxygen tank is almost 100 percent pure oxygen.

You know how compressed air from your blower will increase the temperature of a flame. Adding the same amount of oxygen (at the same pressure in pounds) will increase the heat much more. With oxygen you will get a white heat in much less time, and the temperature will go higher.

Ordinary gas with compressed air simply will not melt platinum, no matter how much you use nor how long you try. The same gas, plus a little oxygen from a tank, will melt it easily.

One reason why a compressed air and gas flame is so noisy is because of the rush of the useless nitrogen. An oxygen-gas flame that will do the same work will be smaller and much less noisy.

* * * *

Q. I have been advised not to melt platinum because the fumes that come off are very dangerous. Is that true?

A. Pure clean platinum melts easily under the oxygen flame, without unpleasant fumes, and it is perfectly safe to do this work without a flue. See Chapter A of the Appendix. Impure platinum, however, often produces fumes, as many substances are volatile at the temperature at which platinum melts. Crude platinum ore, as obtained from the mines, often contains osmium and ruthenium, and these metals when heated strongly produce fumes that are both unpleasant and dangerous. This point will come up again in Chapter XVII and elsewhere. However, crude platinum is always refined at least once, possibly several times, before being used in jewelry or dentistry, and all the osmium and ruthenium are normally removed. Accordingly you are not apt to be exposed to any hazard when melting your platinum scrap, filings, or recovered metal.

* * * *

Q. Why is it I have so much trouble with these test tubes ? They are always breaking, or the liquid spurts out when I heat it, and they never look clean.

A. Practice with a little plain water until you get the knack. Do not put too much liquid in the tube—an inch to an inch and a half is enough, and experienced workers use less. Have the tube perfectly clean and dry on the outside before heating it. Use a small flame such as that of a Bunsen or Meker burner, and hold the tube in a slanting position, being careful not to let the flame touch the glass above the level of the liquid. While it is warming shake the tube gently so that steam will not accumulate in one part of the tube. Remove it from the flame as soon as it boils. Hold it with a wooden or wire clamp; do not use your bare fingers.

Immediately after finishing the test, wash the tube well with plain hot water. Never let material dry inside it. The test tube brush with a sponge on the end is useful, but must be kept scrupulously clean itself. Invert the clean tube so that it will be dry when you need it again.

Most pictures of chemists at work show them holding a test tube. You will soon come to understand the popularity of this modest piece of apparatus. The larger size—about 6 inches by ¾ inch—is preferred by beginners because it is easy to clean and less apt to boil over, but the smaller size—say 4 inches by ½ inch—is more economical of material.

CHAPTER IV

ARRANGEMENT OF EQUIPMENT. DISPOSING OF FUMES

Disposing of fumes. Material for hoods. Lighting. Burners. Fans and blowers. Water and plumbing. Storage of chemicals. Hazards.

* * * *

In Chapter III we produced a few fumes and handled a minimum of equipment. Let us now consider both of these subjects more deeply. When a shop has very little refining to do, as in a repair shop, or one that handles platinum only, the space given over to refining will be small. Once a month, perhaps, the end of a bench will be cleared off, dishes and bottles will be brought from beneath a cupboard, and the task will be completed in a few hours. For such shops the main problem is fume disposal, and several inexpensive plans are being used. One man will place a wooden box outside a window, and heat the dish with a small movable gas burner, electric hot plate, or even by frequently-changed hot bricks. Another will work only when the weather is such that he can operate outdoors. ~~Another will shut himself up in a small room where there is no machinery to be damaged, open the window, and hope that the fumes will drift out~~.

This book, however, is written mainly for the shop that makes refining a routine process, not an occasional experiment. While it offers many suggestions for the smaller shops, its main concern is for the average user.

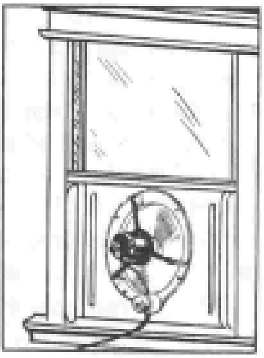
Many jewelry factories and dental laboratories already have a good part of the equipment required for refining, especially the tables, heaters, running water, possibly furnaces, and perhaps a means of disposing of fumes.

You will need a table about 3 by 6 feet, more or less. Set it waist high; that is easy to work at and leaves room below for cabinets, a drawer or two, and space for storing jars or crocks.

Many different materials have been proposed for table tops; probably wood is as good as any. Stone tops are handsome, but unless covered with a rubber pad they are certain to cause the fracture of many a dish and flask. Metal tops are useless in this work.

DISPOSING OF FUMES

Every jewelry shop needs a method of carrying off acid fumes. Acid fumes are produced when gold or silver or platinum is refined, also when gold or silver is cut down for the preparation of plating solutions; also when articles are boiled up in sulphuric acid for the removal of fire coat; also when enamel is dissolved in hydrofluoric acid; and in several other processes well known to the jewelry maker.



One inexpensive device for removing fumes, suitable to the small establishment. The fan is detachable and portable. It should be placed low, close to the work table.

Most shops already have a hood or flue for this purpose, but many of them are both inefficient and unhandy. The reason is that some of them were made in imitation of the canopies that jewelers have over their melting furnaces.

When we recall that the job of boiling acid is quite different from the job of melting gold, we see that the hood requirements for the two processes must be different also.

Thus: (I) melting gold furnishes a high temperature, enough to produce a draft up the chimney, while boiling acid does not. (2) The fumes from acids will destroy metals, while furnace fumes do not. (3) The furnace works admirably in a dark corner of the shop, while the acid hood should be lighted by daylight if possible, or by powerful and well-placed bulbs. (4) It is sometimes necessary to let the work with acids stand overnight; the melting furnace is almost never in operation overnight. This means that the acid hood alone should be so fixed as to permit closing up at night, with all openings fume-tight. . . And there are other differences.

What are the requirements of an acid hood?

First, it must carry off fumes.

Second, its walls must be of some material that will not scale off and drop down, but that will last reasonably well.

Third, if it can possibly be arranged, its platform should be large enough for carrying on all of the work that evolves fumes. Some solutions must be left to stand, and while standing they give off fumes; so build your hood large enough to accommodate these solutions as well as all others. A working space of 3 by 6 feet is excellent for a small shop, and when not actively in use with fuming solutions, can be used as a storage space for material that might possibly give off fumes, and so is always in profitable operation.

Fourth, it must be extremely well lighted.

Fifth, it must be so arranged that if a vessel of acid breaks or boils over, there will be neither loss nor damage.

Sixth, the platform must be at a comfortable height for a standing worker; waist high is about right.

Seventh, the gas cocks, if any, should be placed outside the hood, for easy adjustment without opening the hood door.

In addition, the door or window (or windows) should open and close easily, and the whole arrangement be easily cleaned.

Some plants are lucky enough to have a tall smoke stack that furnishes enough draft for an acid hood. But in most cases a fan or blower must be utilized.

If only a small fume hood is available, place your work table near it, with one gas burner thereon, and have one or two burners in the hood.

The chemical supply houses sell hoods made of slate, glass, etc., that are handsome, efficient, and well designed. However, they are apt to be expensive, and possibly more ponderous than the jewelry factory really needs. It is suggested that a study of the catalogue of such a supply house would be useful, as it would provide ideas for arrangement and design.

Another suggestion is that the jeweler visit some neighboring school or college, where chemistry is taught. Most teachers of chemistry are happy to display their equipment to any inquirer that shows a normal interest, and will take pleasure in explaining to a visitor how the fume-hoods work, their advantages or faults, and so on.

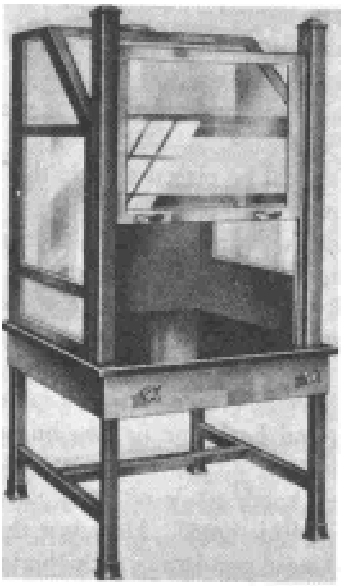
Also, it is usually wise when building a hood to employ a contractor who has had experience in such work; your neighboring laboratory, whether scholastic or commercial, is usually happy to give you the name of the firm that installed its hoods.

The frontispiece of this book illustrates a large hood, designed for a busy laboratory.

MATERIALS FOR HOODS

The chemists normally use glass-walled hoods, with flues of terra cotta or stoneware. Wire fire-proof glass is excellent. The back walls are usually stone.

The jeweler may not wish to use such expensive materials. Glass set in wood frames will serve excellently for years, especially if the wood be coated with acid-proof paint. Back walls of Transite or other fire-proof composition are moderate in cost and will give years of service.



A standard chemical fume hood, with glass sides.
Courtesy of the Laboratory Furniture Co., Inc.

The platform of the fume hood, because of its closeness to the heaters, is usually made of cement or stone. If wood be used, place asbestos or stone slabs under the burners. Keep some distance between the heaters and the glass sides or windows of the hood; otherwise the glass may crack.

A hood with a floor-space of say 3 by 6 feet would require two windows. These should be similar to ordinary windows—with counter-weights, running up and down in grooves, and fitting properly on all sides.

The objections to sheet metal are two—the fumes cause it to flake off and drop flakes into the solutions; and sheet metal cuts off the light.

The platform of the hood should be smooth and easily cleaned—not made of rough brick. Sometimes a dish of acid is spilled; let the platform be made with a slight slope, and with a slight raised edge across the front, and at the lowest corner a hole should be bored, and underneath the hole an earthenware crock should be stationed.

LIGHTING

The lighting of the hood is easy if its walls are of clear glass. Since most of these operations call for close watchfulness on the worker’s part, see to it that the lighting is extremely good. So-called “daylight” bulbs are advised, as they do not obscure the colors of the solutions.

BURNERS

The arrangement of the gas burners is important. Run the gas supply-pipe along the front of the hood, *underneath* its platform. Bore holes through the platform, some three or four inches back from the front of the hood, just large enough for flexible gas hose to pass through. The gas cocks are then situated underneath the hood, quite outside it, so that they can be manipulated without opening the window or exposing the hand to heat or vapors.

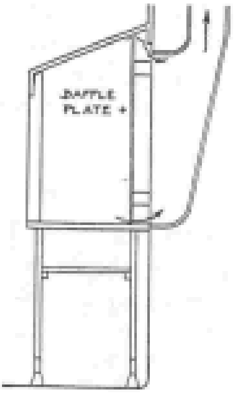
Most workers prefer movable heaters instead of stoves that are piped in permanently, because movable ones are more easily cleaned. The little stoves used in cooking are cheap and satisfactory. Unless your insurance rules forbid rubber tubings for connections, we advise them; flexible metal tubing is not so safe when acids are present.

Electric heaters are not satisfactory for work involving strong acids and corrosive fumes; their essential element is a coil of wire that is affected by the acids in a short time.

FANS AND BLOWERS

There are fans and blowers on the market made especially for use with corrosive fumes; their motors are either specially enclosed and ventilated, or skilfully placed so as to be outside the reach of the fumes. These models are not unduly expensive.

Practically all the fumes occurring in these processes are *heavy* fumes that tend to settle downward. Remind your contractor of that when he designs your hood—he will see to it that there is a good draft at the bottom of the hood. Sometimes this is accomplished by locating the fan low; sometimes a baffle plate is so arranged as to draw air through a slot near the bottom of the hood, Usually there is another slot higher up, to take care of such fumes as do ascend.



The width of the slots at top and bottom should be established by trial.

Remember that when the fan is working, in order to provide good draft the windows must not be entirely closed. Leave a small opening for fresh air to enter as the foul air is pulled out. But there will be many times when you will wish to shut the hood up tight and leave it so. . . Because of these considerations we sometimes find a small port or slit that can be easily closed at will.

Even with the best ventilating equipment there may be some escape of acid fumes. Accordingly the space used for refining should, if possible, contain no electric switchboards and as little machinery as possible.

Let us repeat—most chemical laboratories, whether in college or industrial plant, are open to visitors, and the chemist in charge will be genuinely pleased to escort a guest through his establishment, explaining the operation of hoods, drying ovens, steam baths, filters, and many other devices.

WATER AND PLUMBING

Running water should be available if possible; otherwise provide a supply jar and a good vessel for slops. Do not let the spent solutions from the refining run into your settling barrels—they will injure the plumbing and may cause losses in other ways. Remember that acids corrode the metals used in plumbing; therefore wash the sink out well at frequent intervals. Though much strong acid is used in the refining, comparatively little of it is poured down the sink until after it has been neutralized or otherwise weakened. Even so, frequent flushing is advised.

STORAGE OF CHEMICALS

In large shops nitric and hydrochloric acids are purchased in carboys holding 5 gallons; these should be supported in a cradle device that permits tipping. The small shops will buy acid by the gallon. It is convenient to have a smaller bottle, say 16 ounces or about 500 cc., in addition, for use when your task calls for only a small quantity of acid, as the large bottles are not easy to pour from. Dealers normally grant an allowance on the return of empty bottles or carboys.

Dry chemicals should be stored in crocks, jars such as Mason jars, or in clean wooden boxes, or left in the original container if it has a good cover.

Filter papers should be stored in a drawer or box within easy reach.

HAZARDS

With one very minor exception (sodium chlorate) the chemicals used in refining do not present any fire hazard. (Indeed, some of them would make excellent fire extinguishers.) But since many of them are corrosive in their nature, they should be stored where wandering feet will not kick them, nor aimless wheelbarrows fracture their bottles.

~~The refining processes do not produce explosive materials~~. When your contractor is designing your fume hood, he will probably ask you if you are apt to have explosives, that he may govern his design accordingly. There is just one possibility of explosion: if gas should be permitted to escape from the gas burner, it will provide the hazard that is present in every gas cook-stove, but no more.

In general, when chemicals are spilled upon hands or clothing, the *first* thing to do is to *wash them off with plenty of plain water*. *After* that, neutralize an acid stain with a little weak ammonia, or bicarbonate of soda. Do not attempt to neutralize until *after* you have removed all acid possible with plain water! If you spill caustic or lye on skin or clothing, again wash off thoroughly with plenty of water; *after* which it may be well to neutralize with a little vinegar, lemon juice, or extremely dilute hydrochloric acid solution. Keep a jar of clean water beside you, in which you can quickly place your hands in case of need. Use paper towels, and if they show stains of solutions that may contain precious metal, put them in the "paper storage" for ultimate refining.

* * * *

In Chapter XX will be found a further discussion of equipment and its care. In Chapter B of the Appendix will be found additional information on the personal hazards to which the refiner is exposed, with suggestions on how to minimize them.

* * * *

CHAPTER V

THE COMMONEST CASE—REFINING GOLD SCRAP THAT CONTAINS NO PLATINUM METALS

The first refining. Equipment and chemicals. "Acquaintance experiments." Beginning work, (I) Preliminary treatments. (2) Melting into a button, if desired. (3) Treatment with nitric acid. (4) Dissolving gold with aqua regia. (5) Removing excess nitric acid. (6) Recovering the dissolved gold with copperas. (7) Washing the fine gold. (8) Melting the fine gold. (9) Saving the silver. Old filter papers. What to do if you spill acids or caustic.

* * * *

This type of scrap is found in almost every shop or laboratory that handles precious metals, so we shall discuss fully the different methods of refining it. First we shall describe a method of general applicability, and in later chapters mention the possible modifications. The reader should in time acquaint himself with several procedures, then adopt the one that best fits his needs.

For our first refining, let us handle only high grade gold, such as clean yellow dental gold, clean sprues clipped from castings, or bench clippings and filings, or old solid gold jewelry. For this first refining let us carefully exclude all platinum-group metals, or alloys that may contain them; also anything that might contain soft solder (this means most cheap jewelry, rolled and filled goods, and jewelry that has been repaired); amalgam and mercury; all white-metal dental scrap; and all green gold of 16 karat or higher. In later chapters we shall take care of these materials now being excluded.

The procedure will differ with the purposes of the worker. Thus, sometimes he wants merely to get his gold into a clean button of good working qualities, for use in making up new jewelry. Ultimately, however, he will separate the metals to obtain fine gold and fine silver, each free from alloy of any kind. The first case is not true refining; it should be described as a cleaning or re-melting.

Filings will be contaminated with the same sorts of dirt that were in the platinum filings described in Chapter III—emery, binding wire and the like, possibly plaster of paris and vulcanite. The metal will consist of gold alloyed with copper, silver, and probably zinc, cadmium and other base metals. The only precious metals present are gold and silver.

For your first refining handle 50 dwt. or less; 10 dwt. is an excellent quantity to begin on. After the methods become familiar, you will find it easier to handle much larger quantities.

EQUIPMENT AND CHEMICALS

We shall use all the equipment listed in Chapter III: frying pan, magnet, sieve, casserole, funnel, filter paper, funnel support, test tubes, stirring rod, wash bottle, glass pitcher, burner or stove, wire gauze or thin asbestos. In addition, the following:

An evaporating dish. A small shop will want Eimer & Amend's No. 21966 or its equivalent, 8½ inches across, at $1.20. A larger shop will also need the 10½ inch size at $1.80, and probably others both larger and smaller. A large evaporating dish is shown in the foreground of the frontispiece; also in the hands of one of the workers.

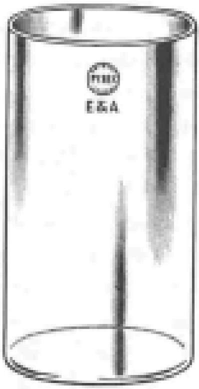
Graduate glass, No. 24697, 16 oz., $1.10. A large shop might want the 32 oz. size instead; $1.80.

Pyrex glass beakers, with lip, are especially useful when handling small lots of material. No. 17614. The 2000 cc. size (something over two quarts) will be used in the first refining, and you will find use eventually for other sizes as well; a nest consisting of the following sizes—150 cc., 250, 400, 600, 800, 1000, 1500, and 2000 cc.—will cost about $3.75. The smallest of these is about the size of a teacup.

A sand bath is an inexpensive piece of apparatus; it is merely a flat shallow pan of sheet metal, filled with an inch of clean sand. No. 17288, 6 inches across, is about 15¢. Kitchen ware such as a pie-pan, is also adequate, or a pan can be shaped up out of a piece of sheet metal. A more expensive device that is used for the same purpose is a steam bath—a metal container filled with hot water, its top carrying circular openings upon which dishes of different sizes can rest. Sometimes the water is heated by live steam, sometimes by a gas burner underneath the bath. E. & A. No. 17352, water bath or steam bath, is one of several models; $30.50. The

Graduate glass.

Beaker.

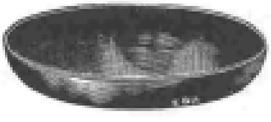


Glass cylinder.

One type of steam bath.

Earthenware crock.

Stoneware crock.



Sand bath.

price may seem high, but it will be a good investment, as you will have many occasions to use it. Its great advantage is that with it work can go on without supervision, and without danger of spattering.

Large jars of earthenware, stoneware, or glass of various sizes, will be needed. For storing dilute acid solutions, and for water or slops, the earthenware crocks sold in department stores will serve; the 1 gallon size at about 65¢ and the 5 gallon size at $1.50 are handy.

Strong acids destroy cheap earthenware; accordingly get stoneware or glass jars for strong solutions and those containing much value, and for cases where trouble would come from admixtures of substances that have soaked into the ware. A good acid-proof crock is E. & A.'s No. 25637; the 5 gallon size is $6.50. Heavy Pyrex glass jars, cylinder shaped, E. & A. No. 25592, are especially desirable because of their transparency. Sizes and prices are as follows: two gallons, 6 by 18 inches, $3.25; four gallons, 8¾ by 18 inches, $4.50; five gallons, 12 by 12 inches, $6.00.

For melting your metal a furnace or blow-pipe is needed, also crucibles and a flux such as borax. Rolls, or an anvil and hammer, are useful but not always essential.

The chemicals used in Chapter III will be used here also. These include caustic or lye, and nitric acid. In addition: hydrochloric acid, preferably the chemically pure; a 6 lb. bottle costs about $1.20; ferrous sulphate crystals, U.S.P., called "copperas"; these are pale green when fresh, and should be kept in a tight jar or box, as they deteriorate on exposure to air; they cost about 20¢ a pound in 5 lb. lots. Sulphuric acid, concentrated; a pound bottle is about 25¢.

"ACQUAINTANCE EXPERIMENTS"

Gold. Obtain a scrap of fine gold (it will not be wasted). Also some 14-k or 12-k yellow or red gold, and a bit of low-karat yellow gold, preferably 6-k or lower. This can be made on the spot by melting a little high grade gold into a button with the proper quantity of brass.

In Chapter III we learned what nitric acid does to certain base metals and to platinum. Repeat these experiments, using gold. The fine gold and the 18-k gold will show no change. The low-karat gold will first darken, then seem to dissolve, giving off the usual brown fumes. But on closer inspection you will see that a heavy dark powder remains undissolved. What happens is this: the base-metals dissolve; they constitute about three-fourths of the bulk; the remaining one-fourth that is gold remains as this brown powder. Save this material, which is valuable; it will be handled again soon. The solution obtained will probably be of a green color, because most low-karat gold is alloyed with copper.

Silver. Obtain a bit of fine silver, and repeat the tests with it. Many shops have no fine silver, and will probably use Sterling or coin silver. Nitric acid acts promptly on either, even without being warmed, producing the usual brown fumes. Sterling and coin silver yield a green liquid, the green color being again due to the copper they contain. Fine silver yields a colorless solution, which, if exposed to light, will gradually blacken. Place it to one side in a little bottle or corked test tube, labeled “Silver Nitrate,” as it will be needed again shortly.

Aqua Regia. This name means “royal water,” and was applied by the Alchemists to a mixture of nitric acid and hydrochloric acid, because it was the first solvent known that would attack the “noble” metal, gold. Prepare a little by mixing the two acids, preferably in a graduate glass; use one part nitric acid to four parts hydrochloric. Note that bubbles appear; in hot weather they are conspicuous. Do not stopper the mixture or these bubbles will blow the stopper out or possibly rupture the bottle.

Aqua Regia and Gold. Cover a small piece of fine gold with a small quantity of aqua regia. Note the fumes; they resemble the brown fumes of nitric acid, but are not quite the same. Fine gold dissolves promptly, leaving no residue. Note the effect of heating. Notice also that the color of the solution is a clear yellow—not green.

Repeat, using karat gold, such as 14-k or 6-k. Note that after the aqua regia has acted all it will, and the bit of metal has gone to pieces, there is a residue, usually of a gray color. This is silver chloride—the result of interaction between the hydrochloric acid and the silver that was present as an alloying element. Note also that the solution is not clear yellow, but greenish yellow. The green is due to dissolved copper.

Save these solutions, labeling them “Aqua regia gold solution.” They contain a mixture of substances, including gold chloride, copper chloride and copper nitrate, unused hydrochloric acid, and unused nitric acid.

Aqua Regia and Silver. Cover a small piece of silver (fine or alloyed) with a little aqua regia. If desired, warm the vessel. Most beginners are surprised at the result. They think of aqua regia as a powerful acid—which it is—and so expect it to dissolve silver. It does affect it; it changes its color and soon coats it with a firm adherent layer of gray or whitish substance. This is silver chloride. This can be rubbed off, exposing a fresh surface to the onslaught of the acid, which may in time convert all the metal into the grayish silver chloride, but it would be a slow process.

Let us learn more about silver chloride. In a test tube take a few drops of the silver nitrate that you saved from a previous test, and add a single drop of hydrochloric acid. . . Notice the white cloud that forms. Shake the test tube and see how the cloud seems to fill the whole bulk of the liquid. Set it aside for a few hours and notice how the white cloud settles. Place it in sunlight for a time, and notice how the white stuff darkens, going through lavender and gray into black. (Incidentally, this change is the basis of the science of photography.)

Again take a few drops of the silver nitrate solution in a clean test tube, and this time add a single crystal of table salt. (Table salt is sodium chloride—made up of sodium and chlorine in combination.) As the crystal dissolves, a white cloud will again form; this again is silver chloride, formed by a rearrangement of the molecules in the solutions. It is identical with the stuff formed when hydrochloric acid reacted with silver or with silver nitrate. It can be formed in other ways as well.

These acquaintance tests cover only a few of the many that could be made. You will learn other characteristics of the metals as you go along, and your own ingenuity will suggest other acquaintance tests that you can make from time to time. Beginners usually take too large a sample; use only a few drops of solution, and a small bit of metal, and you will save both time and materials.

BEGINNING WORK

In outline, the method consists of the following steps:

(1) Preliminary treatments as required.

(2) If necessary, melting the material into a button and rolling it thin, or granulating it.

(3) Removing as much base metal as possible with nitric acid.

(4) Dissolving the gold in aqua regia.
(5) Removing excess nitric acid.
(6) Recovering the dissolved gold with copperas.
(7) Washing the fine gold.
(8) Melting it.
(9) Saving the silver, if worth while.

(I) PRELIMINARY TREATMENTS

You first want to get your material in such form that it will be easy for the nitric acid to reach the base metals and dissolve them. The treatment will differ for different kinds of material.

Old gold jewelry, clippings, and old dentures should be hammered flat and rolled thin, the thinner the better. Every minute at the rolls saves many minutes at the acids. Feed the pieces into the rolls with a little scoop whose sides have been cut out so that they will fit against the rolls closely; or put them on a piece of paper, and feed in paper and all.

Cut the rolled pieces up into short lengths, twisting them so they will not lie flat in the acid; then anneal.

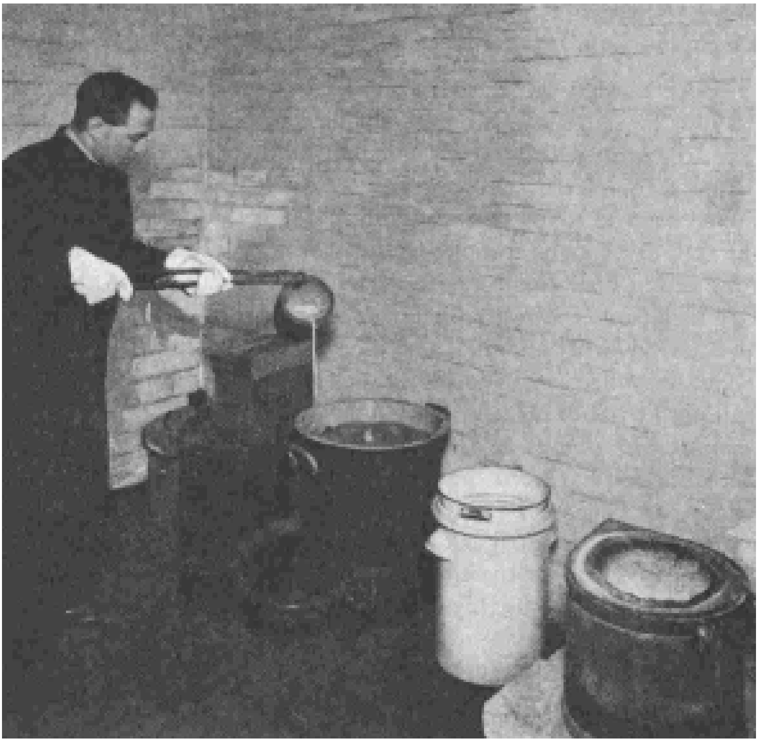
Filings, or “lemel” as they are often called, always contain dirt. Lemel is derived from the French word “limaille,” which means filings. In Chapter III you were told how to sieve filings, how to remove iron with a magnet, burn out trash, and dissolve grease and shellac by boiling the material in caustic soda or lye solution. These same operations are usually carried out on gold filings.

(2) MELTING INTO A BUTTON, IF DESIRED

This may or may not be necessary. It is often done with very dirty filings, or with dental wastes that contain much carborundum or emery; also in some other cases that will be discussed later. One way of melting dirty filings is to mix them with their weight of some flux, such as crushed borax glass and soda ash, with or without nitre, and melt them in a gas furnace, using a sand crucible. Another and quicker method is to use an oxygen-gas torch, the kind used when melting platinum, with a shallow open sand crucible.

If you have melted your filings into a button, the next step is to get the button into such form that the acid can act upon it readily. Sometimes it is so soft that you can roll it easily. Cut the rolled strips up short and twist them so that they will not lie flat in the acids. Roll them very thin; a few minutes at the rolls will save hours in later steps. Anneal.

Usually it is easier to granulate the button than to roll it. Remelt the button in a clean crucible with a little flux, and pour it while molten into a big bucket or tub of water. Pour it in a thin stream, and the molten metal will break up into fine shots or pellets when it hits the water. Collect these pellets carefully.



Granulating gold. The molten metal is being poured into water, Later the small pellets will be captured in the strainer.

(3) TREATMENT WITH NITRIC ACID

The metal, whether filings, scrap, old jewelry rolled thin, or pellets, should now be placed in a casserole. Cover it with nitric acid. Add the acid slowly, as it will tend to boil over. Cover well. Add a little water, say one part of water to four or five of acid. Some people use much more water.

Heavy, poisonous brown fumes appear, which are disagreeable and bad for machinery. Therefore do this work near an exhaust fan, or outdoors, or in a hood, or outside a window.

This treatment dissolves all the copper, silver, and base metals that the acid can reach. The thinner your clippings and the lower the karat, the more base metal the acid can reach.

As you learned in your acquaintance tests, nitric acid works rapidly on low-karat gold such as 6-k or under, which soon crumbles to pieces. The copper and silver with which it is alloyed go into solution, and the particles of gold are left as a brown powder.

Gold that assays 12-k or higher does not crumble. The acid dissolves most of the solder, and a piece of jewelry will drop apart for that reason, but the 12-k gold will not be acted upon much. Later we treat this gold with aqua regia, in which it dissolves promptly and easily. As for gold between 6-k and 12-k: the effect of this treatment will depend upon the strength of the acid, the character of the alloy, and the thickness of the pieces.

The amount of acid needed will therefore depend upon the kind of metal you are refining. So if your material is mostly high grade gold, you will not use up much nitric acid in this process.

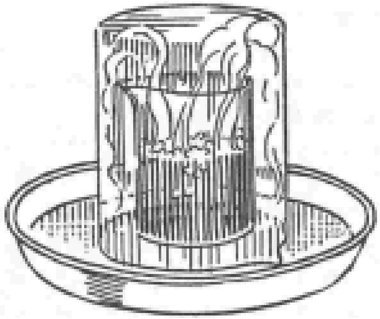
With low-grade material, the tendency to boil over is much greater. Stir the acid well with a glass rod or porcelain spoon as soon as you see there is no danger of boiling over. The treatment with nitric acid must continue until there are no more brown fumes.

After the acid has acted a while, you may want to heat it to boiling. See that the whole bottom of the dish is clean and dry, and then place it on a gas stove, with a thin piece of asbestos between it and the flame. Or, heat the dish in a pan of sand or on the steam bath. A thin sheet of metal, or a square of strong metal screen (wire gauze) can be used instead of the asbestos, to protect the dish from the direct flame.

The metal may be left in the acid overnight, or longer. But do not let it evaporate or boil dry. Also keep out dust and dirt.

Here is a way to keep fumes from getting into the room. Set the casserole or other vessel into a big flat pan or tray containing a half-inch of water. Now invert over the dish a bucket, or a crock, letting it rest in the water. A glass cake-cover is excellent for this job. This holds the fumes in, and they are absorbed by the water.

When there are no more brown fumes on stirring, add a good quantity of water, preferably hot, to dilute your acid, and pour it off through a clean filter paper folded as already described. Leave the metal in the dish. Let the liquid run through into a big jar or crock which we shall call the Silver Jar. This liquid contains dissolved silver, copper, zinc, nickel, etc.



A trap for fumes.

Sometimes there is so little silver in this solution that it does not pay to bother with it; if so pour it down the sink, being careful to flush the sink out well with plenty of water, to protect the plumbing.

But if you wish to recover silver, store this solution in a big jar or crock (not bottle), and keep it covered. Usually the solution is not strongly acid by this time, partly because the acid has been killed, partly because it has been diluted with wash water; therefore ordinary inexpensive earthenware jars are suitable for storing it. Directions for saving the silver will be given later—See Chapters V and VIII.

Rinse the metal (the gold) with some hot water, filtering the washings in with the main solution. Now add a little more nitric acid to the metal, as before, so as to be sure you have dissolved all the base metal and silver that you can.

With a little experience you will learn how much acid to use. Let each lot of acid be thoroughly killed before you pour it off and add a new lot. You will get better results in less time by using two or three small lots of acid than one large lot.

It is not easy to calculate exactly how much acid will be needed, partly because the process never acts with 100% efficiency, partly because you rarely know exactly the composition of the metals you are putting into solution, and partly because you rarely carry the acid to complete exhaustion. Experience shows, however, that about 4 to 6 lbs. of concentrated acid will be used for each pound of metal that dissolves. As was pointed out before, the acid works with less waste when diluted, but more slowly.

Finally when you are sure that everything has dissolved that will dissolve, rinse the metal well, filtering the wash water in with the acid.

* * * *

Under some conditions the metal remaining in the dish is nearly pure gold. If your original metal ran 6-k or less, and if you rolled it thin and boiled it well in nitric acid, the remaining gold may be pretty nearly fine gold, in the form of a brown powder. But under most conditions it still contains considerable base metal, and often is in the form of flakes or lumps.

As we said at the beginning of this chapter, some workers desire merely to get their gold into a clean button of good working quality, without going through the final process of obtaining fine gold free from all alloy. If such is your purpose, wash the remaining metal thoroughly, to remove the dissolved copper, etc., then dry it and melt it.

But to obtain high quality fine gold, you must carry your metal, in most cases, through this next process.

(4) DISSOLVING GOLD IN AQUA REGIA, IF DESIRED

For every Troy ounce of metal in the dish (more or less), mix up at least

I fluid ounce nitric acid,
4 fluid ounces hydrochloric acid.

Mix the acids in a graduate glass. Use “Technical” or C.P. Acids. Use enough to cover the metal well, but add it slowly, a little at a time, as it soon boils vigorously and might boil over.

Poisonous fumes appear again, different from the nitric acid fumes but just as bad. In cold weather you may have to warm the acid to start it to work. Stir now and then with a glass rod or porcelain spoon, so that the acids can reach all parts of the metal mass.

You want to use just enough aqua regia to dissolve your gold, but no more. It is better to use three or four small lots of mixed acid than to put on one large lot in the beginning. Let each lot be well killed before adding the next lot.

As each lot of acid is killed, pour it off into a big pitcher or crock. Do not filter it yet.

Toward the last you may want to heat your acids. If your metal is in small or thin pieces this will not be necessary. A big funnel, inverted over the dish, will prevent spattering.

Whatever silver is present in the metal is changed by aqua regia into the mud or scum of silver chloride. It dissolves to only a minute degree. If your metal is in thick pieces, the scum will cover the metal and keep the acids from reaching it, so stir often, and crush the lumps with the rod or spoon, to loosen this scum. The more you stir, and the hotter the acids, the sooner the work will be done. Finally there will remain a fine mud of silver chloride in the bottom of your casserole, and all the metal will be dissolved.

Rinse this mud to free it of dissolved gold, adding the washings to your main solution. If the mud looks clean, put it into your Silver Jar; but if it is dirty, with cinders, emery, etc., it may be better to put it into your sweeps.

(5) REMOVING EXCESS NITRIC ACID

You were told to use no more aqua regia than was required. Beginners always use too much. Experienced workers often do the same thing, especially when in a hurry, because fresh acids work more rapidly than those that are partly exhausted.

Sooner or later you must get rid of the unused nitric acid. Most workers think it pays to do so right away, as follows:

Put the aqua regia solution into a big evaporating dish. It will contain some sediment, mostly silver chloride; this does no harm at this point, so do not filter it yet. Now add a little sulphuric acid, stirring all the time, and working slowly, as it might spatter. Use about an ounce or less of the sulphuric acid to each quart of liquid. Now ~~boil~~ the solution down gently, to a syrup, being careful not to spatter. The purpose of the sulphuric acid will be explained later.

This evaporation is a tiresome process. It goes rapidly at first, but soon the liquid begins to spatter and you must lower the flame. Do not cover the dish, as that merely impedes evaporation. A sand bath or a steam bath is useful; these have already been described.

When using a sand bath, start work by pushing the sand to the sides of the pan, so that the heat can quickly reach the evaporating dish; later, as evaporation has progressed, scrape the sand down underneath the dish, to lessen the tendency to spatter.

The advantage of the steam bath is that it does not cause spattering, and a dish can be left on it without supervision, without danger of overheating.

Let the evaporation continue until the liquid becomes syrupy; then slowly add a little full-strength hydrochloric acid. Brown fumes will bubble off; this is the unused nitric acid being expelled. Usually this evaporation must be repeated at least once, maybe twice —evaporating to a syrup and adding a little hydrochloric acid—in order to get rid of all the unused nitric acid.

Do not carry the evaporation far enough to form a hard crust. One reason for the sulphuric acid is that it hastens the expulsion of the nitric acid, and when it is present there is less tendency for a hard crust to be formed. The sulphuric acid also serves another purpose—to get rid of lead—which is described fully in a later chapter.

When you are sure that the excess nitric acid has been driven off, let the dish cool, wash down its sides with a little water (use the wash bottle) and get the solution into a jar or pitcher, preferably a tall one.

Now dilute the solution with three or four times its bulk of water, preferably hot, and let it stand (for some days if possible) for the silver chloride to settle. The solution must be perfectly clear and separated from the sediment before you go to the next process. Usually it settles well in a couple of days, and you can pour off the bulk of the solution, filtering only the last part.

The sediment of silver chloride should be collected and washed, and put in the Silver Jar (or in the sweeps if very dirty). If there was any lead in your original material, the silver chloride will be contaminated with lead salts.

The clear solution contains dissolved gold, copper, zinc, etc. If there is much copper or nickel in it, it will be greenish brown. When gold is the main element it is yellowish brown. If it is not perfectly clear and free from sediment, let it stand another day or two for the sediment to settle; then pour off again into a clean widemouthed vessel of generous size.

(6) RECOVERING THE DISSOLVED GOLD WITH COPPERAS

If possible, have the solution in a transparent vessel—a glass jar, beaker, or pitcher. If it is transparent you can see what goes on and understand the process better. Later, when you handle large quantities, you will carry out this process in a chemical stoneware crock, but while learning the processes, use transparent vessels whenever possible.

In another vessel, dissolve in warm water about a pound of green copperas for each 50 pennyweight of fine gold that you expect to recover. Use fresh green copperas, with about a quart of water to a pound. Add a little hydrochloric acid, enough to make the copperas solution a clear green.

Pour the copperas solution slowly into the gold solution, and stir. Metallic gold will appear as a dark cloud. Let this settle some hours, or overnight, and you should find your gold in the bottom of the dish, as a heavy brown powder.

Sometimes an impatient worker will cut short the evaporation described in Section 5, and will fail to remove all the excess nitric acid. When this has happened, bubbles will arise on the addition of the copperas to the gold solution, sometimes so freely as to make the mixture boil over. So add the copperas slowly at first. These bubbles are the same brown fumes that you notice when nitric acid interacts with anything. In this case the nitric acid is reacting with the copperas. Gold will not come down until all the nitric acid has been disposed of. The solution will turn dark, but no gold will precipitate. When this happens you must do one of two things to get rid of this nitric acid.

One way is to add an extra quantity of copperas and hot water, stirring constantly. Keep on adding copperas until the mixture stops fuming and the gold comes down. Before trying this method, however, take out about on ounce of the solution and get a rough idea of how much copperas is needed. The other way to get rid of nitric acid is to evaporate the whole solution down to a syrup again, and again add hydrochloric acid, as in Section 5.

After a while, as we said, you will find the fine gold in the bottom of the dish as a brown powder. Test the liquid to see if you used enough copperas to throw down all the gold that was in solution; take a few drops of it in the porcelain spoon, and drop in a clean green crystal of copperas. Watch the crystal closely; if nothing happens in two minutes, you used enough copperas. But if a dark cloud forms around the crystal, add more copperas and hot water to your main solution, and let it settle again. You may have to do this more than once.

(If your original material had contained platinum or palladium, these metals would now be in this solution. If there is any possibility of their being present, test the solution for these metals. Full directions are given in Chapter IX.)

When, after satisfactory tests, you are sure that all the gold has been precipitated, and that the liquid now contains no dissolved precious metal, pour or siphon it off and throw it away. You will have to filter the last part of it. Finally wash the mass of gold powder into the casserole, as it must now be cleaned of the copperas solution. In this operation the wash-bottle is helpful.

(7) WASHING THE FINE GOLD

Fill the casserole twice with hot water, letting it settle, and pouring off (or filtering) the liquid, which is thrown away. Now and then a thin film of gold floats on the surface; this is so light that it does not amount to much. You can avoid this by having your casserole quite clean before using it. Wash it with soap, rinse well, and do not touch the inside with your fingers. It is the grease from your fingers that floats this film of gold.

Using the wash-bottle to direct a thin stream against a certain spot. Hold your left thumb against the stopper. This also shows how to wash heavy materials, such as fine gold powder, out of a dish.

Washing a powder, such as the gold powder, while it is in the funnel.

Wash down the sides of the funnel, so as to get the powder into a compact clean lump.

Next, cover the powder with hydrochloric acid and heat it to boiling. This dissolves the light yellow mud that is mixed with it;

(it comes from the copperas), which must be washed out well. Stir. Pour off this acid and throw it away. Add a little more acid, to be sure your gold powder is clean.

Then wash off the acid with plenty of hot water.

Finally get the gold powder into a clean filter paper, washing it down into a lump. See illustrations.

Let the gold powder dry in the funnel. After it has dried partly you can lift the paper out of the funnel, spread it out on a plate in a warm place, and it will dry quickly. You will note that clean gold powder dries more quickly than powder containing dirt of any kind.

(8) MELTING THE FINE GOLD

Place the gold when dry in a clean sand crucible that has been rubbed well inside with borax. Put borax on top, and melt as usual in a gas furnace, or with a Hoke-Phoenix oxy-gas torch. When molten, add a pinch of nitre or saltpetre from time to time. This burns out impurities. Let the gold cool in the crucible. Then break the crucible and remove the button.

If the refining is properly done, this button will be of high quality gold. If it does not roll perfectly, remelt it in a clean crucible with borax and more nitre, as before. Or, add some ammonium chloride, or a little ~~bichloride of mercury~~. Do not inhale the fumes. Pour into an ingot if desired, or let cool in the crucible.

Your gold should now be ready to be used again, or to be sold as fine gold. Sometimes, either because of faulty refining, or because of the presence of certain impurities that this method does not remove (these will be discussed later), the gold button is not as pure as you wish. If this happens, turn to Chapter XV on the special repurification of gold.

(9) SAVING THE SILVER

Going back to the Silver Jar, which contains silver, copper, etc., dissolved in nitric acid: add some table salt, dissolved in a little water, roughly ½ ounce or more of table salt for each ounce of silver in solution. A white cloud of silver chloride will form. Let it settle.

To see if you used enough salt, add a little more salt after waiting until the cloud has settled some. If more white cloud forms, add still more salt. Hydrochloric acid can be used instead of the table salt. It forms silver chloride in the same manner.

After a satisfactory test, in which no new clouds form, let the chloride settle well. Let it stand in the dark, preferably for several days.

Then pour off the clear liquid and throw it away.

Leave the chloride in the crock, covered to keep out dust, and next time you refine pour the nitric acid solution in on top of it. Add hydrochloric acid or salt as before, let settle, test, pour off the liquid and throw it away as before. Repeat this until you have a pound or two of chloride. Keep it moist.

It usually pays to let this silver chloride accumulate for some time before refining it. We shall therefore leave it now, returning to it in Chapter VIII.

OLD FILTER PAPERS

These sometimes contain considerable value. Tear off and throw away any paper that is plainly worthless, and spread out the rest to dry. When you have several papers, burn them in a frying pan; ~~pour on gasoline~~ and burn until they will burn no more. If the remains are very dirty, put them in your sweeps or your paper storage. If fairly clean, add them to your next lot of filings.

WHAT TO DO IF YOU SPILL ACIDS OR CAUSTIC ON HANDS OR CLOTHING

Wash them at once with much water, and little or no harm will be done. With acids: *after* you have washed off all the acid possible, it may help to put on a little very dilute ammonia water, or a little bicarbonate of soda. With lye or caustic: *after* washing well with plenty of water, neutralize with a little lemon juice or vinegar, or some extremely dilute hydrochloric acid, say three drops of acid to a glassful of water. However, if you use plenty of water at once, you will not need any neutralizing treatment. In Chapter B of the Appendix, this subject is discussed in greater detail.

* * * *

As we said at the beginning of this chapter, there are several ways to refine this kind of scrap. In the next chapter we shall discuss some of the alternative methods.

CHAPTER VI

MORE ABOUT GOLD. ALTERNATIVE METHODS

(I) Alternative preliminary treatments. (2) Melting the material into a button. Quartation. (3) Removing base metals with acid. (4) Dissolving the gold in aqua regia. (5) Evaporating off the excess nitric acid. (6) Recovering the dissolved gold by alternative methods: sulphur dioxide; oxalic acid; sodium nitrite; metallic precipitants—copper, iron, zinc. (7) Washing and (8) Melting the fine gold. (9) Saving the silver. Summary. Questions and Answers.

* * * *

In Chapter V we described a standard way to handle high grade gold scrap. Briefly the steps were as follows:

(1) Preliminary treatments as required.
(2) If necessary, melting the material into a button, and rolling it thin or granulating it.
(3) Removing as much base metal as possible, using nitric acid.
(4) Dissolving the gold in aqua regia.
(5) Evaporating off the excess nitric acid.
(6) Recovering the dissolved gold with copperas.
(7) Washing the refined gold.
(8) Melting the refined gold.
(9) Saving the silver if worth while.

In this chapter we shall describe several alternative methods that are frequently employed. *The student should be thoroughly familiar with Chapter V before attempting to use or even to understand the present chapter, which indeed may well be skipped for the present.* He should carry through at least two small lots of metal according to the procedures of Chapter V, then try those outlined below. With that background of experience he can adopt for regular use the method that best suits his material and purposes.

In this chapter also we shall handle only high grade gold scrap or filings or dentures; no platinum-group metals, soft solder, rolled, filled or plated gold, amalgams, green gold of 16-k or better, or white-metal dental alloy.

Since we are assuming that the reader has already acquired some facility in handling acids and equipment, our descriptions will be less detailed than in earlier chapters.

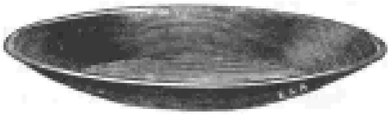
(I) ALTERNATIVE PRELIMINARY TREATMENTS

In Chapter V you were told to sieve your filings, then to remove iron with a magnet, then either to burn out the trash or to boil in caustic solution. Some workers burn them first, especially if they are very linty, then sieve, and finally use the magnet. Thus the order of procedure will be governed by the nature and proportions of the dirt to be removed.

At this point many workers weigh the filings; since it would be misleading to weigh them while wet, such operators will burn the trash rather than use the caustic treatment, which leaves the filings damp. Considerations such as these often determine the nature and order of the treatments.

Before using the magnet, give your filings time to cool completely after being burned; iron has no magnetism when hot. Remember also that some types of white gold are attracted to a magnet. In any case, there is always the probability that some particles of gold are caught up by the magnet, mixed with the iron particles. Some workers place all these particles in a jar of acid, usually dilute hydrochloric or sulphuric acid; the iron and steel dissolve, and at intervals the remaining gold is collected and refined.

Some workers like to pan their filings, the way miners pan dirt when looking for gold dust. If there is a chance that the stuff contains small pearls or other objects that could be harmed by heat, pan it without burning it. Some workers boil in caustic, or burn, to get rid of grease, and then pan. It takes only a little practice to get the trick of panning. Shift the flat pan round and round, with water, letting the water and the lighter particles slip over the edge, while the heavy bright metal collects in the bottom.



Gold washing pan. Eimer and Amend No. 29698.

When burning paper and trash out of filings, it hastens matters to add a little ~~gasoline~~ or alcohol.

(2) MELTING THE MATERIAL INTO A BUTTON. QUARTATION

In Chapter V we said that this step may or may not be necessary. But it is usually employed when much sand or emery is present. There are two other cases where it is advised: when there is good reason for reducing the metal to 6-k or lower, and when you have green gold that is 16-k or higher. (Green golds will be discussed again in Chapter VII.)

You will recall that when 6-k gold is treated with nitric acid, it promptly goes to pieces, the silver and copper dissolving, and the gold remaining as a dark powder. This gold powder, after thorough treatment with nitric acid, is frequently of high purity. Many shops, therefore, make it a practice to melt up *all* their gold scrap, adding enough other metal to reduce the gold content to 25% or less—that is, to 6-k or lower.

In that way they avoid steps 4, 5 and 6—dissolving in aqua regia, evaporating off the excess nitric acid, and precipitating with copperas.

The disadvantages of this plan are that it uses up much more nitric acid, and calls for large crocks, etc., for handling the bulky solutions that are required. Also,—for reasons that will be clear in Chapter XII—it is not suitable when platinum-group metals are present. But when platinum-group metals are absent, it offers certain advantages, and the student should become familiar with it.

It is necessary to decide what metal to add, and how much of it. Many shops add silver. Since they recover it later on and use it over and over again, this involves comparatively small expense. Other shops use copper or brass; this does not cost much initially, but since it is not feasible to recover the copper or brass for re-use, the expense may be considerable in time. Rolled- or filled-gold scrap, or electroplated gold scrap, and old jewelry made of these materials are often used for this purpose, and if you have such scrap on hand you will want to use it. However, for this first refining, we ask you to use silver, or clean copper, or clean brass. Later, after you have studied Chapter VII, which covers rolled and filled stuff, we advise you to make up a button with it. But for reasons that will then be clear, we ask you now to use silver, or clean copper, or clean brass.

You must next decide how much metal to add.

You want the resulting button to be about 6-k (25% gold) or less; the other 75% to be metal that will dissolve in nitric acid. Suppose your original scrap ran about 15-k on the average and weighed 100 dwt. Fifteen-karat gold is $^{15}/_{24}$ or $^{5}/_{8}$ gold; $^{5}/_{8}$ of 100 dwt. is 62½ dwt. The rest, or 37½ dwt., is metal that will dissolve in nitric acid. You want to make up a button that will be one part gold to three (or more) parts metal that will dissolve in acid; 3 times 62½ equals 187½. Your metal already contains 37½ dwt. soluble metal, so, if you add 150 dwt. of silver or copper or brass, your button will be one-quarter gold.

(This practice of making a button that is one-quarter gold, is called *quartation* or *inquartation* and has been employed for many years in assaying and refining.)

If you have doubts as to the fineness of the original material, add more silver or copper, rather than less.

The resulting button should be rolled thin if possible, and cut up into small pieces, which are then twisted and annealed. Usually the metal is too brittle to be rolled, so it is melted again and granulated.

(3) REMOVING BASE METALS WITH ACID

In all cases, the object of this step is to remove as much as possible of the base metals and silver. Nitric acid is used in the majority of cases, especially in the small jobs. When very large lots, running 100 ounces and over, are treated, sulphuric acid may be chosen; but it is suitable only when the added metal is silver, when the copper content of the resulting button is 10% or less, and when the lead content is low. Sulphuric acid is cheaper than nitric, but more unpleasant to handle. Since your purpose at this time is to learn the various modifications of these processes, we suggest that you now take a button in which silver is the added metal, which contains little or no lead, and in which copper runs not over 10%, and treat it with sulphuric acid instead of nitric acid.

A small lot would be treated in a casserole or flask. Large lots are treated in cast iron pots; sulphuric acid, so long as it is concentrated, has surprisingly little effect on cast iron. Heavy fumes are produced, differing chemically from those yielded by nitric acid, but equally offensive and dangerous. The mixture should be stirred often.

From two to three ounces of concentrated sulphuric acid are needed for each ounce of metal (more or less), and the mixture is heated cautiously until action begins.

When the action of the acid ceases or becomes very slow, let the vessel cool. This takes some time, because boiling sulphuric acid is much hotter than boiling nitric acid. Then cautiously ladle the liquid into a barrel or big crock of water. Pour this acid into the water, slowly. (*Never pour water into sulphuric acid*—it would instantly become steaming hot and spurt out. Instead, *pour the acid slowly into the water,* giving the mixture time to cool.) Leave the remaining metal in the vessel and treat it with a small lot of fresh acid, breaking up the lumps. Finally scrape it into a porcelain dish. Do not put water into the iron pot, because dilute sulphuric acid attacks iron rapidly.

The solution in the barrel contains dissolved silver, copper, and other base metals in the form of sulphates. Often when ladling it into the barrel of water you will see a white cloud form, which may or may not redissolve as you stir it through the water; this is silver sulphate. Silver sulphate dissolves scantily in water. That is, if much water is present, all the silver sulphate may dissolve. Since the quantity of silver present may be considerable, your next task is to save it. As before, you add either hydrochloric acid or a solution of table salt, and the insoluble silver chloride will be precipitated as a white cloud, which does not redissolve on stirring. Let it settle, then test the top liquor with another drop of salt to see if all the silver is down. If not, add more salt, and let it settle again.

After a satisfactory test, pour off the liquid and throw it away, as it should contain nothing of value. Methods of recovering the silver from the silver chloride are given in Chapter VIII. (If your original material had contained platinum or palladium, this liquid would be of value, but that is another story.)

Returning now to the gold in the porcelain dish: wash it well, to remove all sulphates of copper or silver. As we said before, this gold may be as pure as you require. The exact purity will depend mainly upon the nature of the metal you started with, partly on your skill and patience, and partly on the composition of the button you obtained by inquartation. Thus, if the gold in your button is too high, say 30% or so, the gold you recover will be of doubtful purity. (That is why some workers make up their buttons with a gold content of only 10% or 15%, although this means added expense in acid and time, and rarely pays.) Note also that if your original material contains much lead, sulphuric acid may not remove all of it.

When highest purity is required, this gold must be dissolved in aqua regia and precipitated again. Chapter XV on the special repurification of precious metals tells you more about this.

(4) DISSOLVING THE GOLD IN AQUA REGIA

When you handle large quantities of metal, you will use larger vessels, but the processes will not differ in principle. Filtering a big jar of solution is slow work, but it can be hastened by such devices as the filter pump and the Büchner funnel. These are described fully in Chapter XX. Hot aqua regia works more rapidly than cold, but you are advised not to let it boil, because boiling drives off the acids and wastes them; gentle heating on the steam bath is better.

(5) EVAPORATING OFF THE EXCESS NITRIC ACID

Here again the steam bath is advised, especially for large quantities of material. Sometimes this evaporation may go too far, and brown metallic gold will bake out onto the dish. You can easily dissolve this baked out gold (without adding any nitric acid) in this way: cover it with a few drops of full-strength hydrochloric acid, then slowly add a few drops—not more—of a solution of sodium chlorate in warm water. A very small amount of this sodium chlorate solution will do the work; add it a drop at a time, tilting the dish to wash the dissolved gold into the syrup. Stir well, as this mixture of chlorate and hydrochloric acid can form an explosive gas, especially when cold, but if your dish is warm, and your chlorate solution is warm, and if you work slowly, little if any of the explosive gas will collect.

(6) RECOVERING THE DISSOLVED GOLD BY ALTERNATIVE METHODS

In Chapter V you were told to use copperas (ferrous sulphate) to precipitate the gold that was dissolved in the aqua regia. Copperas is not the only reagent that will accomplish this, though it is the most popular one. It is cheap, easy to use, obtainable everywhere, and offers no hazards; in time it will lose its strength if exposed to air, but with ordinary care it lasts for years. It is the small refiner’s standby.

There are several things to be considered when choosing a precipitant: its cost; the ease of handling; and the completeness and cleanness with which it works. That is, you want it to bring down 100% of the dissolved gold, and nothing else. This final consideration—the cleanliness with which it works—is one that has been somewhat neglected, with the result that some recovered gold is not pure enough to use.

Reagents that we shall describe here are: sulphur dioxide gas; oxalic acid; sodium nitrite; and the metallic precipitants such as copper wire, sheet iron and zinc. This does not complete the list of possible precipitants, but covers those in general use. Each has its advantages and its disadvantages.

SULPHUR DIOXIDE GAS

A new way of precipitating gold from aqua regia solution employs sulphur dioxide gas. This method is destined to become very popular, especially among large users.

Sulphur dioxide gas is dispensed in steel cylinders, something like oxygen tanks; several sizes are on the market. It is one of the gases used in refrigerators such as Frigidaire. In the past it has not been generally available, but its sale is becoming common, and it is now available in most parts of the country at a price within the reach of even the small user. In most cases the dealers sell the tank with its contents, and then will refill the tank or exchange it when empty for a full one, at a reasonable charge.

When bubbled slowly through your regia aqua solution, it throws down the gold as that same brown powder that you obtain with copperas.

It is normally much cheaper in operation than are other methods equally suitable. Even with beginners the gas is cheaper, and time and labor costs are less. It is also less bulky than copperas or other materials. Thus, suppose you have two gallons of solution containing gold; if using copperas you would dissolve the copperas in two or more gallons of water; that means four or more gallons to handle and filter. Other reagents, such as the oxalic acid that is shortly to be described, also involve bulky solutions, which sometimes require heating, an operation which involves further time and expense.

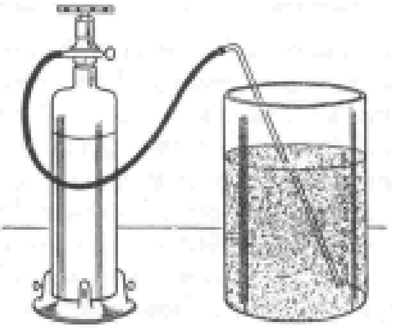
Sulphur dioxide gas is simply passed into the original two gallons of solution. This saves floor space, equipment, and time—especially when filtering. The gas keeps indefinitely until used.

Most workers report that they get purer gold with sulphur dioxide than with any other precipitant. Even when soft solder is present, the fine gold obtained is apt to be of high quality. In other words, sulphur dioxide is not likely to “carry down” other substances with the gold, and the chemist speaks of it as giving a “good separation.”

Sulphur dioxide has two disadvantages: first, the initial cost is high, since you have to buy the first cylinder, as well as its contents. After that, the expense is low, as you return the tank to be refilled, or exchange it for a full tank. The average medium sized shop will find that a tank will last for a year or more, so the bother of changing tanks does not come often. The second great disadvantage is that the gas has an extremely evil smell—the smell of burning sulphur. If it escapes from the tank it is stifling and dangerous, also it tarnishes shop machinery, jewelry and other metal objects. When using it you must work near a fan or under a hood. However, you have already had some experience in handling dangerous fumes, and this is no worse than those you are already familiar with. Store the tank in a safe place and handle it intelligently, and it will be no more dangerous than your illuminating gas.

HOW TO RECOVER DISSOLVED GOLD WITH SULPHUR DIOXIDE

As in Chapter V, you must remove the excess nitric acid by evaporating the solution to a syrup, adding hydrochloric acid, and ~~boiling~~ down again, finally diluting with considerable water and getting rid of all sediment. This procedure is necessary when you use copperas, or sulphur dioxide, or any other precipitant. Be sure that the resulting solution is perfectly clear and free from sediment or cloudiness.



Precipitating gold with sulphur dioxide gas.

The solution should now be in a jar or crock, preferably one that is tall rather than wide. A glass vessel is pleasant to work with, since it permits you to watch the operation. Simply bubble the gas through the solution, a bubble at a time, as shown in the sketch. Use tubing of at least ¼ inch inside diameter; smaller tubing might become clogged by the gold. Fasten the tank in an upright position, so that it cannot tip over; the gas within is really in liquefied form, and if the tank were on its side, the liquid would run out, which would be wasteful and very unpleasant.

At first the bubbles of gas will all be absorbed. Let them pass in slowly, say sixty to a hundred bubbles a minute. After five or ten minutes let them run more slowly. The solution will soon become dark with the precipitated gold. Stir gently, to bring all parts of the liquid in contact with the bubbles.

The length of time required will depend upon the quantity of solution you have, the amount of gold it contains, also whether you removed all excess nitric acid or not. Normally it takes about 45 minutes to throw down 10 ounces of gold contained in two gallons of solution, assuming that you had removed practically all the excess nitric acid.

The beginner sometimes finds that the gold is very slow to come down. Usually the trouble is that the liquid contains too high a concentration of acid; that is, maybe he failed to evaporate off all his excess nitric acid; or maybe he used too much sulphuric or hydrochloric acid in previous steps. One remedy is to add water to dilute the liquid and reduce the concentration of acid; another is to add pinches of sodium carbonate, a very small quantity at a time, stirring well. When the acid concentration is right, the dark cloud of precipitated gold will appear promptly.

Let the powder settle as usual; take out a few drops of the liquid and test it to be sure that you have used enough of the sulphur dioxide to throw down all of the gold; place a few drops in a test tube, heat it gently to boiling, and then add a clean green crystal of copperas and watch to see if any more gold powder appears.

When you are sure that all the gold has been precipitated, let it settle, pour off the solution as usual, and collect the gold powder, and wash it with plenty of hot water, then with hot strong hydrochloric acid (to remove dissolved copper, etc.), then rinse well, dry, and melt as usual.

If your material had contained no platinum metals, the solution will now be worthless and ready to throw away.

PRECIPITATING GOLD WITH OXALIC ACID

Oxalic acid is often used to precipitate gold from aqua regia solutions, but since it is relatively expensive, it is usually saved for occasions where the purpose is to obtain specially pure gold; that is, when the gold you start with is already nearly pure enough for your purpose. Thus, suppose you had your gold content down to 6-k or less, had dissolved out the base metals with nitric acid, and had obtained a gold residue that was almost pure enough to be used again. This in turn you had dissolved in aqua regia, and you are now ready to re-precipitate it. This aqua regia solution therefore contains only small amounts of other metals. This is a case where oxalic acid might well be chosen as the most suitable reagent.

You will observe that copperas and sulphur dioxide were employed on solutions that contained (in addition to dissolved gold) much dissolved copper, zinc, and possibly nickel and other metals.

Oxalic acid has this advantage over copperas: it does not introduce any iron or other material which, if melted in with the fine gold, could hurt its quality. The disadvantages are its cost, and the fact that when using it you must heat your solutions, both the aqua regia solution and the dissolved oxalic acid that is added to it, preferably to the boiling point. Hot solutions, especially when bulky, are awkward to handle, and may be dangerous. For these reasons, as we said, oxalic acid is usually reserved for jobs where the quantity of solution is relatively small, or when you are working with a solution that contains little or no dissolved base metals.

The method of using it, therefore, will be described in Chapter XV on the special purification of gold. You should become acquainted with this method, even though you do not plan to use it regularly.

PRECIPITATING GOLD WITH SODIUM NITRITE

This method is mentioned in British Patent 380,324, February 12, 1931. One of its advantages is that this reagent, if melted in with the fine gold, will cause no trouble; sodium nitrite is chemically related to sodium nitrate, and the latter, often called Chile saltpetre, is used as a flux and purifier when gold is melted. Sodium nitrite is not expensive, but it may weaken on long standing and eventually lose its power to react with gold solutions.

The method of using it is simple—practically the same as for copperas. The aqua regia solution is evaporated to a syrup as usual, taken up with water and a little hydrochloric acid as usual, and filtered clear as usual. Do not use too much hydrochloric acid;

the final clear and filtered solution should contain not more than about 5% of total acids. This includes the sulphuric acid you added to your aqua regia. If too much acid is present, the acid will react with the nitrite and waste it, producing reddish fumes, but no gold will come down. The nitrite may be added in solid form, a little at a time, or may first be dissolved in water, as convenient. The gold appears as an attractive yellow or brownish powder, which settles promptly under normal conditions—that is, when the solution is not too concentrated. If it seems slow to settle, add water.

Finally, after proper tests, pour or filter off the solution, discard it, and wash the gold as usual.

METALLIC PRECIPITANTS—COPPER, IRON, ZINC

One of the oldest ways to get gold out of solution is to hang bunches of copper wire in the jar. The copper slowly dissolves and grains of metallic gold appear in its place, clinging to the remaining copper. (The process is often spoken of as "cementing the gold out," as the same method can be used to take silver out of solution, and the resulting grains of silver bear a fancied resemblance to cement and are called "cement silver." The phrase was then extended to cover the similar process when applied to gold.) At intervals the grains of gold should be knocked off, to expose a fresh copper surface.

The process is slow, and you must test the liquid now and then to see if the copper has had time to remove all the gold. When you are sure that this has taken place, the liquid (which by now is deep green with dissolved copper chloride) should be dipped or filtered off and thrown away. The remaining metal consists of gold and probably bits of unused copper wire. It should be washed, boiled in nitric acid to remove all the copper, and finally washed, dried and melted as usual.

This method has the disadvantage of being slow, and also more expensive than other methods except in those rare cases where you can use the dissolved copper in some manner or other. Its less obvious disadvantage is this: if any platinum or palladium should be present, they will come down with the gold, in metallic form also. This means that your "refined" gold will simply have to be refined over again in order to save these two metals and provide you with pure gold. In this respect the method differs conspicuously from copperas, sulphur dioxide, sodium nitrite, or oxalic acid methods; you will recall that when these latter are used, any platinum and palladium will remain *in solution* while the gold alone is thrown down. This difference is important.

Iron and zinc may be used in the same way; wire, foil, shavings, or granulated metals are used. The reaction is similar to that between copper wire and dissolved gold; the iron or zinc dissolves and the metallic gold is cemented out in its place. Iron and zinc work somewhat more rapidly than copper. The disadvantage here is the same as with copper; if platinum or palladium be present, they also will come down with the gold. In addition, whatever dissolved copper is present will also come down. The result is a mass of granular particles of gold, copper, platinum, and palladium, mixed with any iron or zinc that may not have been used up in the reaction.

These methods, therefore, are not true refining methods, since the gold they bring down is mixed with quantities of other metallic particles. Accordingly "cementing out" is done only when the purpose is simply to *recover* precious metal, without regard to its purity. Instances of this will come up in later chapters.

(7) WASHING THE FINE GOLD

In Chapter V we washed the fine gold powder first with water, then with hydrochloric acid, then with water again. Some people use two acid washes. Sometimes sulphuric acid is used instead of hydrochloric, thus: cover the powder with cold water and add a few drops of acid, slowly, and stir well. (Do not add the water to the acid.) Work slowly or it may spatter. Heat to boiling, then wash well with plain water to remove the acid, following the routine suggested in Chapter V.

(8) MELTING THE FINE GOLD

(9) SAVING THE SILVER

Melting the fine gold and saving the silver will be discussed fully in chapters of their own Chapter XV, Chapter A of the Appendix, and Chapter VIII so no more will be said about them now.

* * * *

To summarize:

High grade gold scrap is treated as follows:

(1) Preliminary treatments: sieving, burning, panning, treatment with caustic and with the magnet, as required by circumstances.

(2) Melting into a button if necessary. In some cases a metal such as silver or copper or brass is added in sufficient quantity to

reduce the gold content to 25% or less. Rolling the button thin, or granulating it.

(3) Treatment with nitric or sulphuric acid, to remove base metals and silver.

(4) Dissolving the remaining gold in aqua regia, if desirable.

(5) Evaporating off the excess nitric acid.

(6) Recovering the dissolved gold, using copperas, or sulphur dioxide, or, in certain cases, oxalic acid, sodium nitrite, or a metallic precipitant.

(7) Washing the fine gold.

(8) Melting the fine gold.

(9) Saving the silver when advisable.

In Chapters XXI and XXII of this book, other alternative methods, suitable primarily to the large plant, are described.

* * * *

In this chapter the following equipment and chemicals are mentioned for the first time:

Flat pan for "panning" filings; metallic silver, copper, or brass, to serve as added metal; cast iron pot; sodium chlorate; sulphur dioxide; oxalic acid; sodium nitrite; metallic precipitants such as copper, iron or zinc; rubber and glass tubing for use with sulphur dioxide.

Note that all of these materials are employed in alternative methods; none are absolutely essential, and many workers will not find them desirable.

* * * *

QUESTIONS AND ANSWERS ON CHAPTER V AND VI

AQUA REGIA. Q. What is the best mixture of nitric and hydrochloric? Some people say one part nitric to three parts hydrochloric; you say use four parts hydrochloric.

A. The most efficient mixture for dissolving gold contains at least four parts hydrochloric acid or more. However, remember that any mixture of these two acids will dissolve gold to some extent, the action ceasing when one ingredient is used up. Also, nitric acid plus a chloride such as table salt or ammonium chloride, will dissolve gold; and hydrochloric acid plus a nitrate such as saltpetre, will also dissolve gold.

CHEMICALLY PURE ACID VS. COMMERCIAL ACIDS. Q. Chemically pure acids cost much more than the ordinary acids. Would it not pay to use the cheaper one?

A. In some cases the cheaper acids are satisfactory. This book endeavors to indicate which kind to use. In general the purer acids are more concentrated than the cheaper ones, and are therefore more economical in the long run. However, concentration is not the only thing to be considered. Thus, when you treat gold filings with nitric acid to remove base metals, you do *not* want any gold to dissolve; you are told to use C.P. nitric acid for this work because cheap nitric acid normally contains a little hydrochloric acid as an impurity. Any mixture of nitric and hydrochloric acids will dissolve gold to some extent; in other words, cheap nitric acid will, because of this impurity, dissolve a little gold, and therefore should not be used in this procedure. These same facts apply to the platinum filings in Chapter III.

It should now be clear that when you want aqua regia, the cheap nitric acid is not objectionable. However, if you do not wish to keep two kinds of acid in stock, choose the C.P. grade, as it is suitable for every purpose.

* * * *

PURITY OF RECOVERED GOLD. Q. What will be the purity of the gold that I recover by these methods? Can I make really fine gold?

A. It depends first upon the amount and nature of the impurities that you start with, and then upon your own skill and patience. The final rinsings are very important.

Since these factors differ with each refining, it is impossible to make any statement regarding the purity of your final product. You will learn more from the next chapter about the effect of such impurities as tin and lead, and from Chapter XV, in which this point comes up again, you will learn how to repurify such metal as may require it.

In general we can say this: a careful worker, even a beginner, can expect to obtain gold fine enough for making up new alloys, if his original material contains no unusual impurities, and if he follows properly the procedure that takes care of the impurities that are present, and carries out the final washings with due patience. On the other hand, an experienced worker using the best methods known, will expect impure gold from stuff that originally contained large proportions of certain elements that are hard to remove, and he will repurify at least once.

For example, one worker reports: "Recently we had occasion to test the purity of our gold, by assay, by wet analysis, and by hardness. In all respects it corresponded with the Mint's one thousand fine (999.9) gold. This gold we have gotten without any re-precipitation, using simply the first precipitation with sulphur dioxide and boiling twice with hydrochloric acid." But such high purity should not be expected every time. In this case the original material is high-karat dental alloys. The same man, using the same methods, might not get such good results if his material had been, for example, dirty low-grade scrap containing much soft solder.

* * * *

RECOGNIZING QUALITY. Q. How can I tell whether my fine gold is really of good quality and fineness or not? Do I have to assay every lot?

A. The usual procedure is to melt the gold powder into a button, then roll or hammer it. With a little experience you can tell by the appearance of the button whether it is good or bad, closely enough for most commercial purposes. A good button has a characteristic yellow color, which rarely appears when impurities are present even in small amounts. It also shows a characteristic depression or “pipe,” a sort of dimple on its surface where the metal contracted on cooling.

When placed under the hammer or rolls, a good button flattens smoothly and easily. As the melters say, “It rolls like butter.” Most of the very large bullion dealers, whose business is to manufacture gold of definite purity, do assay each batch, but the jewelry shop whose business is simply to get gold for re-use, does not assay its refined gold. The beginner would do well to obtain some fine gold of unimpeachable quality, such as that sold by the U. S. Mint, and melt it and roll it, in order to see the characteristic color and “pipe” and to appreciate its characteristic softness under the rolls.

* * * *

COPPERAS. Q. What is copperas? Does it contain any copper?

A. Copperas does not contain any copper. The name is definitely misleading; it is an iron salt. One way to make it is to dissolve iron in sulphuric acid, then crystallize out the salt that forms. Its chemical name is ferrous sulphate, and it is also called green vitriol. When exposed to air the surface turns yellow. Only the green salt is useful in precipitating gold, the yellow stuff being worthless for this purpose.

CHAPTER VII

SOME SPECIAL CASES

Green gold. White golds. Rolled, filled, and electroplated gold, and gold scrap, containing soft solder. Procedure to be followed when tin and lead are present.

* * * *

It is now time to take up some of the materials that were excluded from study in Chapters V and VI.

GREEN GOLD

Acquaintance Experiments: Cover a piece of 16-k or 18-k green gold with nitric acid, and warm it. There will be no action; this is not surprising, since it contains so much gold. Now add a little hydrochloric acid to the nitric acid in the vessel, thus forming aqua regia. . . You expect aqua regia to dissolve gold, but in this case it acts for a few minutes, and then stops. Warm the aqua regia, and watch carefully. . . A firm coating of a grayish substance will collect on the green gold, and even prolonged heating in aqua regia will have surprisingly little effect.

The explanation is that green gold contains considerable silver, and, as you know, aqua regia does not dissolve silver but merely converts it into this whitish silver chloride. Eighteen-karat green gold is usually 25% silver.

These facts leave the beginner in a quandary. He says to himself: it contains so much gold that nitric acid will not dissolve it; and so much silver that aqua regia will not dissolve it; what is there to do?

One answer is to melt it with enough copper, silver, brass, or zinc to reduce it to 6-k or less; then it will yield to nitric acid and crumble to a powder. A second answer is to melt it up with enough gold (or other metal) to make it yield to aqua regia; this means reducing the silver percentage to 10% or less. And there is a third way out, as will be described in Chapter XVI, that is especially suitable when green gold is soldered to, or mixed with, platinum, as in the case of platinum-topped jewelry with a green-gold base.

You are already familiar with the idea of inquartation, or adding enough silver, copper, or brass, to reduce the gold content to 25% or less. This is the usual plan when green gold is refined.

The other alternative, of melting it up with some metal that will make it soluble in aqua regia, is not so popular, but the student should understand it. A button that contains more than 12% silver is very slow to dissolve in aqua regia. With silver as low as 8%, aqua regia works readily enough, especially if hot. (We are assuming that the other constituents are metals that are themselves soluble in aqua regia, such as gold, copper, zinc, or nickel.) We can easily imagine a situation wherein a jeweler might have on hand a little green gold, and considerable yellow gold, red gold, or fine gold. By melting all these together he would obtain a button of less than 12% silver, that would dissolve in aqua regia, and that could be refined by familiar methods.

WHITE GOLDS

White golds, to the refiner, are of two classes: those that are whitened with nickel and those that are whitened with palladium. The nickel golds are the cheaper and commoner class. Palladium golds are used frequently in the dental laboratory, sometimes in high grade jewelry, and sometimes in chemical apparatus; it is not unusual for platinum to be another constituent in these special dental golds. The refiner's first task, therefore, is to establish which class his white gold belongs to. If it contains palladium, with or without platinum, it must be handled according to the plan described in Chapters XI, XII and XIII, in order that the valuable platinum-group metals may be saved.

Chapter IX describes methods of determining whether your gold belongs to the nickel class or the palladium class. If after reading Chapter IX and utilizing the tests described, you are still in doubt, you are advised to assume that your white gold may contain palladium, and treat it accordingly.

And if you are sure that no palladium or platinum can be present —and if the gold is low karat, or of low price, you can be reasonably sure they are absent—your white gold should be refined exactly as described in Chapters V and VI, with which you are now familiar.

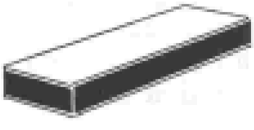
Nickel, which is such an important element in the commoner white golds, has a rather high melting point; you notice this when melting the scrap into a button. The button is apt to be brittle and difficult to roll; therefore it is customary to granulate it at once. Some nickel golds are attracted by the magnet and may be confused with steel.

With these facts in mind, the student is now ready to handle any of the nickel white golds.

ROLLED, FILLED AND ELECTROPLATED GOLD, AND GOLD SCRAP, CONTAINING SOFT SOLDER

Rolled and filled gold consist of thin shells of a gold alloy—usually low-karat gold—soldered onto a heavier core of brass or nickel silver.

Even in the better grades of filled goods, the quantity of gold is small. Thus, goods stamped "$^1/_{10}$ 12-k" at best will assay one-twentieth fine gold, the other 95% being base metal. Old jewelry whose surfaces are worn down will contain even less gold than the karat-mark will indicate. Electroplated gold contains an even lower percentage of precious metal.



Billet of base metal with thin layer of karat gold soldered to top and bottom, ready to be rolled.

For our convenience we shall group these three kinds of scrap together as "cheap" scrap. They have two things in common—they contain very little gold, and usually they contain soft solder. The scantiness of the gold, and the presence of the soft solder, combine to make this type of scrap relatively unprofitable and troublesome to handle.

Soft solder contains tin and lead, both of which are difficult to remove. Moreover, if small amounts are left to contaminate the recovered gold, they will make it brittle and useless.

When the depression of the 1930's forced many jewelers to go into the business of buying old gold, many shops that had previously handled only high grade gold bought old cheap jewelry, old spectacle frames, old jewelry that had been repaired with soft solder, and so on. They quickly found themselves in difficulty with their refining; many a refiner with years of good work behind him began to turn out brittle buttons, pale and crumbling “fine” gold, and unworkable alloys. In most cases the trouble was due to the tin and lead, which he had failed to remove completely.

The fact that some of this cheap jewelry is hollow, and is weighted with sealing wax, shellac, or lead, did not help matters.

It is the purpose of this chapter to clear up these various problems.

At certain times the United States Assay Office has not bought cheap scrap—rolled, filled, or plated stuff. However, the regulations change from time to time, and at certain times it may be wise to sell all this material to Uncle Sam. The reader is advised to apply for new rulings from season to season.

There are several ways in which this cheap scrap may be disposed of. The larger handlers sell it to a copper refinery. The stuff will then be treated as though it were impure copper, and the gold and silver will become by-products. When several hundred pounds are available, this method is normally chosen.

A second plan utilized by large shops is to melt it with low-grade wastes such as floor sweeps or polishings. Low-grade waste must be melted up with considerable clean metal in order to collect its precious metal particles into a button. If there is some rolled-gold scrap on hand, for example, it can be melted in with the sweeps; that saves the expense of buying clean metal for this purpose, and all the precious metals are collected and refined together. This is referred to again in Chapter XVIII.

A third plan, suitable to the average shop, is to use cheap scrap as the added material in the inquartation of high grade scrap, as described in Chapter VI. This gives the worker a button similar to that described in Chapter VI except that it probably contains tin and lead.

In a shop that handles gold and silver only—no platinum-group metals—this is an excellent scheme so long as the worker understands the effects of the tin and lead, and knows how to get rid of them. We urge the student to become familiar with this plan, as he will have many opportunities to use it.

Two other plans, less advisable, are mentioned now simply for the sake of the record:

(a) Stripping the gold layer off the base metal core, using a “reversed” electric current and a cyanide solution. The idea is to dissolve the gold layer only. This is hard to do economically, and is dangerous to the workmen. People who have equipment for electroplating or gilding, and who have had experience in handling cyanide, should experiment with this process, but others are advised not to. More will be said on this subject in Chapter XVI under the heading of "Green Gold with Platinum."

(b) Stripping the gold off by dipping the articles into aqua regia, and fishing them out as soon as all the gold is dissolved. This also is hard to do economically; sometimes the acid works in and acts more rapidly on the core than on the outside gold layer. We do not recommend this method.

* * * *

Sometimes the worker has on hand only cheap scrap, such as old spectacle frames, and wants to refine them as they are. That is, he does not wish to melt them up with sweeps, nor with high grade gold. Perhaps he has no facilities for melting them up at all. In that case he will use an acid method similar in principle to that described in Chapter V, making only such changes as are demanded by the tin and lead.

For your first refining of cheap scrap—rolled gold, filled gold, electroplated goods, or goods that have been repaired with soft solder—we suggest that you employ this modified acid method, which will now be described fully, in order to learn to recognize the effects of tin and lead, and to get rid of them. Having learned these important things, you can then use the method of inquartation when desired, as it employs the same general principles.

Acquaintance Tests: Obtain from your supply house small samples of pure tin and pure lead. A pennyweight of each will be enough. Do not use metals of whose purity you have doubts. The metals may be in pellets, foil, grains, or any other convenient form.

First take a bit of tin about the size of the head of a pin and cover it with a few drops of hydrochloric acid, plus a couple of drops of water. Heat to boiling and watch the results. Now do the same thing with a little lead; use a clean test tube or beaker for each test.

Note that hot hydrochloric acid dissolves tin promptly. It is slower in its action on lead. Now, let the lead-hydrochloric acid mixture cool. . . Note that a heavy precipitate of white crystals appears. This is lead chloride. Add some water to make up for evaporation, then alternately heat and cool the mixture, observing that considerable lead chloride will be held in solution by a little hot water, only to crystallize out when it cools.

You will note that the tin chloride, formed when the tin is acted on by hot hydrochloric acid, is not so markedly affected by heat.

Because of the above facts, we use hot hydrochloric acid to dissolve solder (tin plus lead) in cases where the hot acid can reach the solder. So, if your old jewelry shows lumps of soft solder, boil it in hydrochloric acid until the solder loosens and can be scraped off. But if the solder is inside the article, the hot acid will not reach it.

Second: Try the effect of hot strong nitric acid, first on a scrap of tin, then (in a clean test tube or beaker) on lead. . . The effect is quite different. In both cases the acid goes to work at once, giving off the usual brown fumes. . . The tin goes to pieces, and in its place appears a white pasty or slimy substance. We call this tin paste. The chemists call it meta-stannic acid. If you add some water the tin paste will thin out, like jelly, but it will not dissolve. This tin paste, which forms when nitric acid acts on tin (and at other times as well) is the main reason why tin is troublesome in refining.

The lead, as we saw at first, reacts promptly with the nitric acid, but in a few minutes it becomes coated over with a white salt, which soon becomes so thick that action ceases. When this happens, add a little water. . . The white salt will dissolve.

This means that lead, treated with strong nitric acid, forms a white salt of lead nitrate, which may coat over the lead so closely that the acid cannot reach it. But this lead nitrate will dissolve if water is added. In other words, lead nitrate is fairly soluble in water, less soluble in concentrated nitric acid.

Because of these facts, we dissolve lead metal in diluted nitric acid. But when it comes to tin we see that, while nitric acid acts on it, it does not really dissolve it, but merely converts it into that troublesome tin paste.

Third: Repeat these tests, using clean test tubes and fresh samples of tin and lead, with sulphuric acid. Have the test tubes dry when making the first of these tests; just cover the small samples with a few drops of the strong acid, and warm cautiously.

Strong sulphuric acid, powerful as it is in some respects, acts rather oddly on metals. If diluted with an equal volume of water, or more, it acts much more like the other acids. Try this: take a clean cup or beaker, place in it an ounce of water, and then add slowly a quarter ounce or less of sulphuric acid. Add the acid slowly, and stir it between additions. Note how hot it gets.

(Never pour water into sulphuric acid. If you should it would at once boil and spurt out of the dish. Always pour the acid, slowly, into the water, stirring all the time.)

Now try the effect of the diluted acid on samples of tin and lead. . . We find that, if heated, the acid will dissolve tin promptly, but it does not dissolve lead at all; merely converts it into a white salt (lead sulphate) which does not dissolve in more water. If you still have some tin paste, left over from an earlier experiment, try the effect of sulphuric acid upon it. . . It dissolves it, whether dilute or concentrated.

It is valuable to repeat these tests using aqua regia, first strong, then diluted, to see what it does to these two metals. Use small new samples, and write down the results of each test.

By this time you will see that tin and lead are quite different in their reactions; also different from copper or silver. This means that each one demands attention in the refining process.

You are now familiar with the regular acid refining of high grade gold—the method described in Chapter V. By making a few changes you can adapt this method to take care of tin and lead.

PROCEDURE WHEN TIN AND LEAD ARE PRESENT—ACID METHOD

For your first refining of rolled, filled, or plated scrap, take clean stuff such as old spectacle frames, or old jewelry or collar buttons. Sometimes the thin outer layer of gold is firm enough to keep the acids from reaching the base metal core; therefore roll this scrap out thin, cut up the pieces and twist them to keep them from lying flat in the acid. In many cases the gold layer is so thin that this precaution is not necessary.

If there are visible lumps of soft solder, cover the articles with full strength hydrochloric acid, and heat to boiling until the solder loosens and can be scraped off. Then pour off the acid and throw it away, and wash the metal thoroughly to get rid of all traces of this acid. Wash till the washings ~~have no more sour taste, or~~ fail to turn blue litmus paper red. (See Chapter IX.)

Next, treat the metal with nitric acid and a little water, as usual. Since low grade scrap is mostly base metal, you will need much more acid than in Chapters V and VI, and there is much more chance that it will boil over, so add the acid slowly. This dissolves all the copper, silver, brass, zinc, iron, cadmium, and nickel, that the acid can reach. Tin is converted to the gelatinous tin paste. Lead turns into the scantily soluble lead nitrate; add a little more water, and all the lead nitrate will dissolve.

Pour or filter off this solution, looking out for flakes of gold. Usually the liquid contains so little silver, if any, that it should be thrown away. Repeat the nitric treatment if necessary, then wash the residue well, but do not let it dry. The residue is gold, plus tin paste, plus such base metals as were not reached by the nitric acid.

Next, mix up a little sulphuric acid and water, half and half (pour the acid into the water, slowly, and stir all the time) and cover your residue with this solution. Warm gently. This dissolves the tin paste, dissolves any remaining tin metal that the acid can reach, and changes any remaining lead into white insoluble lead sulphate.

The next task is to pour off and get rid of this sulphuric acid solution. This is not as easy as it might appear; it is so strongly acid that it would destroy a filter paper, so it must first be diluted. The best way to do this is to pour everything—acid, residue, and all—into another larger vessel which contains considerable water. Let it settle somewhat, and you can then easily pour off and throw away the bulk of the liquid. Then get the washed residue back into your casserole for the next treatment.

From here on, follow one or another of the methods with which you are already familiar. Some workers will melt this gold residue (it usually is in the form of thin flakes) into a button first, but usually the most economical plan is to dissolve it at once in aqua regia. Its value will depend upon the type of stuff you started with, but it rarely runs as high as 14-k. It may still contain a little tin and lead, which must be taken into consideration in later stages.

Thus, when making up aqua regia, add some sulphuric acid, say an ounce of the concentrated acid to each pint of aqua regia, more or less. As we said in Chapter V, this sulphuric acid serves two purposes: it hastens the expulsion of the excess nitric acid, and it also helps to get rid of lead. You will now see how it does this: by converting the lead into the insoluble white lead sulphate, which will remain with the mud of silver chloride that is left after the other metals dissolve in aqua regia, and which is filtered out at the same time.

Tin dissolves in aqua regia, and will go along with the dissolved gold. Small traces of lead sometimes do the same. If you precipitate your gold with copperas, some tin paste may be carried down mechanically with the gold, and some lead may be precipitated with it as lead sulphate. (With sulphur dioxide there is less tendency for tin to be dragged down.) But if you use special care when washing the gold powder you can expect good results. Thus, without letting the gold powder get dry, wash it first with much hot water; then (second) boil it in hydrochloric acid to remove compounds of tin, iron, and copper; wash (third) in hot water to remove the acid; then (fourth) boil it in a strong solution of caustic soda to dissolve lead sulphate; and finally (fifth) rinse again in much hot water.

But the cautious worker does not melt up all his recovered gold at once; he takes about a pennyweight and makes a small test button. If it is good, he melts the whole quantity. If it is brittle or off color, he turns to Chapter XV and follows the suggestions given there for the further repurification of gold that is already of fairly high quality.

* * * *

NOTE.—As we go to press, we learn that the Western Electric Co. is working on a process for stripping the gold from gold-plated articles. Details are not yet available.

CHAPTER VIII

SILVER

Forms of silver encountered by the refiner. Characteristics and properties of silver; acquaintance experiments. Metallic silver wastes—scrap, filings, polishings. Silver chloride, and its conversion into metallic silver. Silver in solution: silver nitrate; silver sulphate; stripping and pickling solutions. Cyanide solutions of silver or gold; plating baths. Mirror solutions. Alternative methods of reducing silver chloride. Photographers' wastes.

* * * *

The reader is already familiar with many of the more important characteristics of silver. He knows that it is a white metal popularly included in the group known as "precious" metals. This inclusion has sometimes had unfortunate consequences, because silver, in spite of its beauty and usefulness, is much less expensive than the other precious metals. Thus, during the last few years the highest ratio, in terms of gold, was reached in November, 1919, when silver was quoted at $^1/_{15}$ the price of gold. In December, 1932, it fell to $^1/_{84}$ and in July, 1939, "foreign" silver was exactly $^1/_{100}$ the price of gold. This relative cheapness must not be lost sight of by the refiner, especially the beginner, when deciding how to handle a given lot of material.

FORMS OF SILVER ENCOUNTERED

The jeweler, dental mechanic, and refiner will encounter silver in several forms. These may be divided into two kinds—metallic and non-metallic. Of the metallic group the most valuable form is clean metallic scrap such as old anodes, old Sterling silver tableware, old silver jewelry, or the clippings from the silversmith's bench. Good quality silver filings are nearly as valuable. These will be discussed in this chapter. The fine metallic particles found in polishings, floor sweeps, and wash-barrel deposits will be discussed in Chapter XVIII on Low-Grade Wastes.

Silver is also present as an alloying element in most gold alloys. Even the higher grade dental golds usually contain silver, and some of the green golds used in jewelry contain as much as 25% silver. In the processes of refining, this silver is separated from the gold and other elements, usually in the form of silver chloride.

Non-metallic wastes include silver salts such as the silver chloride and silver sulphate which the reader has already met in Chapters V and VI; and the solutions used in pickling, stripping, and electroplating. Most of these solutions are acid in reaction; a few, such as the cyanide plating solutions, are alkaline.

Photographers' wastes, and the solutions left over from the making of mirrors, do not come strictly within the scope of this book, but so many people are interested in their treatment that a brief discussion of them will be included.

This chapter will try to cover the ways in which these forms of silver—metallic and non-metallic—may be converted into clean pure metallic silver, ready to be used again or sold.

METALLIC SILVER WASTES

Clean scraps of silver metal, such as clippings of Sterling silver, old Sterling tableware, wire, sheet, and the like, if perfectly free from solder or Britannia metal, are usually melted, cast into ingot form and used again. Impurities are apt to get in, however, and bits of solder, binding wire, iron from the shears, etc., will cause brittleness if melted into the bar, and a good proportion of what seems to be clean scrap will yield a bad ingot. The process of melting often changes the fineness of the Sterling silver, and in large plants these ingots are assayed to establish their quality before they are re-used.

Good quality silver filings should be sieved, gone through with a magnet, and the organic matter should be burned out before they are melted and cast into ingot form. The result, however, is frequently a brittle bar, which may be sold as is, or perhaps used as the "added metal" in the inquartation of gold.

Obviously these metallic wastes could be refined by acid methods; the process is simple and the reader probably has guessed the steps that might be used. But with prices at present levels it would not pay; much acid and labor would be required, and it is better to return brittle bars to the professional refiner, who will refine them in large quantities according to methods described in Chapter XXII.

Old suspension wires used in silver-plating become coated with silver and finally break. These may be melted up with filings or scrap that is to be sold.

NON-METALLIC WASTES

These include various salts of silver, either in solid or liquid form. Of these the most important is silver chloride, and its recovery will be discussed fully in this chapter.

Before going further, it would be well for the reader to recall the several acquaintance experiments in previous chapters, in which he handled silver. Thus in Chapter V he observed that silver dissolved readily in nitric acid, and he prepared some silver nitrate, laying some aside for later examination. When freshly made from fine silver, the silver nitrate solution is colorless, like water. If made from coin silver it will be greenish, the green color being due to dissolved copper nitrate. If exposed to light, silver nitrate (as well as most other silver salts) darkens and finally becomes black.

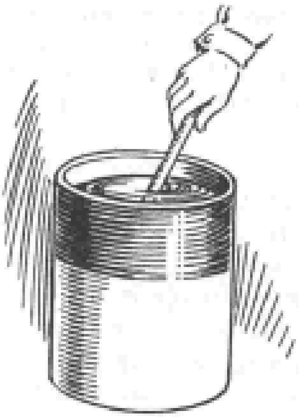
Silver also will dissolve in hot concentrated sulphuric acid, to form silver sulphate. (See Chapter VI.) Aqua regia does not dissolve silver, but attacks the surface layer and converts it into a coating of silver chloride. Straight hydrochloric acid if hot and concentrated does the same thing; cold dilute hydrochloric acid has almost no action on silver.

One of the Acquaintance Tests of Chapter V was the addition of a little hydrochloric acid or table salt to a solution of silver nitrate. The resulting precipitate of silver chloride was seen to form as a white cloud which gradually settled to the bottom of the vessel.

For the last five chapters silver has been accumulating in our Silver Jar, in which we originally placed the nitric acid with which we had dissolved as much as possible of the base metals that contaminated our gold scrap. This liquid contained dissolved silver nitrate, copper nitrate, probably zinc and nickel nitrates as well. We added some hydrochloric acid (or perhaps some table salt) and we obtained the white precipitate. This silver chloride was allowed to settle, and when we were sure that the liquid over it had been freed from all dissolved silver, we threw the spent liquid away, leaving the deposit of silver chloride in the jar. At our next refining we put the new nitric solution in on top of the old white chloride, and again we added hydrochloric acid or table salt, and again let the heavy chloride settle, and again, after proper tests, threw away the spent liquid.

Silver chloride obtained as above, or secured in other ways that will soon be mentioned, is on hand in almost every shop that handles precious metals.

Many jewelers, especially those who are cramped for room, do not refine it; they wash and dry it and sell it as silver chloride because of the difficulty in obtaining recovered silver of sufficient purity for the manufacture of new alloys. However this book would be incomplete without full instructions for carrying out this step.



It is almost as easy to refine a large lot of chloride as a small lot, and in general you are advised to refine silver salts only in fairly large quantities.

RECOVERING SILVER FROM SILVER CHLORIDE

There are several ways to reduce silver chloride to metallic silver. We shall first describe a standard method; you are advised to learn later the alternative methods described at the end of this chapter, then to choose the one best suited to your requirements.

In all methods you begin by collecting the deposit of silver chloride and washing it well, with much hot water, breaking up the lumps and washing until all green copper stains are gone. You will recall that lead chloride, which may be present and which looks like silver chloride, will dissolve in hot water. Lead sulphate, unfortunately, will not dissolve.

(Sometimes, when breaking up lumps of silver chloride obtained from dissolving gold alloys in aqua regia, you will find that some gold remains undissolved. Beginners often have this experience. If such bits of residual gold do appear, pick them out and return them for further treatment. This mistake is one that is easily recognized and should not happen to the careful worker. In later chapters you will learn that when alloys containing gold plus silver and platinum-group metals are dissolved in aqua regia, there are occasional complications and the silver chloride thus obtained may require special treatment, which will be discussed in the proper place. For the present we are considering silver chloride in which gold and platinum-group metals are absent.)

After the chloride has been thoroughly washed, cover it with diluted sulphuric acid, using about one part acid to fifteen or twenty parts water. (Pour the acid into the water, slowly, stirring all the time; it may spatter.) Use enough to cover the chloride well. Next add zinc, preferably in the form of shavings or thin foil. Zinc plates or shot work more slowly. The zinc will begin to dissolve at once, giving off many bubbles; as the zinc dissolves, the silver chloride that is in contact with it is changed into grains of metallic silver. Stir often. The bubbles consist of hydrogen gas; this gas will burn, and if confined may become a fire hazard; therefore it should be permitted to escape freely into the outside air.

For each pound of chloride, you will use about one-quarter to one-half pound of zinc (more or less) and about one-half pound of concentrated sulphuric acid.

The chloride changes to granules of metallic silver, called “cement silver.” Dip some out with a porcelain spoon and look at it, and you will see it looks quite different from the chloride.

Stir the mass often to permit all parts of the chloride to come in contact with the zinc as it dissolves. Stirring hastens matters, and also reduces the loss of zinc that dissolves while not in contact with chloride.

When all the silver chloride has changed over into cement silver, pour off the liquid and throw it away. The length of time required will depend upon the rapidity with which you bring zinc and chloride into contact with each other; that is why zinc shavings or thin foil work faster than thick plates; they present more surface.

The cement silver must now be freed of the unused zinc. This can be done by picking out any pieces large enough to be seen, then by dissolving the rest in weak acid. Mix up some weak sulphuric or hydrochloric acid—say one part sulphuric acid to twenty parts of water, more or less; or one part hydrochloric acid to fifteen parts water—and cover the cement silver with either mixture and watch for bubbles. When there are no more bubbles on stirring, you may conclude that all unused zinc has dissolved. Wash well with plenty of clean hot water to remove all salts and acid, and let the cement silver dry.

This process is entirely comparable to the precipitation of dissolved gold by means of copper wire or other metallic precipitants, as described in Chapter VI.

Usually the next step is to melt the cement silver into a bar or button; use a flux containing borax with charcoal or sugar, in a graphite crucible. The silver thus obtained is rarely pure enough for new alloys, and most jewelers sell it as is. However, if you use the inquartation process described in Chapter VI, this silver is precisely what you want for reducing your scrap gold to 6-k or less.

(Alternative methods of reducing silver chloride will be given later in this chapter.)

RECOVERING SILVER FROM SILVER NITRATE AND SILVER SULPHATE

These salts are formed by dissolving silver in nitric acid or sulphuric acid. Examples will be found in Chapters V and VI, in which we removed the silver from gold alloys. Nitric acid acts quickly on silver, dissolving it rapidly even when cold. Moreover, a small amount of acid will hold in solution a relatively large amount of silver, which is another way of saying that silver nitrate is a very soluble salt—100 grams of water being able to dissolve 213.4 grams of silver nitrate at room temperature. Sulphuric acid acts less readily, and the silver sulphate thus formed is only scantily soluble in water, only .55 gram being held in solution by 100 grams of water. If any larger quantity of silver sulphate should find itself in a scanty supply of water it would appear in solid form, that is, as a precipitate. This precipitate will dissolve on the addition of more water, as you will recall from Chapter VI.

The first step toward the recovery of dissolved silver from silver nitrate or from silver sulphate is, as you have already learned, to add hydrochloric acid or table salt, to bring down the insoluble white chloride. A consideration of the figures just given will show you why a nitrate solution may require more salt than a sulphate solution.

In general, a better precipitate is obtained if the solutions are fairly dilute; also if warm rather than cold. To explain: a "good" precipitate is one that settles quickly and completely, and that does not carry other substances down with it. Here is an interesting experiment to illustrate this point: divide a small amount of concentrated silver nitrate solution into halves, placing each in a beaker or glass. Make up a concentrated solution of table salt, and divide it also into halves. Now pour the strong salt solution into the strong nitrate solution, and set aside. Next, dilute the remaining salt solution with considerable hot water, and dilute the remaining silver nitrate solution with considerable hot water, finally adding these two hot dilute liquids together, and set aside as before.

In both cases you have a precipitate of silver chloride; but watch the two vessels and compare the way in which the precipitates settle. . . . You will find that when silver chloride precipitates in the presence of considerable hot water, it settles much more promptly than when formed in cold concentrated solution. Analogous experiments would show that when other substances (for example dissolved lead or palladium) are present, the precipitate obtained from a dilute solution carries down much less of the other substance.

Accordingly, in most cases—not all—when recovering dissolved silver we add hot water, and we dissolve our table salt or hydrochloric acid in hot water before adding it. The exception to this rule appears when a bulky or dilute solution is objectionable for one reason or another, such as lack of room, or when the solution remaining must undergo further treatment that would be made difficult by the presence of much water.

The second step in the recovery of silver from solutions of silver nitrate or silver sulphate is to collect the precipitated silver chloride, to wash it well, and then to treat it with zinc, as described in the previous section of this chapter.

ACID STRIPPING AND PICKLING SOLUTIONS

In this classification come old sulphuric acid stripping solutions used to remove deposited silver from electroplated articles before replating. Such solutions contain strong sulphuric acid to which has been added some nitric acid, or perhaps potassium nitrate. To recover the silver in as pure form as possible, dilute such solutions with considerable hot water, and let any deposit or sediment settle overnight. Pour or filter off the clear liquid, and add to it a solution of table salt, or some hydrochloric acid diluted with warm water. Treat the precipitated silver chloride as usual.

The sediment that was filtered out of the solution above should be examined, as it may contain considerable silver or silver compounds, mixed with material from the walls of the vessels, organic trash, and so on. If a lead vessel had been used, more or less lead sulphate, also particles of metallic silver deposited out on the lead walls, may be included. The deposit, therefore, may well be worth salvaging; usually it is melted into a button and sold with other impure silver.

The pickling solutions used to strip firecoat from silver articles belong to the same group, except that they may not require dilution. Otherwise they are treated the same as above: the sediment is filtered out and saved if worth while, and the silver is precipitated as silver chloride, as usual.

CYANIDE SOLUTIONS OF SILVER OR GOLD; PLATING BATHS

Old silver cyanide solutions, such as foul electroplating baths, sometimes contain enough silver to justify treatment. All cyanides are poisonous, and when mixed with acid they are doubly so. The fumes are deadly if breathed, and the solution should not be permitted to touch the skin if the latter is broken or chapped.

It is possible—possible but not advisable—to recover silver from cyanide solutions by the same method we used on acid solutions, namely to add plenty of hydrochloric acid. This method is not advised, however, for two reasons: the fumes are extremely dangerous to the worker, and in addition they may cause the solution to froth over and be lost.

Another way, safer and better, is to add zinc to the cyanide solution, and let it stand for some hours or days, stirring often. It is not necessary to add any acid; some workers do add a little acid, however (sulphuric or hydrochloric), because it hastens matters. We do not advise this because it produces the poisonous hydrocyanic acid gas, which may cause the liquid to froth over. The zinc may be in the form of turnings or foil, or zinc sheets may be suspended so as to hang free in the solution. Stir often. An ounce of zinc will reduce about a gallon of solution if agitated well, the exact quantity depending upon the amount of metal present and the thoroughness with which it is brought in contact with the zinc.

This process is essentially the same as the precipitation of gold by metallic precipitants (Chapter VI) and the reduction of silver chloride with zinc (this chapter). Silver appears in fine grains, called cement silver. Most old plating baths contain impurities such as dissolved copper, and the treatment with zinc will carry down the copper too, in grain form, and as a result the recovered silver will be impure. The usual procedure is to wash it well and melt it, the impure silver button being used in inquartation or sold to a refiner.

A second way to recover silver is to evaporate the old solution to a crust. This takes time, but if your shop has facilities for the task, the method has advantages. Be sure the fumes escape into the outer air. Heat the dried crust in a crucible; the salts that are present serve as a flux and on stronger heating a silver button will collect. The button is apt to contain copper and other base metals, and usually is sold with other silver-bearing wastes.

A third way to get silver out of cyanide solutions is to plate it out electrically, using steel or platinum anodes and a silver cathode. This is slow and the last few grains of silver are hard to recover, so in general the method is not recommended.

Gold can be recovered from cyanide solutions in the same ways. Thus old gilding baths are dried to a crust and melted down; or they may be treated with zinc (without acid) exactly as above, the cement gold being washed extremely well, then refined as in Chapter V or XV. Sometimes it pays to plate the gold out electrolytically, as described in Chapter XVI in the section on 18-k green gold with platinum, to which you are referred.

In an article entitled RECOVERY OF GOLD AND SILVER FROM PLATING SOLUTIONS,[1] Frank K Savage describes the methods used in the C. G. Conn plant at Elkhart, Indiana. The silver rinse waters pass over glass baffles that force it to travel some twenty-five feet before reaching the sewer. The space between the baffles is packed with zinc shavings, held in place with excelsior. In this particular plant the gold is plated out electrolytically from the drag-out solutions, work from the various gilding operations being rinsed into a tank where the free sodium cyanide concentration is kept at ¼ to ½ ounce per gallon. Carbon anodes and brass cathodes are used, the cathodes having cloth bags to catch any gold that may drop off after deposition.

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[1] The Metal Industry, New York Page 159, April, 1939

Further information on the recovery of these metals from cyanide solutions will be found in S. B. Christy's 171-page pamphlet entitled ELECTRO-DEPOSITION OF GOLD AND SILVER FROM CYANIDE SOLUTIONS.[2]

SOLUTIONS USED IN MAKING MIRRORS

These solutions are made up with silver nitrate and ammonia, to which is added a reducing agent such as sugar, or Rochelle salt, or formaldehyde, or the like. The compounds formed are apt to be highly explosive, and care must be taken to prevent any residues becoming dry. This hazard is emphasized in a pamphlet[3] published by the U. S. Bureau of Standards, and the reader is told that all vessels containing silver solutions should be carefully cleaned at once, and all residues disposed of without delay. The proper method of disposal is to dilute with cold water, then add enough hydrochloric acid to neutralize the ammonia (in which process the solution becomes warm) with sufficient excess to throw down the silver as silver chloride.

From here on the process is familiar, the silver chloride being collected, washed, and reduced to metallic silver as usual.

ALTERNATIVE METHODS OF REDUCING SILVER CHLORIDE TO SILVER

You are already familiar with the standard method, in which the washed silver chloride is covered with acid and left in contact with zinc to form cement silver, which is washed and melted into a button.

There are however several other ways of reducing silver chloride to metallic silver. The standard method is susceptible of variations. Thus aluminum or iron may be used instead of zinc. Aluminum, as powder, foil, or sheet, works more rapidly than zinc, and is much more apt to make the jar boil over. Also aluminum is more expensive than zinc. It is chosen only when rapid action is required, and the worker is warned to add it very slowly, with frequent stirring, because its action with acid produces heat, sufficient to crack the jar if produced suddenly.

Iron is cheaper than zinc and works more slowly. Flat iron plates may be used, the silver chloride being spread over them in a thin layer, the whole being covered with dilute sulphuric acid as before.

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[2] Bulletin 150 of the Bureau of Mines. Obtainable from the Superintendent of Documents, Washington, D. C. Price 25¢.

[3] THE MAKING OF MIRRORS BY THE DEPOSITION OF METAL ON GLASS. Circular No. 389 of the Bureau of Standards. Price 5¢ January 6, 1931.

Rake the chloride back and forth at intervals, to bring all parts of it in contact with the iron. Finally lift out the iron plates, which possibly can be used again.

The liquid which covers the cement silver now contains iron sulphate, also called ferrous sulphate or copperas; this was formed by the interaction of iron and dilute sulphuric acid. It is impure, and contains ferrous chloride and possibly other salts as well. However, you will recall that you used ferrous sulphate (copperas) to precipitate your dissolved gold. Some refiners, therefore, collect this ferrous sulphate solution and use it for this purpose; they let the cement silver settle, pour off the supernatant liquid, and sometimes evaporate it down and get the green crystals of copperas. In most parts of the country, however, fresh pure copperas can be obtained so cheaply that this expedient does not pay.

The cement silver obtained as above should be washed in dilute acid as before, to remove all unused aluminum or iron, and dried and melted as usual. If any copper salts were present in the original silver chloride, metallic copper will be present now, mixed with the cement silver.

REDUCING SILVER CHLORIDE THE DRY WAY

Here is another method which involves a different principle, and is quicker than the first method, but requires a furnace with a good draft.

After the chloride has been washed well with plenty of hot water, spread it out and let it dry. Mix up a flux of equal parts dry borax glass and soda ash; or use a prepared flux made for this purpose. When the silver chloride is perfectly dry, mix it well with an equal weight (or more) of flux.

Put the mixture into a large graphite crucible, filling it less than half full. Melt in a gas furnace, slowly. Unpleasant fumes come off and the crucible tends to boil over, so watch it and reduce the heat if necessary. As it boils down, add more chloride-flux mixture. Continue until everything becomes quiet, then let the mass cool in the crucible. The button will be metallic silver, the chlorine having gone off as fumes.

Here again the metal obtained is of doubtful purity, but convenient to use in the inquartation process described in Chapter VI.

PHOTOGRAPHERS' SOLUTIONS

With silver at present prices, there is small profit in these wastes, except when handled on a large scale. Photography produces silver wastes of several kinds: old films and prints, and the solutions used in developing and printing, the latter being the stuff that commands most interest. Large quantities of silver go into photography, at least one hundred tons of silver salts being dissolved annually by America alone, and the jeweler or small refiner may have occasion to handle hypo solutions to his advantage.

Several ways of recovering silver from old hypo (thiosulphate) solutions are in use, and by an unfortunate coincidence, at least three essentially different methods are commonly referred to as "electrolytic." This has caused confusion both in the literature and among users.

When silver is to be recovered from ordinary quantities of old hypo baths, such as accumulate in the average photo shop, the commonest procedure is to add sodium sulphide, which immediately precipitates the black silver sulphide; the liquid is discarded and the sulphide is washed and melted with a flux (litharge and soda ash perhaps) which gives a lead-silver button ready for further purification.

A second method, equally applicable to small or medium-sized lots, is the familiar one of adding metallic zinc, which gradually deposits cement silver. This method is cleaner than the sulphide method, but takes longer. The cement silver is melted into a button, which as before is often of doubtful purity. Since the reaction between the zinc and the dissolved silver depends upon the fact that zinc is higher than silver in the electromotive series of metals, the method is loosely referred to as an "electrolytic" method, even though no generator is involved.

Indeed, the name "Electrolytic Unit" has been given to a prepared device, which when immersed in an old hypo bath will collect silver upon itself, the solution being saved for re-use. Such a device is being provided by refiners for the use of their clients; it utilizes in a convenient form the principle that is employed when zinc dissolves to displace a heavier metal.

In both the above methods, the metallic silver obtained requires further purification. When large quantities of such silver are available, the most popular methods of purifying it are the Thum and

Moebius processes, described in Chapters XXI and XXII. These are true electrolytic methods, employing electric generators, an electrolyte, a heavy current of electricity, etc. The impure metal is made the anode in an acid bath, it is carried into solution by an electric current, and is then deposited out again on a cathode as pure silver, the impurities being collected in the electrolyte.

The Eastman Kodak Co. has worked out another and quite different method. It is truly electrolytic, in that the bath is traversed by an electric current provided by a generator, and silver is deposited on the cathode. The equipment required is extensive, and rigid control of the process is imperative; hence the method is one that has found successful application only where large quantities of film are being treated.

The Eastman Kodak Co. controls several patents covering both the principles and details of this method, which is described in an article entitled ELECTROLYSIS OF SILVER-BEARING THIOSULPHATE SOLUTIONS,[4] written by engineers of its staff.

The process is carried on in large cells containing 100 square feet of cathode surface, through which a current of 300 amperes is passed at 1 to 1.5 volts. At the anode, thiosulphate (hypo) is oxidized to tetrathionate and trithionate sulphate; at the cathode silver is deposited with small inclusions of silver sulphide and gelatin from the film; some of the tetrathionate is reduced to thiosulphate, which is then available for re-use.

The electric efficiency varies between 65% and 80% in large installations, and the yield per million feet of film is about 1200 ounces of silver. By utilizing the solutions from which silver has been removed, the consumption of fixing baths is reduced to 35% of that previously demanded.

When a simple silver-bearing hypo solution is electrolysed under ordinary conditions—with fixed electrodes, for example—as soon as the current is applied a stream of brown colloidal silver sulphide falls away from the cathode, yielding a dirty unfilterable liquid. For this reason earlier workers on this problem dismissed as impracticable the electrolysis of hypo solutions.

However, by strictly regulating several factors, electrolysis can be accomplished with the deposition of high-purity, mirror-bright silver. Vigorous agitation, together with proper concentration of acid, sulphite, and certain promoting agents, is essential.

In general, cells should be as large as will pass through a doorway, and the cathode assemblies, plus their load of deposited silver, should not be too heavy to be lifted by hand. The choice of building material for the

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[4] By K. Hickman, W. Weyerts, and O. E. Goehler. Journal of Industrial and Engineering Chemistry, pp. 202-212, vol. 25, February, 1933.

cells was found to be difficult, partly because of the corrosive action of acid hypo solutions, and also because, as the action proceeds, silver tends to deposit and spread from any spot where the cathodes touch the wall, eventually causing short circuits.

Carbon or graphite anodes are used; the cathode may be of Monel metal or Alleghany metal. The silver complex that deposits out is melted in 100-lb. lots in an iron crucible, with a little nitre. In the first six months of operation, the Metro-Goldwyn-Mayer plant at Culver City, California, with one tailing and four working cells, recovered 60,000 ounces of silver. There was a saving of 65% in fixing and precipitating chemicals.

OTHER PHOTOGRAPHIC WASTES

Old print paper containing silver can be burned, and the ashes collected and melted. Old film contains two valuable ingredients, the silver-bearing emulsion and the celluloid base. Some large establishments are salvaging both of these. They remove the emulsion with caustics, and the clean celluloid is sold for use in making campaign buttons and the like. At present silver prices, the profit on this kind of waste is small, even when relatively large lots are handled.

Several other metals, including gold, platinum, iron, palladium, uranium and selenium, find employment in photography, in printing papers and toning solutions. Occasionally it pays to burn such papers and to add sodium sulphide or zinc to such solutions. Chapter IX gives tests for the identification of such precious metals as these residues may contain. Photographic solutions normally contain complex organic chemicals, some of which inhibit the reactions of the heavy metals. Chapters XII, XIII and XIV describe recovery methods, some of which can be adapted to residues of this kind. The salvaging of these wastes by the non-chemist is not advised, partly because of their small intrinsic value, partly because of the complications occasioned by these organic chemicals.

CHAPTER IX

IDENTIFYING METALS IN SOLUTION

The need for identification. Definition of “in solution.” Equipment for making tests. Testing for gold in acid solution, with copperas. Testing for gold in alkaline or cyanide solution. Testing for silver. Stannous chloride testing solution, for all precious metals. Standard solutions of gold, platinum, and palladium. Using stannous chloride with platinum. With gold. With palladium. With silver. Usefulness of stannous chloride. If the tests are not conclusive. . . . Two or more precious metals. Dimethyl glyoxime for palladium. DMG and nickel. Other chemical tests—The glow test. Copper. Iron. Acid and alkaline solution: litmus paper. Other tests. A warning. Identifying metals in solid form.

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An important part of the refiner’s job is to know whether solutions do or do not contain dissolved metals, and, if so, roughly in what quantity.

Thus you have frequently been told to throw away a solution which had once contained precious metal. For example, in Chapters V, VI, VII and VIII you are told to discard solutions from which gold or silver has been precipitated. The beginner is always reluctant to do this, and as a result his shop is soon cluttered with jars and bottles of worthless solutions. Before long his troubles are further complicated by his forgetting what the various liquids originally contained. Finally in desperation he packs them up expensively and ships them off to some refiner, who naturally gives him nothing in return.

It is therefore advisable to test all spent solutions at once, and to throw them away promptly if they are worthless. Wash the sink out well afterwards with plenty of water, to protect the plumbing. In general it is well to send worthless solutions ~~directly down the drain~~, not into the settling tanks; being acid they may dissolve precious metals that are present in the settlings and cause their loss.

But before throwing away any solution, you must assure yourself by proper tests that it is indeed worthless. Fortunately there are several such tests, all easy to perform and so dependable that the most self-distrustful worker can soon use them with confidence. Two of the most useful ones are already familiar to you.

DEFINITION OF "IN SOLUTION"

But before describing these tests, we must first make clear what we mean by "dissolved metals" or metals "in solution." We mean that they are distributed throughout the fluid in the sense that sugar may be dissolved in water. Sometimes we may see particles in the solid form as a sediment in the bottom of a dish, like undissolved sugar in a teacup; this sediment is a different thing from a metal "in solution"—do not confuse the two. Some workers, especially those to whom English is an acquired language, make this mistake, and when they are told that there is no metal in a given solution, they will say: "But I see little pieces of it there in the bottom of the jar!" When metal is present in solid form, no matter how small the particles, we call it a sediment, or a residue, or a precipitate; it is not "in solution." Substance "in solution" will pass through a filter paper; if a substance will not pass through a filter paper, it is not "in solution."

(When you wish to test metal in solid form, your first step, as will be described on page 102, is to get it into solution.)

All of these tests consist of taking a small quantity of the suspected solution—which we shall call the "unknown"—and adding to it a substance that will show the presence of a *small* amount of the precious metal in question. That is the whole story in one sentence. Certain ways of handling the solutions tend to make the tests more delicate or more sure, and these will be described in turn.

EQUIPMENT FOR MAKING TESTS

Chemists generally use test tubes for making tests of this kind. Small glass beakers are almost as good. Porcelain spoons and the porcelain spot plates that will be described shortly are excellent in many cases. The porcelain spoon and spot plate are especially useful when the test involves a change of color, but they cannot be used when the solution must be boiled.

All testing equipment must be kept scrupulously clean.

TESTING FOR GOLD IN ACID SOLUTIONS, WITH COPPERAS

You will recall that you recovered dissolved gold by means of copperas. After the gold powder had settled, you tested the remaining liquid to see if you had thrown down *all* the gold, by taking a few drops of the liquid in a porcelain spoon and adding a clean green crystal of copperas. If after a few minutes a dark cloud formed around the crystal, you realized that your “unknown” still contained some dissolved gold. This is one of the most useful tests for gold, especially as it can be used even when other heavy metals such as the platinum-group metals are present in quantity.

Note that your unknown was originally an aqua regia solution, and you had driven off the excess nitric acid by repeated evaporations. You will also recall that copperas will not throw down the gold until all the unused nitric acid has been disposed of; it will produce brown bubbles but no brown powder. This fact must be remembered when using this same reaction as a test; that is, if on adding copperas you observe a brownness or darkening remember that this may be gold or it may be merely brown bubbles. To settle this doubt, repeat the test using a test tube or beaker, and heat the solution to boiling; brown bubbles will be driven off but brown powder (gold) will remain. Add enough copperas to be sure that you have “killed” any nitric acid that may be present, and if the gold is indeed present, you will soon observe the brown powder.

In order to gain assurance in making this test, practice first with solutions whose compositions you know, noticing for example how a concentrated solution behaves—how instantly the dark cloud forms; then take a few drops of this same solution and dilute it with three or four ounces of water and test it again; notice the difference in the appearance of the dark cloud. Repeat a third time, taking a single drop of your rich solution and diluting it with a pint of water, then testing the result; as your skill increases you will be able to detect smaller and smaller quantities of gold. This skill is especially useful to the man who buys old solutions for their metal value.

TESTING FOR GOLD IN ALKALINE OR CYANIDE SOLUTION

The test with copperas works only in acid solutions; it will not work at all in alkaline or cyanide solutions until the alkalinity is destroyed.

Thus, suppose you have an old cyanide gilding solution, and wonder if it might contain dissolved gold. Take about five drops of the suspected liquid in a small test tube or tiny beaker, stand near a window or an exhaust fan, and add four or five drops of hydrochloric acid. The fumes evolved are extremely poisonous—hence the need for working near an exhaust. Bring the mixture cautiously to a boil; this drives off the cyanide. Let it cool, and you can now test with copperas as usual.

TESTING FOR SILVER IN SOLUTION

This test also is already familiar. On several occasions in the past you have added hydrochloric acid (or table salt) to solutions that contain silver, and you have seen silver chloride form and settle as a white precipitate. You observed that a small amount of silver produced a surprisingly large amount of chloride.

Your purpose when examining spent solutions, to see whether they are worthless or not, is to recognize *small* quantities of precious metals—dissolved in a relatively large quantity of liquid. Accordingly you must give your eye some practice in recognizing small precipitates and thin clouds. Thus, take one drop of silver nitrate solution (left over from the acquaintance experiments of Chapter V, for instance) and dilute it with an ounce or so of plain water; then add a few drops of hydrochloric acid. You will see the same white cloud of silver chloride, but much less dense than before.

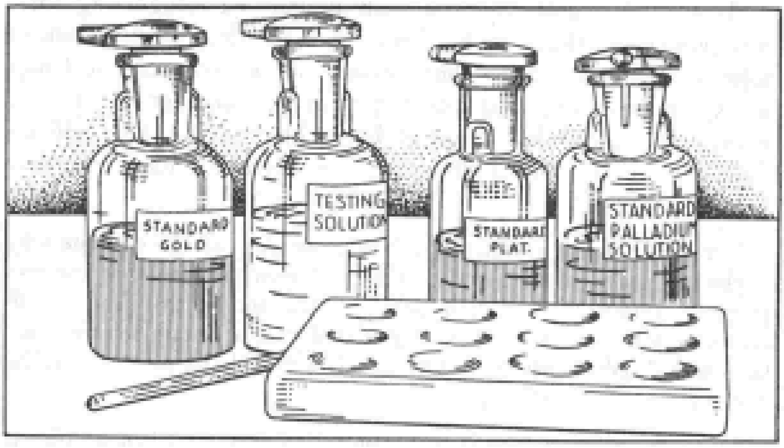
It is interesting to repeat this, diluting one drop of silver nitrate with a pint of water, stirring well. This will convince you that the test, properly conducted, is indeed delicate. Do not let this fact lose its economic significance—that is, if you find that a certain solution contains so little silver that the test gives only a thin cloud, you must realize that it is not worth refining.

This test for silver can be used on either nitric acid or sulphuric acid solutions; also on pickling solutions (which contain both nitric and sulphuric acid). Cyanide or ammonia solutions require slightly different handling; use a test tube or small beaker and take only a few drops of the unknown solution, and cautiously add five or six drops of hydrochloric acid; the ammonia mixture will become hot; with cyanide solutions there will be bubbles of the deadly hydrocyanic acid gas, which should be driven off by gentle heating. As soon as all the alkalinity is neutralized, the familiar silver chloride cloud will be visible.

A few other metals beside silver will give a white cloud with hydrochloric acid. You will recall from Chapter VII, that lead has a white insoluble chloride; so has mercury. In other words if your unknown gives a white precipitate on the addition of hydrochloric acid, it may contain silver, or lead, or mercury. Here is a way to settle all doubts: separate out a pinch of the white stuff. either in a filter or by letting it settle; wash it with considerable hot water, and if it dissolves it is lead chloride. Suppose it does not dissolve—that means it is either silver chloride or mercury chloride; add a few drops of strong ammonia... mercury chloride turns black, and silver chloride dissolves. These tests are easy and to most people fascinating.

STANNOUS CHLORIDE TESTING SOLUTION, FOR ALL PRECIOUS METALS

This solution, often called “Testing Solution A,” is extremely useful; rightly handled it reveals the presence of gold, silver, platinum, iridium and palladium in solution, and suggests the proportion in which they are present. It is easy to prepare and the ingredients are inexpensive.[1]



Dropping bottles, spot plate with cavities, glass rod.

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[1] For a full discussion of the testing of metals in solid form, see TESTING PRECIOUS METALS, by C.M. Hoke, Published by the Jeweler’s Technical Advice Co., New York City. Parts of this chapter are direct quotations from this pamphlet.

Purchase the following from any chemical supply house:

1 oz. stannous chloride crystals;

1 oz. or less *pure* tin metal—mossy, granular, or foil;

Porcelain spot plate with cavities—Eimer and Amend No. 29844 or equivalent; about 70¢;

Dropping bottle size 30 to 50 cc; Eimer and Amend No. 18824 or equivalent. (Dropping bottles have grooves in the stopper, and with them it is easy to get one drop, or as many drops as needed, without delay or waste.) Price 30¢ to 50¢.

You will also need hydrochloric acid and water, and a small glass rod. Total cost, not over $2.00; you can hardly make a better investment. These quantities will provide hundreds of tests.

Make up only a small amount of Testing Solution A at a time, as it does not keep indefinitely. Take about a pennyweight of the stannous chloride crystals (also called tin salts) in the dropping bottle, add a pennyweight or less of tin metal, and fill the bottle three-fourths full of water. Ordinary tap water will do. Now add a little hydrochloric acid, about 25 or 30 drops to a 30 cc. bottle. This gives a milky liquid which is ready to use. The tin metal will dissolve very slowly, and it serves to keep the solution in good condition. Label the bottle "Testing Solution A."

As we said, Testing Solution A when properly used shows the presence of precious metals in solution. In order to get acquainted with the color changes involved, you should first make up some solutions containing these metals. You should have a solution containing gold, one containing platinum, and another containing palladium. This method is so useful and fascinating that most users wind up with a whole series of standard solutions, so perhaps you might as well get a half dozen dropping bottles in the first place.

STANDARD SOLUTIONS OF GOLD, PLATINUM, AND PALLADIUM

To make a standard solution, dissolve a weighed piece of metal in a definite quantity of solution. Thus, dissolve two grains of fine gold in a few drops of aqua regia, wash it into a two-ounce bottle, and fill the bottle up to the mark with water; label it "Two Grains Gold in Two Fluid Ounces Water."

When your only object is to become acquainted with the various solutions, it is not necessary to use exact measurements. But later on, when trying to estimate precious metal in a solution, it will be extremely helpful to have standard solutions made up with a definite weight of metal in a definite volume of liquid. Therefore it saves time to make up your solutions in the beginning according to a definite plan. Some people use 100 milligrams to 100 cc. of solution. It makes no difference which unit you use, but use the same unit every time.

Use pure metals; not alloys. The gold and the palladium will dissolve readily in cold aqua regia, but it will be necessary to heat the platinum. Use as little aqua regia in each case as will do the work, then evaporate the solutions gently to get rid of excess acid, finally washing them into their respective bottles with a little water.

USING STANNOUS CHLORIDE WITH PLATINUM

Take the spot plate and drop one drop of the standard platinum solution into a cavity. Notice the pale yellow color. Add a drop or more of Testing Solution A. If properly prepared the two will react instantly to give a deep yellow or brown color. If too concentrated, the color will be almost black; in that case, dilute the platinum solution with an equal volume of water. This deep yellow color with Solution A is a characteristic of platinum and iridium.

WITH GOLD

In another cavity, place one drop of gold solution, and add a drop of Solution A. After several moments add several more drops of Solution A. Note the first intense dark color, deep purple or black. This is characteristic of gold. After it stands a few minutes, notice the purple stain on the white porcelain.

Now, in another cavity, take just one drop of your gold solution, and dilute it with five drops of plain water. Take one drop of this dilute gold, in another cavity, and add a drop of Solution A. Note that the color is still definite. Dilute with five more drops of plain water, and try again. See how dilute this gold solution must be before it becomes so weak that you cannot detect a change with Testing Solution A. If you figure this out, you will find that Solution A constitutes a delicate test, and will reveal the presence of a very small percentage of gold.

WITH PALLADIUM

In the same way, learn the color changes shown when mixing standard palladium solution with Testing Solution A. This color change is even more interesting than the others. When the two drops are first admixed, you see a deep yellow, not unlike the effect produced by platinum. After some minutes the yellow turns blue-green. This blue-green color is characteristic of palladium.

WITH SILVER

Silver solutions, such as silver nitrate, do not give any color reaction with Testing Solution A. What you will see when the two are mixed is the white cheesy precipitate of silver chloride, similar to that obtained when table salt is added to a silver nitrate solution.

USEFULNESS OF STANNOUS CHLORIDE

By the time you are familiar with the color changes produced by gold, platinum, and palladium in solution, you will also be able to gauge the approximate quantities of metal present. This knowledge is especially valuable when you are examining spent solutions to decide whether they should be discarded or not. You will also have occasion in later chapters to use Testing Solution A to decide upon what methods of recovery to use. If you are a professional refiner who buys old solutions, you will find this solution invaluable when making quick appraisals of your purchases.

IF THE TESTS ARE NOT CONCLUSIVE . . . .

Of course the beginner sometimes gets confusing results. Sometimes the colors fail to appear. This may mean that the testing solution has lost its strength, or, more likely, too much strong acid is present.

(Testing Solution A must be made up freshly from time to time. It loses its virtue completely in a few weeks. Therefore, begin the day's work by checking your Solution A against a drop of standard gold solution. If it fails to respond, throw it away at once.)

Solutions containing only such base metals as iron, copper, zinc, nickel and cadmium give no color change with stannous chloride. Lead may give a white precipitate of lead chloride, which may be confused with silver chloride—see page 92 for a way to distinguish between them. Another base metal that is apt to confuse the beginner is mercury, which under some conditions gives a heavy grey precipitate with stannous chloride. If you suspect mercury, make up a standard mercury solution and make a few acquaintance tests in order to recognize this reaction.

Here is another complication: solutions of the platinum metals, especially iridium, to which much ammonia has been added at certain stages of the procedure, sometimes fail to respond to the usual tests. The ammonia can form a sort of complex which ties up the metal and the usual reactions may not occur. This will be spoken of again in Chapter XIII. Organic substances sometimes do the same sort of thing. In this book we go to some pains to avoid the formation of these complexes, hence this difficulty is not apt to occur when following these routines. If it should occur, however, do this: evaporate a sample of the solution to a crust, and heat the crust to redness. This breaks up the complexes and reduces the precious metals to metallic form. Dissolve the residue in a little aqua regia and the usual tests can be made.

If your unknown solution contains a very large concentration of iron salts (as from copperas) or of copper salts, the test with stannous chloride may seem slow to appear, and you will need more testing solution than usual. This is because of a by-reaction that consumes some of the stannous salt before it reacts with the precious metal.

Remember that Testing Solution A spoils on standing. The standard solutions do not spoil; but when you make them up, do not use an excessive amount of acid to dissolve your bits of metal, or the tests will be weakened or even destroyed.

TWO OR MORE PRECIOUS METALS

If your unknown contains two or more precious metals—say gold and platinum—you may at first be confused, especially if one or the other is in large excess. The answer is to practice with mixtures of the standard solutions, varying the proportions and concentrations, and in a short time your eye will become skilled.

Remember also that gold reacts with copperas, and platinum does not. Therefore, if your stannous chloride test is confused, it may be helpful to repeat the test using copperas instead.

Instead of the spot plate, some people use white blotting paper or white filter paper. Place on it a drop of the unknown solution, then drop one drop of Testing Solution A on top of the first drop. The colors will spread through the paper, and if two or more metals are present the characteristic colors of both will appear.

Another situation that may confuse a beginner is to find an unknown containing much platinum and very little palladium; or much gold and very little palladium. He finds that the palladium color is obscured by the intense reactions of the platinum or the gold. As his eye becomes skilled he can detect smaller and smaller proportions; however, he will be glad to know that there is another solution that is especially valuable in detecting small amounts of palladium.

DIMETHYL GLYOXIME SOLUTION AND PALLADIUM

This solution has the added virtue of showing up nickel even in small amounts. It will show up nickel in a platinum alloy; in a white gold alloy; in a dental alloy. It will show up palladium and nickel when both are present in small amounts in an alloy that is largely platinum or gold.

One gram of dimethyl glyoxime will be enough for several hundred spot plate tests. It is a white or pale yellow powder. The name is pronounced “dye-methyl glyoxeem,” but no one will blame us if we refer to it as DMG.

Dissolve this gram of DMG by bringing it to a boil in about 100 cc. of water—about 4 fluid ounces. It dissolves rather slowly. If possible let it stand overnight; then filter. It is important that the solution be free from sediment or crystals. It is now ready to place in a dropping bottle, which should be labeled DMG. It keeps quite well for years, except that you may have to filter it again.

Let us get acquainted with DMG. Its most interesting characteristic, as we said, is to show up palladium and nickel, in the presence of other metals and in the presence of each other.

You can see this more clearly by using a few small test tubes. In No. 1 place a few drops of standard platinum solution; in No. 2 a little of your standard palladium solution; in No. 3 some standard gold solution. All three have a pale yellow color. Be sure that all the solutions are free from sediment. Now add a few drops of DMG to each test tube, and note the change in the palladium tube.

Note the *precipitate* that forms, and its color. The pale yellow colors do not change, but in the test tube containing palladium you will see a precipitate. Note carefully that while Testing Solution A gives prompt change in color, DMG distinguishes between palladium and the other metals by forming a precipitate.

In a fourth test tube take several drops of water and a very small amount of palladium solution; add DMG and see how small a quantity of palladium is the smallest that you can detect. With practice in looking at precipitates, your eye will detect smaller and smaller percentages.

Be sure that all your solutions are clear and free from precipitates or flocculence; otherwise you will be deceived.

DMG AND NICKEL

Rub a piece of nickel—a five-cent piece will do—vigorously on the unglazed bottom of your spot plate, so as to obtain a "streak" of metal particles. Dissolve the streak with a drop of nitric acid or aqua regia. Add a drop or two of DMG. Nothing special will happen.

Now repeat, but with this difference: after dissolving the nickel streak in acid, add a big drop of ammonia. Then add the DMG. If you used enough ammonia to kill the acid, you will see a very beautiful and characteristic color change.

From one point of view it is a waste of time to describe these color changes, since they become of value only through being seen by each observer. However, for the sake of the record we may say that this color, produced by DMG, nickel, and ammonia, is a striking rose-red. And the precipitate produced by palladium and DMG in acid solution is canary yellow.

Note this particularly. The test for palladium appears only in acid solution; the test for nickel must be made in ammoniacal solution.

This is very handy. Thus, suppose you have a piece of white dental alloy as an unknown, and you suspect that it may contain nickel or palladium. First get some of it into solution with aqua regia. Then add DMG. If palladium is present you will see the copious precipitate, canary yellow in color. Now add enough ammonia to make the mixture smell faintly. If nickel is there, you will at once see the beautiful rose-red. All in one test tube. Continue to use various scraps of metal, such as cheap white gold (which is almost sure to contain nickel) and high grade dental alloys (which are almost sure to contain palladium). These tests are so fascinating that it will be no hardship to practice until your eye is quite thoroughly trained.

OTHER CHEMICAL TESTS THE—GLOW TEST

There are other chemicals, in addition to Testing Solution A and DMG, that can be used in identifying precious metals.

~~Mercuric cyanide~~ (poison), which dissolves readily in water, can serve as a test for palladium. It gives a dense precipitate when added to mildly acid palladium solutions.

One interesting peculiarity of platinum and palladium is their ability to soak up gases. This is utilized in several technical applications, including a popular kind of cigarette lighter; a bit of finely-divided platinum or palladium is exposed to the fumes of naphtha; it soaks up the fumes, and in so doing becomes hot, and finally the fumes ignite.

It is essential that the metal be in a finely-divided form; preferably as a fine powder. This phenomenon can be used as a test for platinum-group metals in some cases. To make the test, dissolve your metal in aqua regia, dip into the solution a bit of thin asbestos paper; heat this for a few seconds in a flame to drive off the aqua regia and dry the residue (which by now has been converted into a metallic powder) and let it cool somewhat. Now hold the asbestos over an unlit jet of gas; soon the powder will begin to glow, and finally the gas will be ignited.

This glow test works successfully with platinum, palladium and rhodium. However, if your solution contains considerable quantities of other metals, this test should not be used, as some of them inhibit it, and others, such as copper, may sometimes produce a false glow.

COPPER

The green color of dissolved copper sometimes identifies it. There are several other metals, however, that give green solutions, including nickel, chromium, and sometimes iron. For most purposes, the addition of strong ammonia to a green solution will settle the question. Take a few drops in a test tube or beaker, and add a few drops of ammonia; the mixture may spatter, so work slowly. First there will be a curdlike precipitate, but on the addition of more ammonia, if copper is present, the precipitate will dissolve to yield a clear solution of a beautiful sapphire blue color. This blue color is characteristic of copper, and will distinguish it from chromium or iron. Unfortunately, nickel also gives a blue color with ammonia—though not so deep a blue—which means that you will then have to add a little DMG to settle your doubts; thus nickel with DMG, in the presence of ammonia, gives a rose-pink flaky precipitate while copper does not.

IRON

Iron in solution has sometimes a pale green color—the color of copperas—but more frequently a brown, yellow, or rust color. The rust color is so much like the color of dissolved gold or platinum, that the worker may hesitate to throw away a brown solution because it looks so much like something of value. Here is a quick test that reveals the presence of iron: dissolve a gram of ammonium thiocyanate (potassium thiocyanate works the same way) in three or four ounces of water; place one drop of your unknown solution in a cavity of the porcelain spot-plate, and add one drop of ammonium thiocyanate. If dissolved iron is present a deep blood-red color will appear, usually at once, perhaps only after a few minutes' exposure to the air.

This deep red color constitutes a very delicate test, as it will appear when even a minute trace of iron is present. Indeed, if you drop some thiocyanate on your hand, the chances are that there will be enough iron on your skin, picked up from handling iron and steel articles, to give a red stain. Do not make this test in solutions containing much nitric acid, because the nitric acid itself gives a red color with the thiocyanate. Mercury, oxalic acid, and some other substances also interfere with this test. If copper is present there may be a brown precipitate, which may or may not obscure the red color produced by iron. A few acquaintance tests made with solutions whose compositions are known will be helpful here.

Here is a second test for iron in solution: add a few drops of potassium ferro cyanide, and if iron is present an intense blue color will appear, either immediately or after exposure to the air.

RECOGNIZING ACID AND ALKALINE SOLUTION; LITMUS PAPER

One test is to take a few drops in a beaker and add a little ordinary bicarbonate of soda; nearly all acids will produce an effervescence. Chemists, however, usually use litmus paper. Litmus paper can be bought at any drug store for a few cents. Litmus itself is a dyestuff extracted from a seaweed; it has the valuable property of being red when in an acid solution, blue when in an alkali solution; when in a solution that is exactly neutral, such as pure distilled water, it is lavender-colored.

Get some litmus paper—paper impregnated with this dyestuff—and learn its characteristics. Tear off a small piece, and drop it into a beaker of water and add a drop of sulphuric, or nitric, or hydrochloric, or oxalic acid. (Dozens of other acids will behave the same way.) Litmus paper as bought will probably be of the lavender color; when immersed in the acid it turns red. Now drop a second scrap of litmus paper into a second beaker containing water to which you have added a drop of ammonia, or a very small amount of caustic soda, or a little potassium cyanide or sodium cyanide. (There are dozens of other substances with alkaline or caustic reactions that will behave the same way.) Notice that the paper turns blue.

It is valuable to repeat these tests with many variations. Thus, with a glass rod fish the red scrap out of the first beaker and drop it into the second beaker. Also fish the blue scrap out of the second beaker and drop it into the acid solution. If, as advised, your solutions are fairly dilute, you can repeat this many times, making the dyestuff change from blue to red, from red to blue, over and over again. (Concentrated acids or alkalies will destroy the paper.)

Finally, suspend a piece of damp red litmus paper over the open mouth of the ammonia bottle; note that even the fumes will turn it blue. Suspend a piece of damp blue litmus paper over the open mouth of the hydrochloric acid bottle; and it will soon turn red.

Remember—in acid, litmus is red; in alkaline solution it is blue. College boys have a little rhyme that helps them remember this—they say “Alkaloo turns it blue.” You will have occasion to use these tests often in later chapters.

Another characteristic common to all soluble acids is their sour taste. A single drop of hydrochloric acid will confer a sour taste on a pint of water. However, so many acids are poisonous, especially if concentrated, that it is unwise to taste them.

OTHER TESTS. A WARNING

The foregoing does not exhaust the list of tests that can be made. There are dozens of others, but some of them are so difficult, or so complicated by the presence or absence of this or that other substance, that the non-chemist should not attempt them.

The non-chemist would also do well to confine himself, at least in the beginning, to solutions that originate in his own shop. Strange mixtures may be offered him by itinerant prospectors or old-gold buyers. The non-chemist (or the chemist who is inexperienced in this field) would do well to exercise extreme caution before purchasing such things, no matter what color tests they may produce.

IDENTIFYING METALS IN SOLID FORM

The refiner has frequent occasion to examine buttons, old dentures, sediments, residues, and the like, to learn which precious metals are present. If he is familiar with the reactions described in this chapter, this will be no problem. As we say, the usual procedure is to get some of the metal into solution by warming it in a test tube with nitric acid, or sulphuric acid, or hydrochloric acid, or aqua regia—whatever is found necessary. An excess of acid should be avoided. The solution is then tested by the methods just described.

The familiar touchstone tests, used by jewelers when buying old gold, utilize this principle on a small scale. These are described in the book TESTING PRECIOUS METALS, mentioned on page 92. The metal is rubbed against a stone to leave a streak of metallic particles which are brought into solution with a drop or two of acid. The porcelain spot plate can be used instead of the stone, and reagents such as stannous chloride, copperas, or DMG will be added, as the ingenuity of the operator may suggest.

CHAPTER X

GETTING ACQUAINTED WITH THE PLATINUM GROUP

Especially Platinum, Palladium and Iridium.

The six metals. Their employment in art and industry. Books to read. Familiar characteristics. Platinum and ammonium chloride. Palladium and ammonium chloride. Palladium and acids. Possible experiments. A little about iridium. Questions and answers.

* * * *

Platinum, palladium and iridium are the commoner members of this group, and the ones of greatest general interest. The other three, osmium, ruthenium, and rhodium, will be discussed in Chapter XVII.

These six sister metals share many characteristics, especially rarity, white color, unusual resistance to corrosion, high melting point, and many chemical peculiarities; but like human sisters, each has an individuality of its own.

The reader undoubtedly has had some previous acquaintance with the group. Thus if he is a jeweler he knows that pure platinum is almost as soft as fine gold, and must be hardened for most industrial purposes. He knows that the addition of a little iridium will produce an alloy of beauty and working qualities that make it the supreme jewelry material. The alloy 10% iridium with 90% platinum, called in the trade “10% iridio-platinum,” is the favorite, though lower percentages of iridium are often used.

Pure iridium is rarely seen, except by jewelers who make up their own alloys. So popular are these iridium-platinum alloys that the word “platinum” is now commonly applied not only to the pure soft metal, but to these alloys as well.

The jeweler will also be acquainted with “platinum solders,” which normally contain no platinum at all, the best ones consisting of gold and palladium; the cheaper ones, of gold and palladium plus other metals such as brass and silver. Perhaps the jeweler will have met palladium in other forms as well; in England during the first World War much handsome jewelry was made of it, and it is used today as an ingredient of high grade white golds.

The dentist reader knows platinum and lridio-platinum, and probably several of the alloys of platinum with gold and palladium. Dental alloys, of which more will be said in Chapter XII, are of many kinds, the precious metals being combined in various proportions, oftimes with the addition of base metals.

The desirable chemical and physical properties of the platinum-group metals have insured their use in many other fields as well. Chemical ware is made of platinum because of its resistance to most chemical reagents. Hypodermic needles are made of 20% lridio-platinum because of its strength and the ease with which it can be sterilized. Immense quantities of platinum and its alloys go into radio and electrical equipment. An alloy of osmium and iridium (called osmiridium) is used to tip fountain-pen points, because of its hardness and resistance to corrosion. Most of these uses are familiar to the layman.

The word “platinum” is derived from the Spanish “platina,” meaning “little silver.” Iridium gets its name from its iridescent or many-colored compounds. Palladium was named from the planet Pallas, which happened to be discovered at about the same time, Pallas in turn being named for the Greek goddess of Wisdom.

The history of the platinum metals, and the story of their occurrence in nature, are interesting and romantic, but have no place in this book. Nevertheless, a knowledge of that history will have a dollar-and-cents value to every man who refines, works, buys or sells these metals, because it gives him that familiarity that is the basis of successful business.

BOOKS TO READ

Chapter E at the end of this volume, on “Books to Read,” might be consulted at this point. If you are in a business that employs the precious metals, you can without cost obtain several publications of high merit, simply by writing for them on your letterhead. While they are primarily advertisements, they contain general information of especial interest to the refiner. The following are notably useful:

TECHNICAL AND INDUSTRIAL PLATINUM, put out by J. Bishop and Co., Malvern, Pa.

PLATINUM, A THUMBNAIL HISTORY, by Sigmund Cohn, 44 Gold St., New York City.

DATA CONCERNING PLATINUM, by Baker & Co., Newark, New Jersey.

PLATINUM-PALLADIUM-GOLD IN DENTISTRY, by the International Nickel Co., Inc., 67 Wall St., New York City.

LABORATORY APPARATUS OF PLATINUM, GOLD, SILVER, by the American Platinum Works, Newark, N. J.

THE HANDY BOOK FOR JEWELERS, by Handy & Harman, Bridgeport, Conn. Price, $1.00.

FIFTY YEARS OF PROGRESS, by Thomas J. Dee & Co., Chicago, Illinios.

FAMILIAR CHEMICAL CHARACTERISTICS

The reader who has studied previous chapters of this book will already be familiar with several characteristics of interest to the platinum refiner. Thus in Chapter III, in which he removed dirt and base metal from platinum filings, he observed the following:

(1) Platinum may be boiled in nitric acid without dissolving or suffering other change.

(2) Platinum is not attracted noticeably by the magnet.

(3) Platinum does not dissolve in caustic soda or potash.

(4) Platinum shows no tarnish after being heated to redness.

(5) If he has done electro-plating he has observed that platinum does not dissolve in cyanide solutions, even under the electric current.

(6) In Chapter VI he learned about the use of metallic precipitants such as copper wire, or zinc shavings, to get gold out of solution. In the discussion on this method he read "One disadvantage is this: if any platinum or palladium should be present in the solution, they will come down with the gold, in metallic form also. . . . In this respect the metallic precipitants differ from copperas, sulphur dioxide, sodium nitrite or oxalic acid; when these latter are used, platinum or palladium will remain in solution while the gold alone is thrown down. This difference is important." Indeed, as he will shortly learn, differences such as these are the basis of most of our refining procedures.

(7) In Chapter IX, when making up his standard solutions, he dissolved weighed samples of pure platinum, palladium and gold; he observed that gold and palladium dissolved readily in cold aqua

regia, but that platinum reacted so slowly that he heated the dish to hasten matters. This difference in *speed* with which gold and platinum are attacked by cold aqua regia is important and will be referred to again later.

There is another respect in which platinum differs from gold. You will recall from Chapter VI (See Quartation) that gold can be separated from silver by treating a silver-rich alloy with nitric or sulphuric acid. That is, if an alloy containing three times as much silver as gold is boiled with either of these acids, the silver will dissolve and all the gold will remain as a brown powder, thus effecting a separation. This method cannot be used to separate platinum from silver, as platinum-silver alloys behave quite differently from gold-silver alloys. Thus, if you should expose an alloy of 95% silver and 5% platinum to boiling nitric acid, everything will dissolve, the platinum forming a soluble platinum nitrate, from which it is not easy to recover the platinum. If you should expose an alloy of 75% silver and 25% platinum to nitric acid, most of the silver and some of the platinum will dissolve, and there will be a considerable residue which contains both metals. In other words, you will not effect a separation.

Silver-rich platinum alloys react to boiling *concentrated* sulphuric acid in about the same way—no separation is effected. With sulphuric acid that is slightly diluted, a fair separation can be obtained. This point will be mentioned again in the latter part of Chapter XII.

Before the reader becomes an accomplished refiner he will come to know several other characteristics of platinum, but for the moment (since we are anxious to begin actual work) we shall content ourselves with only one or two further observations.

(Several new chemicals and pieces of equipment will be needed in Chapters XI, XII and XIII. These are described in Chapter XI. Of these, the following will be employed now: the porcelain crucible and the clay triangle that supports it; sodium chlorate; ammonium chloride.)

PLATINUM AND AMMONIUM CHLORIDE

Place in a small beaker a half ounce or less of the platinum solution you prepared in Chapter IX. This is a solution of platinum in hot aqua regia, made up with as little aqua regia as would do the work, plus water; its chemical name is “Platinum Chloride” or “Chloro-platinic acid.” Notice the yellow color. In a second vessel dissolve a tablespoonful of good quality *ammonium chloride* in a little water, to make a clear concentrated solution. (Cheap ammonium chloride gives a muddy solution that must be filtered before use.) Add one-third of the ammonium chloride solution to your platinum chloride solution, stir, and let settle.

The orange-colored powder that forms is called *platinum ammonium chloride* or *ammonium chloro-platinate*. These names are long, and it is usual to refer to it simply as the "orange powder."

Next, let us separate the orange powder from the liquid, using a small filter paper, and collecting the clear solution in a clean beaker. Test a drop of the clear solution in a cavity of the spot plate with stannous chloride solution. . . . You will find that it still contains a little dissolved platinum.

In other words, the ammonium chloride precipitated most of the platinum, but not all. Naturally you will add a little more ammonium chloride with the idea of completing the precipitation, after which you will test the clear liquid again with stannous chloride. . . . You will find that it still contains a little platinum—enough to be detectable.

In this respect ammonium chloride differs from reagents like the copperas with which you can precipitate gold so completely that no ordinary test will show its presence.

There are at least two good ways to reduce the orange powder back into metallic platinum: by heating it strongly in a crucible, and by boiling it in formic acid; and even the amateur refiner should know both methods.

The first way is the older method, and the one we shall use now. (Later, in Chapter XIV, we shall use the formic acid method.) Let the powder dry, then brush it into a porcelain crucible and heat it, gently at first, then more strongly. Use a Bunsen flame, or a small gas flame such as is used in cooking, or a gas-fired muffle furnace. Do not use a gold-melting furnace.

Observe the effect of heat. The powder shrinks and changes color, and fumes appear which are hard on machinery as well as on human lungs, so work under the hood. If the fumes are white you are working at proper speed; black or yellow fumes mean you are heating too rapidly. Soon you will have left a lump of gray metallic powder, called *platinum sponge*, all the ammonium chloride having gone off in fumes.

This sponge is (if these directions have been followed) quite pure, and should be saved. Residues such as the liquid above, which contain a trace of dissolved platinum, should be saved too, though of small value. Place this liquid aside for the moment, and later add it to the "Stock Pot" which will be described in Chapter XI.

PALLADIUM AND AMMONIUM CHLORIDE

Place in a small beaker a half ounce or less of the palladium solution you prepared in Chapter IX. This was made by dissolving pure palladium in a little aqua regia, evaporating off the excess acid, and adding a little water; its chemical name is "palladium chloride." In appearance it resembles both gold chloride and platinum chloride. To this add a little of the ammonium chloride solution you prepared for the previous test—a quarter ounce, more or less. Does anything happen ?

If your palladium is pure, and if your standard solution was prepared as directed, nothing will happen. This experiment shows that palladium differs from platinum in that it is not precipitated with ammonium chloride from an aqua regia solution from which excess nitric acid has been boiled off.

Warm the mixture gently, and add a single crystal of sodium chlorate. Or, dissolve a pennyweight of chlorate in a little warm water, and add a drop at a time. There will be considerable fizzing, and as it subsides, add another small crystal or another drop. The solution should be just short of boiling. After the addition of a little more of the chlorate, a change in color will be noted. Stir the mixture with a glass stirring rod; soon a dark red precipitate will be seen, floating on the surface and then sinking. Continue to add chlorate, a little at a time until the liquid is almost colorless, and then let cool. This red powder is *palladium ammonium chloride*—chemically much like the orange powder above.

If you heat this red powder in a crucible in the same way that you treated the orange powder, the results will be practically the same, as would be expected. However, the palladium sponge that remains after heating will rarely show a clean gray color; usually there are bluish tones suggesting peacock feathers, due to palladium oxides. This is one difference between platinum and palladium;

palladium is apt to form oxides, and the oxides show rainbow colors.

Another and very important difference was hinted at in Chapter III, where you were removing base metals from platinum filings, using nitric acid. You were told not to use the nitric acid treatment if your material contained any pure palladium, or platinum-palladium alloys in which the latter metal ran as high as 40%. The reason for that is that palladium dissolves in nitric acid.

Palladium is the only metal of the platinum-group that shows this characteristic. It also dissolves in boiling sulphuric acid. Hydrochloric acid has little effect upon it.

In the following chapter we shall expose platinum, iridio-platinum, and palladium to a variety of reagents. A full discussion of all the chemical changes that might go on would consume many pages, and the list of acquaintance tests that might be performed, if one had unlimited time, is almost endless. Thus, the reader might profitably take samples of his standard platinum and palladium solutions and expose each in turn to copperas, sodium nitrite, oxalic acid, sulphur dioxide gas, zinc shavings, copper wire, table salt, and many other things.

We have assumed all along that the reader has never formally studied chemistry in school or college; we can assure him that the formal study of this science consists mostly of just such simple acquaintance tests, the addition of one substance to another under varying conditions of concentration, temperature, and so on, with careful observations of the effects. If the reader has performed all the experiments thus far described he has learned a method of approach which if followed will carry him well along toward an understanding of the precious metals.

A *complete* understanding would involve much study and many experiments, as can be judged from a glance at the list of books that have been written about these metals. Indeed, if you should ask any one of the experts on this subject—for example the chemists at the National Bureau of Standards—they would assure you that one lifetime is far too short for a *complete* understanding of this fascinating group. But that does not mean that an intelligent layman cannot learn enough to refine profitably the materials used in his own shop.

Experiments, therefore, will suggest themselves to him from time to time. If he uses small samples, and works slowly, he will run little risk of accident and be sure to learn much. Beginners always use too large samples, which waste time and money, and often by their sheer bulk, obscure the reaction.

Moreover, it is possible also to learn while doing; that is, to proceed with the actual work of refining some jewelers' filings or some dental scrap, accomplishing at the same time the recovery of precious metal and the attainment of precious knowledge. This we shall do, pausing now only to mention a few more facts.

A LITTLE ABOUT IRIDIUM

Pure iridium is a very hard metal, insoluble in any single acid, and attacked even by aqua regia with the greatest difficulty, and only under special conditions. Platinum that is alloyed with 30% iridium can be boiled for hours in aqua regia with only minor loss. In its chemical functions it resembles platinum in many respects; for example, if ammonium chloride is added to iridium chloride, there will soon appear a precipitate of dark iridium ammonium chloride, chemically so much like the orange powder that it is difficult to separate the two. Other characteristics will be discussed in later chapters, as the process of refining reveals them.

* * * *

QUESTIONS AND ANSWERS

Q. I saw a display of platinum-group metals at the World's Fair—a series of buttons, bars, crucibles, articles of jewelry, etc. To my eye all six metals were exactly the same white color. But in a book I read, one metal is described as "steel white," another as "silvery," another as "tin-white," etc. How do they differ?

A. To most eyes, rhodium is the whitest, with iridium and palladium tied for second place, and platinum close behind. The color depends partly on the form of the metal. Thus the platinum sponge obtained by heating the orange powder is gray; melt this sponge into a button and it will be tin-white.

The color of electrodeposited metal will vary with the conditions under which it was deposited, from the mirror-like brilliance of good rhodium plating to a dull leaden hue in badly done work.

A well-polished surface seems whiter than one bearing many small scratches. The usual cause of darkening, however, is an impurity; thus small amounts of other metals, of impurities soaked up from the crucible, or gases absorbed from the torch while the metal was molten, can all cause darkening. But it is generally agreed now that all six metals when pure and properly melted, are so nearly the same tin-white color that experts cannot certainly distinguish them by the eye alone.

CHAPTER XI

JEWELERS' FILINGS AND CLIPPINGS CONTAINING MIXTURES OF GOLD WITH PLATINUM-GROUP METALS

Kind of materials handled. Equipment and chemicals. Beginning work, (1) General cleaning. (2) Removing base metals with nitric acid. (3) Removing gold with aqua regia. (4) Removing silver chloride. (5) Melting the platinum filings. (6) Recovering dissolved platinum. (7) Burning the orange powder. (8) Melting the platinum sponge. (9) Recovering the dissolved gold. (10) Washing and melting the fine gold. The Stock Pot. (11) The Silver Jar. Summary. Questions and answers.

* * * *

KIND OF MATERIALS HANDLED

This chapter covers the filings and clippings ordinarily produced in a jewelry shop where both gold and platinum articles are made. Material of this type is rarely found in dental laboratories, but it is one of the most important encountered in the jewelry industry, and usually offers more profit to the small-scale refiner than any other. Even the smallest jewelry shop will find that these gold and platinum mixtures can be refined easily and with profit.

So important is this type of waste that some readers may turn immediately to this chapter and skip the preceding ones. If so, they should be warned that a knowledge of much that has gone before is essential for the proper understanding of what follows.

We shall exclude from this chapter all buttons or alloys in which *gold and platinum-group metals are MELTED together*. (In Chapter XII we shall discuss such buttons or alloys fully; they are an important part of dental wastes.) This distinction between a mixture of particles of gold and platinum, and an alloy in which these same metals are melted together, is important; the reason will be clear shortly. We shall for the present, exclude amalgams also.

Jewelers' filings of this type contain the usual dirt, such as iron from the files, emery and bits of paper that we found in Chapters III and V.

The platinum used in ordinary high grade jewelry, included in this chapter, normally contains a little iridium to stiffen it. White golds, and the solders used in making platinum jewelry may contain palladium. This iridium and palladium are taken care of in this chapter, and recovered in due time. Included also is old jewelry in which platinum and gold are *soldered* together; for example, platinum-topped gold jewelry.

We shall include in this chapter all the kinds of gold normally used in jewelry, except one. Thus, we include yellow gold, red gold, rolled and filled gold, white gold, and low-karat green gold. We shall exclude only 18-k green gold. You will recall from Chapter VII, that 18-k green gold behaves differently from most gold alloys in that it does not dissolve in aqua regia. For that reason we exclude it from this chapter, reserving it for Chapter XVI.

* * * *

The procedure consists essentially of the removal of first one kind of unwanted matter, then another, from the particles of platinum. That is, we shall remove, in turn, the shellac and grease, the iron from the files, the base metals, and the gold, our effort being to leave the platinum particles unchanged as far as is possible.

With some mixtures this is quite easy; with others it is impossible. That is why we have spent so much time in listing the mixtures that can be handled in this way. Our reasons for including some things and excluding others will be clear to the reader after he has been through the procedure once or twice.

This chapter, then, can be used only when the composition of the mixture is known, in the sense that a jeweler working on his own wastes knows what sort of alloys and materials have been employed. The professional refiner who buys filings, old dental scrap, and the like, usually does not have sufficient knowledge of his purchases to justify him in using this chapter.

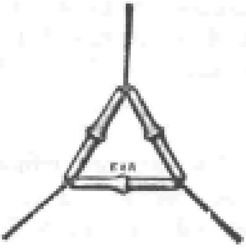
To summarize: This chapter treats of the filings and clippings produced in a jewelry factory where platinum and ordinary gold jewelry are being made, and in which particles of gold and platinum are mixed—not melted—together.

EQUIPMENT AND CHEMICALS

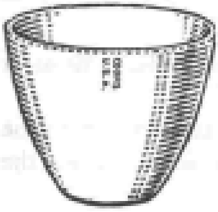
We shall use all the equipment already employed, and a few other things beside. That includes table, burner, exhaust fan or hood, wash-bottle, funnels, funnel support, evaporating dish, graduate glass, glass stirring rods, spoon-spatula, casserole, asbestos to go between casserole and flame, glass beakers, test tubes, the spot plate and dropping bottle used in testing; steam bath, magnet, frying pan for burning out dirt; a crucible for melting the refined gold, and at least one stoneware crock of generous size.

Wash-bottle.

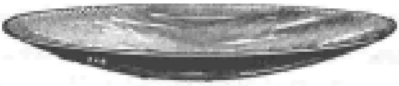
Mortar and pestle.



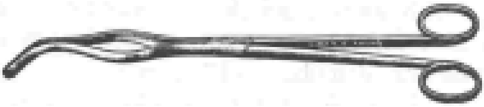
Pipe-clay triangle.



Porcelain crucible.



Watch glass.



Tongs for handling crucible.

In addition you will want the following for use in this chapter and in Chapters XII and XIII: a second wash-bottle, smaller than the first (Eimer & Amend No. 18952, size 500 cc., at 60¢); a mortar and pestle, No. 28688, 5½ inches across, at 95¢. A porcelain crucible No. 21241 or 21243, size 4, at about 50¢, will be big enough for the small shop. Sand crucibles used in melting gold can be used instead, but are not nearly so satisfactory. (Graphite crucibles should not be used at all with platinum.) A pipe-clay triangle No. 32646, size 7½ cm., is needed to support your porcelain crucible while it is being heated; price 13¢. Crucible tongs No. 32553, 9 inches, at $1.10, will be used for picking up hot articles. Watch glasses, to cover dishes and beakers, make for cleanliness; No. 32850, assorted sizes, say one each of sizes 3, 4, 5, 6, and 7 inches, cost about 62¢.

You will use the following familiar chemicals: nitric acid, hydrochloric acid, copperas, sulphuric acid, stannous chloride testing solution, granulated zinc or zinc shavings, and fluxes for melting gold. In addition the following new chemicals: 5 lb. ammonium chloride, U. S. P. or C.P., at about 25¢ per pound; 1 pound cyanide—sodium cyanide, or cyanide-chloride mixture, or "Cyanegg"; (ordinary commercial purity is good enough) price about 40¢; a pound of sodium chlorate, C.P., about 80¢; and a pound of pure ammonia (ammonium hydroxide) at 50¢ or less.

BEGINNING WORK

For your first refining, handle only a small quantity of material, not over three or four ounces. As you become familiar with the procedures, you will handle larger and larger batches with ease.

Briefly, the material will be treated in the following steps:

(1) Removing bits of iron with a magnet; removing shellac and grease by caustic or by burning in a frying pan. These steps were discussed fully in Chapters III, V, and VI.

(2) Removing base metals with nitric acid; this is the same as in Chapters III and V.

(3) Removing gold by means of cold aqua regia; at the same time a little platinum is dissolved. This differs only slightly from the procedure described in Chapter V.

(4) Removing silver chloride. This normally leaves your platinum clean.

(5) Melting the clean platinum filings.

(6) Recovering the platinum that is dissolved in aqua regia.

(7) Melting the platinum sponge.

(8) Recovering the gold that is dissolved in aqua regia, using methods already learned in Chapters V and VI.

(9) Recovering the silver, if worth while.

(10) Laying aside the remaining solution—called the Stock Pot—which contains a little platinum and probably some palladium and iridium, for treatment in Chapter XIII.

Clippings and old jewelry, etc., must be rolled thin; the thinner the better. Hammer them flat; then feed them into the rolls with a little scoop whose sides have been cut out so that it will fit against the rolls; or put them on a piece of paper and feed in paper and all. Roll very thin; a few minutes spent at the rolls may save several hours later. Twist the pieces so that they will not lie flat in the acid, then anneal.

Do NOT melt the filings into a button—no matter how dirty they may be—if you expect to refine them according to the procedure of this chapter.

(I) GENERAL CLEANING

This is in every way similar to the methods used in Chapters III, V and VI. Thus:

A. Take out bits of iron with a magnet. Put these with your sweeps, as they may contain some value. (Some kinds of white gold are attracted to a magnet; so if your white gold is of this kind, do not use the magnet.)

B. Most workers burn out organic matter such as paper, lint, etc., in a frying pan. A few little cinders will be produced; they will be washed out later.

C. But if your filings contain much shellac or grease, instead of burning them, place them in a casserole and boil in lye or caustic, as described in previous instructions, after which wash well, with plenty of hot water. Let the wash-water settle overnight, then throw it away, being careful not to pour over any filings. The mud that has settled out contains some platinum, so put it with your polishings, with old filter papers, or in the sweeps.

(2) REMOVING BASE METALS WITH NITRIC ACID

Base metals, including some of the alloy in the gold, will now be dissolved in nitric acid. Have the filings or clips in the casserole, and cover them well with nitric acid. Use C.P. acid, and add a little water, exactly as described in Chapters III or V. If there is much base metal add the acid slowly, as it may boil over. The familiar heavy brown fumes appear, so you must work near the fan. Dissolve as much as possible of the base metals. The more base metals, the more acid needed. When there are no more brown fumes on stirring, add a good quantity of hot water to dilute the acid, and pour it off through a clean filter, leaving the filings in the dish. Let the liquid run through into a jar with a wide mouth; it contains dissolved silver, copper, and base metals, and is the same as the "Silver Jar" of Chapter V. Wash the filings clean with plenty of hot water, as usual. Filter this wash water in with the acid. The cinders produced when you burned out the organic matter will gradually be flushed out by this and subsequent washings.

Sometimes there is so little silver in your material that it does not pay you to save this nitric acid solution. But if there is enough silver in it to be worth recovering, follow the procedure given in Chapter VIII.

If your original material contained any tin, you will now see more or less of that jelly-like tin paste noticed in Chapter VII in the discussion on soft solder. You can dissolve this tin paste by means of a little sulphuric acid; then wash this off and throw it away.

(3) REMOVING GOLD WITH AQUA REGIA

All the gold is now to be dissolved. A little platinum will dissolve unavoidably at the same time. For every Troy ounce of gold, more or less, add

1 fluid ounce nitric acid,
1 fluid ounce water,
4 fluid ounces hydrochloric acid.

Do not add sulphuric acid yet. Use enough aqua regia to cover the filings well. Do not heat this (unless you are in a great hurry) because the hotter it is the more platinum it dissolves, and we do not want to dissolve any more platinum than necessary. If your material is mainly gold, add the aqua regia slowly, as it may bubble over.

Let this stand till there is no more bubbling when you stir. Usually 24 hours are enough, but the thicker the lumps of gold the longer it takes. In hot weather it works more rapidly. You can hasten action by stirring frequently, by heating, and by having all pieces rolled very thin. In some cases two hours are long enough to dissolve all the gold. If you have much gold, put on a little aqua regia at first, let it act all it will, then pour it off and add more. It is better to do this than to add all the aqua regia at once.

Try not to use any more aqua regia than is necessary to dissolve all the gold. If you use more than necessary, you not only waste acids and time, but also make trouble for yourself later. With a little experience you will learn how to dissolve all the gold, and at the same time have all the acids killed when you are through.

When there is no further bubbling on stirring, pour off the aqua regia solution (do not filter it yet) into a pitcher or jar, leaving the filings in the casserole. This liquid contains dissolved gold, a little dissolved platinum, perhaps some palladium and iridium, and such base metals as were not reached by the nitric acid. This includes a little lead in some cases.

To the liquid now add a little sulphuric acid, to throw down the lead, if any is present, as white lead sulphate. Use say an ounce or less of concentrated sulphuric acid to each quart of solution, add it slowly, stirring all the while. The lead sulphate settles slowly.

Returning now to the platinum filings in the casserole: they are mixed with a greyish mud of silver chloride, formed from the silver that was alloyed with the gold. It forms a tight scum over the metal and may keep the aqua regia from acting on it.

Dump the mass of filings into the mortar, and rub them hard with the pestle, to loosen this scum of silver chloride. Then dump them back into the casserole, washing them in with the wash-bottle. Pour the water and loosened chloride into the pitcher of aqua regia solution, leaving the filings in the casserole. The idea is to wash off as much of this loose chloride as possible, but try not to use more water than is necessary. At the same time you will be flushing off cinders and other light-weight dirt.

Look through your material carefully, and if any large lumps of gold are left, you will see them. Test to see if there are any small pieces by adding a little fresh aqua regia, and watching the effect; if in five minutes you see no bubbles on stirring, then the gold is probably all dissolved. If it is not all dissolved, leave the metal covered with aqua regia for a few more hours, or until all the gold is dissolved.

Wash this aqua regia in with the other aqua regia in the pitcher, washing well but using as little water as will do the work; you can get your filings cleaner with several portions of water, of a few spoonfuls each, than with one large portion, if you stir well and pour off each portion completely before putting on the next. Wash until there is no more color in the wash waters.

(4) REMOVING SILVER CHLORIDE FROM THE FILINGS WITH CYANIDE (OR AMMONIA)

When you are sure that your filings are free from acid, fill up the casserole with hot water, and add a piece of cyanide. For 100 dwt of filings a piece as big as a walnut may be enough. Stir well, and heat to boiling if possible. This treatment dissolves any remaining silver chloride mud, and leaves the platinum clean and bright. Use either sodium cyanide or potassium cyanide, or the chloride-cyanide mixture.

Cyanide is a deadly poison. When mixed with acid it gives off its deadly fumes more rapidly. That is why you must wash off the acid so thoroughly.

If you do not like to use cyanide, you can use ammonia instead, but it is slower. Use it exactly as you use cyanide—wash the filings WELL, then add a strong solution of ammonia, chemically pure, in hot water. Stir often. Do not boil the ammonia, but set it in a warm place.

If there was much gold in your filings originally, there will be so much silver chloride that you may have to repeat this treatment. Finally pour or filter off the cyanide water (or ammonia) and wash the filings well with much hot water. Be careful not to pour off bits of platinum. Washings containing cyanide should not be put in the Silver Jar; if the amount of silver is small you are advised to throw them away at once. But if you want to keep and refine them, keep them in a separate container, and follow the suggestions in Chapter VIII.

As soon as the filings are clean and dry, they are ready to be melted with the oxygen-gas flame. Pick them over well; you may find bits of gold. Remember that small pieces dissolve before the big ones, so if you cannot find any big ones there probably are no small ones. Pick out any tiny squares of metal with a white look; they are a certain kind of platinum solder.

If you have any 18-k green gold, or any gold-platinum dental alloy, in your material, you will find them now. Pick them out, as they require methods to be described in later chapters. Run through the filings with a magnet to be sure all steel is removed. If the filings contain much sand or enamel, see later instruction. A little emery is often seen but it does no harm.

(5) MELTING THE PLATINUM FILINGS

It is always wise to melt about a pennyweight of metal first, to make a test button. If good, melt the whole lot. Remember that it is easy to get dirt out of filings, but very hard to purify an impure bar. So if your sample is bad, now is the time to clean your filings further. Sometimes it is enough to wash them once more with cyanide and water. Sometimes you must soak them again in aqua regia. Clean filings will melt easily and perfectly, without smell or smoke, and without loss. See Chapter A of the Appendix.

(6) RECOVERING DISSOLVED PLATINUM

Return now to the aqua regia solution which contains dissolved gold, also some dissolved platinum; (also dissolved base metals and probably some dissolved palladium and iridium). If the copper or nickel content is high it will be greenish; otherwise it will be brown.

Probably by this time the sediment of silver chloride and lead sulphate has had time to settle. This sediment must be removed sooner or later, and now is one good time to get rid of it, so let it settle well, pour off the clear part, and filter the remainder. The sediment should be washed free of solution and placed in the Silver Jar.

The next step is to drive off excess nitric acid. You were told to use no more aqua regia than was needed, but there is always a tendency to use too much, because fresh acids work much more rapidly than acids that are almost exhausted. Put the solution in an evaporating dish and heat it slowly, preferably on a steam bath, until syrupy. Do not let it spatter. A maximum temperature of 140 to 150 degrees Centigrade is advised. Now slowly add a little full strength hydrochloric acid to the syrup, and you will see the brown nitric acid fumes being expelled. Evaporate to a syrup a second time, possibly a third time, adding hydrochloric acid each time. This is the same procedure that you used in Chapters V and VI.

If you carry the evaporation too far, you will form a hard cake and gold may appear as a brown metallic film on the sides of the dish. Try to avoid this. If metallic gold should bake out, dissolve a crystal of sodium chlorate in a spoonful of hot water, and pour the solution drop by drop where the gold has collected; this dissolves it. Work slowly, drop by drop, as this combination (chlorate and acid) tends to spatter violently.

You may have to evaporate a third or fourth time, each time adding hydrochloric acid, to get rid of all the brown nitric acid fumes. One reason why we added sulphuric acid to the aqua regia solution is because with sulphuric acid the unused nitric acid can be driven off with fewer evaporations. Finally thin the syrup with several volumes of water, and wash it into a large vessel (not a bottle) which should not be more than two-thirds full. There should not be more than about three ounces of precious metal to each quart of liquid. Normally there is still some sediment present—silver chloride and lead sulphate that have managed to escape previous efforts for their removal.

Get rid of this sediment, either by letting it settle and pouring off the clear solution, or by filtering. The solution must be perfectly free from cloudiness before you go to the next step.

The next step is to precipitate platinum by means of ammonium chloride. For each quart of solution you will need about half a pound of ammonium chloride, dissolved in hot water to make a concentrated solution. Good quality (C. P. or T. P.) chloride is best; cheaper stuff contains trash which must be filtered out.

Add the strong ammonium chloride solution to your aqua regia solution, and stir well. Use plenty; for each pennyweight of platinum that is in *solution,* you will need a little over ½ a pennyweight of ammonium chloride, and a definite excess is advisable.

Immediately the orange powder of platinum ammonium chloride will appear. About 95 per cent, more or less, of the platinum that was in solution will be precipitated in this form.

The color will range from canary yellow through orange to a deep maroon. Do not be surprised if the shade is different every time; it depends upon the temperature at which it forms, the impurities present, and other factors as well.

Let the orange powder settle. If your solution contains much IRIDIUM, some iridium-ammonium-chloride may come down, mixed with the platinum salt. The longer it stands, the more of this dark iridium compound will come down.

(Moral: if you want your recovered platinum to be free from iridium, filter off the orange powder within an hour or so. But sometimes you want the iridium to come down with the platinum; in that case let the jar stand overnight in a cool place.)

The next step is to get the orange powder into a filter paper; pour the clear liquid through first, and then dump the orange powder in, rinsing it in with a little of the solution that has already run through. Let the liquid (which contains dissolved gold, etc.) run into a big vessel such as a crock—not a bottle.

Some of the powder will stick to the vessel. So dissolve a handful of pure ammonium chloride in a pint of water, making up roughly a 15% solution, and put it in your small wash-bottle. Label this little wash-bottle, so as not to confuse it with the big one containing plain water. Wash the orange powder into the filter with this ammonium-chloride-water, using as little as will do the work. Chemists often use a glass rod tipped with a bit of rubber to wipe off the powder that sticks to the glass; these rubber tips are called "policemen," and can be bought at your supply store.

When all the orange powder is in the filter, and all the liquid has run through, and before the powder dries, wash down the sides of the filter with some of this ammonium-chloride-water, so as to get the orange powder into a lump. We use ammonium-chloride-water because some of the powder would dissolve in plain water, but very little dissolves in ammonium-chloride-water. But use as little as will do the work.

It is now necessary to wash the orange powder, because it is wet with dissolved gold, dissolved copper, etc. A quick way is to pierce the bottom of the filter paper with a glass rod and permit the powder to run through into a clean dish below. Wash it down well, using the ammonium-chloride-water. If you have time, wash the powder into a wide flat vessel, cover it with plain water, and heat it gently on a hot plate or small flame for several hours. Use a large jar so that the layer of powder will be relatively thin. Let cool before you filter again. These schemes serve to rinse and clean the orange powder.

Finally get the powder into a new filter paper, washing it into a lump as before. The liquid that runs through is of value, so add it to the aqua regia solution. Spread the paper out on a plate to dry.

(7) BURNING THE ORANGE POWDER

When the orange powder is dry, dump it into a clean shallow porcelain or sand crucible, filling it not quite full. Knock all the orange off the paper that you can (if you washed it well this will be easy; if not, very difficult), and put the paper with your other old filter papers. Do not burn the paper with the powder. Porcelain crucibles cost more than sand and are more fragile, but are preferred because the powder does not cling to the smooth surface. If you can afford it, get a fused quartz evaporating dish for this job. It is expensive but should last indefinitely.

Heat the powder, as in the acquaintance test, for some time. A large lot will take an hour or more. The ideal method is to use a gas-fired muffle furnace with a good flue; small shops use a gas burner such as is used for cooking, or a Bunsen burner, supporting the crucible on a clay triangle. Do not use a gold-melting furnace, as the draft may carry the powder up the flue. Do not use an electric furnace unless the wiring is carefully protected against the fumes. The fumes are dangerous to the lungs and should be carried off, preferably through a duct that can be cleaned out periodically to salvage any metal that might collect in it. Refiners handling much metal sometimes play a stream of burning hydrogen gas on the powder as it is being reduced. This method can be dangerous if not performed with the utmost precision and is not advised for the small shop.

Heat the powder gently at first, and hold a cold object, such as a pair of tongs, in the fumes. If a white crust appears on it, all right; but if yellow or black stains appear, you are heating too rapidly and will lose platinum. If you are using a pyrometer, proceed slowly till a temperature of 370° C. is reached; after that the heat can be increased rapidly to 900°, at which all volatile matter is burned off. You now have a mass of grey platinum sponge—metallic platinum, finely divided; sometimes it clings together in a sort of clinker.

Sponge reduced in this way by heat is sometimes spoken of as having been *ignited* or *calcined*. There is an alternative method of reducing the orange powder, preferred by many workers because it involves less chance of loss; it employs formic acid, and is described fully in Chapter XIV.

(8) MELTING THE PLATINUM SPONGE

Sponge is melted in practically the same way as filings; this process will be described more fully in the Appendix. The result, assuming that the refining was properly carried out, should be a button of almost pure platinum—rather soft because it can contain at most only a little iridium.

Beginners sometimes make a bad refining the first time, so it is wise to make a small test button first, before melting the whole lot.

(More trouble and loss in refining is due to neglect of this last paragraph, than all other mistakes put together. The wise refiner takes this precaution every time.)

If you get a bad test button, boil the sponge for ten minutes in strong cyanide water. This generally dissolves the dirt, which is probably silver chloride. Wash well with much hot water, dry, and make another test melt.

Generally this gives good metal; or sometimes one or two remeltings will give a good button. (Another practice, which we do not recommend, is to melt up a small lot of bad metal with a large amount of good new metal, gradually getting rid of bad metal in that way.)

But perhaps you made some serious mistake in your refining, and cannot get good metal. In that case, turn to Chapter XV on special repurification, and follow those directions. It is much easier to purify bad sponge than to purify bad buttons.

(9) RECOVERING THE GOLD FROM THE AQUA REGIA SOLUTION

Return now to the big vessel of aqua regia solution, which contains all the gold. (It also contains base metals, palladium, perhaps some iridium, and a little platinum.)

The dissolved gold is now to be recovered. Use copperas, or sodium nitrite, or sulphur dioxide, as preferred, as described in Chapters V and VI.

When using copperas, be sure to add a little hydrochloric acid to the copperas solution, enough to make it a clear green. Among other things, this precaution tends to prevent palladium from being carried down with the gold.

If, in procedure (6) you did not succeed in driving off all the unused nitric acid in your aqua regia, you will have difficulty here; brown bubbles will appear and gold will refuse to come down. When this happens, you must get rid of this nitric acid by methods described in Chapter V.

(10) WASHING AND MELTING THE FINE GOLD—THE STOCK POT

Let the fine gold powder settle for some hours; then test a few drops of the liquid to see if all the gold has been precipitated, using a clean green crystal of copperas as described in Chapter IX. Watch it for a couple of minutes at least. If nothing happens you have used enough copperas. But if a dark cloud forms around the crystal, add more copperas (or sulphur dioxide) to the main solution and let the gold settle again.

Or, if the solution does not contain too much platinum or palladium, use the stannous chloride test. (Large quantities of platinum or palladium in the solution will mask the gold reaction.)

After a satisfactory test, dip or siphon off the liquid into the largest crock you have, called the Stock Pot. You will have to filter the last part of the liquid.

Dump the mass of gold into the casserole, and wash it as described in Chapter V, first with hot water, then with hydrochloric acid, then with water again. These washings are all filtered and added to the Stock Pot, as they contain dissolved platinum-group metals.

Do not let any gold get into the Stock Pot if you can help it.

The liquid in the Stock Pot always contains a small amount of platinum as well as palladium and iridium. These will be recovered in Chapter XIII. It also contains considerable copper, nickel, etc. If you used copperas as your precipitant, the Stock Pot will contain much ferric iron in solution.

If your original material contained much palladium, some palladium may come down with your gold. If so, the gold powder will look dark, even black, and when melted will give a whitish button. When this happens, turn to Chapter XV on Repurification.

After thorough washing, the gold powder is usually ready to be dried and melted. But here again it pays to make a small test melt, before melting the whole batch. Normally this method gives gold pure enough for most jewelers' requirements; but if the original material contained much tin and lead, or much palladium, for example, it may be advisable to go through the repurification.

(The purity of recovered gold depends, first, upon the kind and quantity of impurities that you started with, and second, upon your skill and patience.)

III) THE SILVER JAR

You will recall that in some instances you were told to throw away silver residues, especially the cyanide residues that are so dangerous to handle. This advice is meant primarily for the small user.

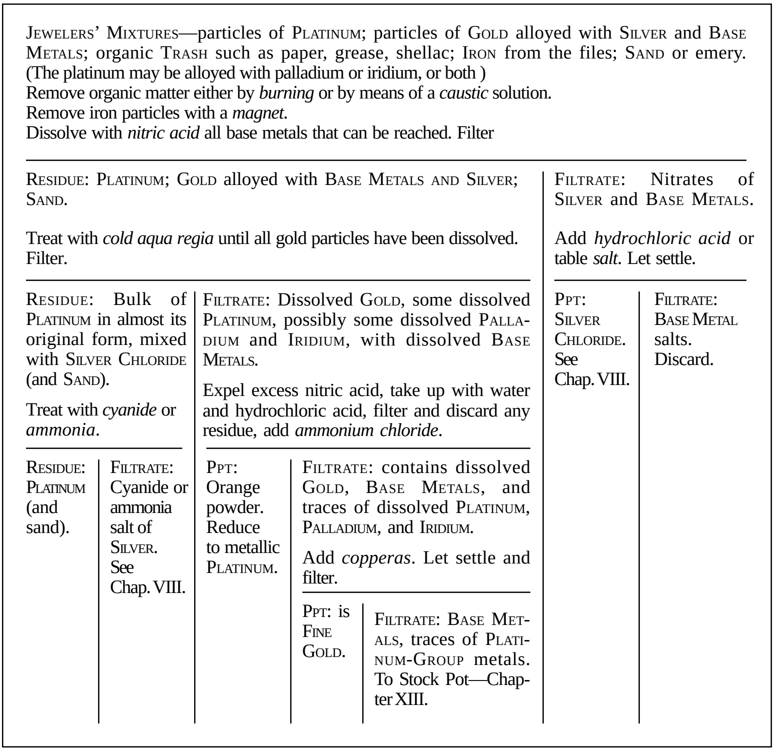
The larger user might do well to save these, if he has good storage facilities, and can keep the cyanide fumes from endangering his health. But he should recall that even at best, silver residues have small value, and usually are not worth refining as such, but should be put in with the sweeps, wash-barrel wastes, or other low-grade stuff.

* * * *

The Stock Pot—the solution from which all the gold and most of the dissolved platinum have been recovered—is set aside for further treatment in Chapter XIII.

SUMMARY

The following diagram, designed for the use of the man to whom the various steps are already somewhat familiar, will be helpful as a reminder and summary. ("Ppt." means "precipitate.")



Jewelers' Mixtures—particles of Platinum; particles of Gold alloyed with Silver and Base Metals; organic Trash such as paper, grease, shellac; Iron from the files; Sand or emery. (The platinum may be alloyed with palladium or iridium, or both)
Remove organic matter either by *burning* or by means of a *caustic* solution.
Remove iron particles with a *magnet.*
Dissolve with *nitric acid* all base metals that can be reached. Filter

- Residue: Platinum; Gold alloyed with Base Metals and Silver; Sand. Treat with *cold aqua regia* until all gold particles have been dissolved. Filter.
    - Residue: Bulk of Platinum in almost its original form, mixed with Silver Chloride (and Sand). Treat with *cyanide* or *ammonia*.
        - Residue: Platinum (and sand).
        - Filtrate: Cyanide or ammonia salt of Silver. See Chap. VIII.
    - Filtrate: Dissolved Gold, some dissolved Platinum, possibly some dissolved Palladium and Iridium, with dissolved Base Metals. Expel excess nitric acid, take up with water and hydrochloric acid, filter and discard any residue, add *ammonium chloride*.
        - Ppt: Orange powder. Reduce to metallic Platinum.
        - Filtrate: contains dissolved Gold, Base Metals, and traces of dissolved Platinum, Palladium, and Iridium. Add *copperas*. Let settle and filter.
            - Ppt: is Fine Gold.
            - Filtrate: Base Metals, traces of Platinum-Group metals. To Stock Pot—Chapter XIII.
- Filtrate: Nitrates of Silver and Base Metals. Add *hydrochloric acid* or table *salt.* Let settle.
    - Ppt: Silver Chloride. See Chap. VIII.
    - Filtrate: Base Metal salts. Discard.

QUESTIONS AND ANSWERS

Q. Is ammonium chloride poisonous? In using the little wash-bottle I got some of the solution into my mouth, and it had a bitter taste.

A. Chemically this salt is related to table salt (sodium chloride), and small quantities will do you no harm. In fact, it is used in some kinds of cough medicine. However, you are advised not to swallow the solution, as it can upset the stomach. Ammonium chloride is also called "sal ammoniac," especially by older chemists.

* * * *

Q. Is there any way of knowing exactly how much platinum will go into solution in aqua regia in a given time?

A. The quantity will depend upon the following factors: (1) the area of platinum—the surface—that is reached by the acids; fine filings expose much area, thick lumps expose relatively little; (2) the temperature of the acids; the warmer the aqua regia the more rapidly it acts; (3) how often you stir; frequent stirring permits fresh acid to reach the metal and hastens action; (4) the composition of the platinum; pure soft platinum dissolves more rapidly than the iridio-platinum that is normally used in jewelry, and the higher the percentage of iridium, the less of the metal will dissolve. Also, some "platinum" is alloyed with more or less palladium, with or without gold and perhaps with nickel and other metals. These alloys dissolve more rapidly than pure platinum; as the percentage of these metals goes up, the rapidity of solution goes up.

* * * *

Q. We are told not to burn the paper with the orange powder. This paper has considerable powder sticking to it. What should be done with it?

A. Discard any part of the paper that shows no stains, and put the rest in with your "Paper Storage," which will be taken care of in Chapter XVIII. We do not burn the paper with the orange powder because the carbon in the paper can combine with platinum, under certain conditions, to form a compound (a carbonyl) that is volatile.

* * * *

Q. Why is it necessary to remove all the excess nitric acid? Could we not add an extra quantity of copperas and get rid of it that way?

A. Several things are accomplished by the removal of the nitric acid, the first being the familiar one of facilitating the precipitation of gold. Also, nitric acid hinders the precipitation of the orange powder, and at the same time causes part of the palladium to come down with the platinum.

* * * *

Q. I have a friend who is doing this work, and he throws down his gold before throwing down the platinum. Is this all right?

A. Under certain conditions it is advisable. There are several possible modifications of this procedure which will be discussed in Chapter XIV.

* * * *

Q. What are the fumes that appear when the orange powder is burned?

A. Several different substances are present: ammonia, hydrochloric acid, chlorine gas, and probably water and other things. This particular reaction has been studied by chemists for a long time, but they are dissatisfied and at least one laboratory has been investigating the matter recently. Undoubtedly some platinum can be carried off mechanically, and apparently a volatile platinum compound can be formed, especially if carbon is present.

* * * *

Q. When I heated the orange powder it darkened and then seemed to creep up the sides of the crucible. Later it clung so tightly to the crucible that I could not get it off. What causes this?

A. This happens when the powder is damp when being burned, also when the ammonium chloride wash water is too concentrated. This excess ammonium chloride is what causes the stuff to cling to the crucible. Impurities such as copper salts will stain the crucible.

* * * *

Q. You tell us to clean the platinum filings with cyanide, to get rid of the mud of silver chloride. Now, I have heard that cyanide will dissolve gold. Isn't it possible that I should lose some gold this way, especially if I do as you say and throw away the cyanide afterwards?

A. Yes, there is a possibility of a small loss of gold here. That is one reason why some people use ammonia for this step, in spite of its slowness. However, cyanide dissolves gold very slowly, even when helped along by aeration, which is not done here. Moreover you were not advised to use the cyanide until after you had reason to believe that the gold was already removed, either wholly or in large part.

* * * *

Q. After evaporating to a syrup to get rid of excess nitric acid, I am told to dilute the syrup with "several" volumes of water. What does this mean?

A. With a little experience you will learn the quantity best suited to your material. Some workers use only three or four volumes of water, others use as much as ten volumes. If you use too much water you waste time in filtering the bulky solutions, and the proportion of platinum recovered as orange powder will be relatively low. On the other hand, if you use too little water, your nickel or copper salts may deposit out as a green crystalline crust mixed with the orange powder. Watch out for this crust, and use enough water to prevent its formation.

* * * *

Q. I have a friend who does this work, and he always adds a little ammonia when he precipitates the orange powder. Does this do any good?

A. It does no good, and it can do harm. For example, if too much ammonia is added (enough to neutralize the acid), all your metals will precipitate together—gold, iron, tin, platinum, zinc—as a mass of pasty compounds, difficult to redissolve and separate. Even a little ammonia can do harm; you will recall in Chapter IX we said that ammonia can form complex substances in which the platinum metals are so tied up that they may not give the usual reactions. If these so-called *amino* compounds do form, they may make your work in Chapter XIII more difficult.

* * * *

Q. I have a friend who is doing this work, and when he precipitates the orange powder he adds alcohol and a big piece of ice. Does this do any good?

A. Ice and alcohol, either together or separately, are sometimes used. Ice is added because more orange powder comes down in a cold solution than in a warm one. Some people put the vessel in the icebox overnight for this reason. However, this chilling may cause nickel or copper salts to crystallize out with the orange powder; accordingly, the method is not generally recommended. Alcohol can also increase the proportion of platinum that comes down. However it reacts with the iridium and palladium (like ammonia) to form compounds that may not be desirable. Accordingly the addition of alcohol is not recommended except—in a few rare cases where this reaction with iridium is desirable.

* * * *

Q. I was reading an old book about platinum, and it said that platinum should be precipitated by sulphuretted hydrogen. Is that a good method?

A. Sulphuretted hydrogen, whose modern name is hydrogen sulphide, is a poisonous gas with an unpleasant odor—the odor of rotten eggs. It will precipitate platinum if the acid concentration is right, but it will also precipitate gold, copper, lead, mercury, and many other metals as well, especially the heavy metals. Because of this latter fact it is rarely used in the recovery of precious metals.

CHAPTER XII

ALLOYS AND BUTTONS CONTAINING GOLD AND PLATINUM-GROUP METALS

Material handled. Jewelers' buttons. Dental alloys. Equipment and chemicals. (A) Preliminary treatments. (B) Melting into a button if necessary. (C) Granulating the button or rolling it thin. (D) Dissolving the metal in aqua regia. (E) Recovering iridium from the silver chloride. (F) Recovering dissolved platinum. (G) Recovering gold. (H) Recovering silver if worth while. (I) The Stock Pot. Summary and diagram. Silver-rich buttons. Questions and answers.

* * * *

MATERIAL HANDLED

In Chapter XI we refined mixtures of gold and platinum particles, the process consisting of the removal of first one, then another contaminating substance, the platinum particles finally being left clean and in practically their original form.

In this chapter we assume that our gold and platinum metals are already melted and alloyed together, as in the case of certain dental alloys. Such material must be dissolved completely, all the gold and all the platinum going into solution and then being precipitated separately. Both jewelers and dental technicians will handle materials of this kind.

It is assumed that the reader is familiar with earlier chapters of this book, has had experience in dissolving and recovering gold, and has performed the acquaintance experiments in Chapter X. If he has carried through a refining according to Chapter XI, so much the better.

JEWELERS' BUTTONS AND ALLOYS

The jeweler occasionally has materials suitable for refining according to this chapter. Thus, after a few weeks of refining the mixtures described in Chapter XI he will have accumulated a number of old filter papers—his paper storage—containing particles of precious metals and considerable dirt. He will reduce this to a button, as described in Chapter XVIII on Low Grade Wastes, which button should be refined according to the procedure shortly to be described.

In past years, when iridium and platinum were much more expensive than they are now, platinum alloys containing gold, palladium, nickel, silver, and even other metals, were sometimes made into jewelry. Scrap and old jewelry made of this stock should be handled according to this chapter. White gold of the highest class (see Chapter VII) contains palladium; scrap and old jewelry made of such white gold should also be handled as described here. Chapter IX on “Identifying” tells how to recognize these complex platinum alloys and how to determine whether a white gold does or does not contain palladium.

DENTAL ALLOYS

Precious metals are employed in dentistry in several forms, some of which have already been discussed. Pure gold in the form of foil or adhesive sponge, is used in fillings; the scrap, which is nearly 24-k gold, should be refined according to Chapter V or VI. There are several kinds of dental gold solders and alloys in which gold and silver are the only precious metals present; these also should be refined according to Chapter V or VI. Amalgams and amalgam alloys contain silver, and sometimes (by accident) other precious metals as well; these should be laid aside and treated according to Chapter XVI. Platinum and iridio-platinum pins also are discussed in Chapter XVI, and generally should be treated separately, but if they are included by accident in the material described below, no harm will be done. Finally, we reach the very important modern alloys that are the main concern of this chapter—the wrought gold alloys and the casting gold alloys in which gold and platinum-group metals are present.

Base metals also find large employment in dentistry, and naturally become mixed with the precious metal wastes. Skinner’s SCIENCE OF DENTAL MATERIALS, listed in the Appendix, describes their application. Thus aluminum is used in making dental plates; so are stainless steel and some of the chromium alloys. Nickel and tungsten are used in dental pins. Steel is employed for dental instruments, drills, etc. “Technic” alloys, which are not used in the mouth, but only for practice, demonstration, etc., are of two types—first the fusible alloys such as the bismuth-lead-tin alloys which are used in dies and counterdies, some of which melt at temperatures as low as that of boiling water, and second the yellow silver-copper technic alloys that look like gold. The workman should try to exclude these base metals as far as possible from his valuable wastes, as they not only consume time and chemicals, but some of them, like lead and tungsten, complicate the refining even when present in small quantities.

Modern dental gold alloys always contain silver and copper, frequently platinum, palladium, zinc and tin as well. Sometimes iridium, rhodium, nickel, and indium[1] are present in small amounts, and the base metals aluminum, magnesium, manganese and iron have been found.

Much interesting research has been done on dental alloys during the last few years, both by the firms that sell them and by the National Bureau of Standards, with the cooperation of the American Dental Association. If the reader is not already familiar with these investigations, he should at once obtain some of the publications described in Chapter E of the Appendix. A familiarity with these recent researches will be of great usefulness both to the user and the refiner of these alloys.

The wrought gold alloys and casting alloys which are the main interest of this chapter, are used for a variety of prosthetic purposes, and many formulas have been proposed. Gold is the principal constituent of most of them, especially the yellow ones. The silver content of the wrought gold alloys ranges from about 5% to as much as 15%; this point will be brought up again later. Platinum and palladium together may run from 10% to as much as 25%. Normally iridium is present in small proportions—less than 1%—and probably got in by accident rather than by design. In the white alloys there is considerable nickel—as much as 18%; copper runs from 9% to 15%, more or less, while zinc rarely runs over 1%. The American Dental Association Specifications[2] require

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[1] Indium is a rare metal, of the aluminum group, sometimes added in small quantities. See U. S. Patents 1,987,451 and 1,987,452, N. O. Taylor, January 8, 1935. Because of its rarity indium is not taken into consideration in this book. If you know that your metal contains indium in sufficient quantity to justify its recovery, see NEW PROCEDURE FOR THE ANALYSIS OF DENTAL GOLD ALLOYS, by Raleigh Gilchrist; Research paper RP 1103, Journal of Research of the Bureau of Standards, vol. 20, pp. 745-771, June, 1938.

[2] These specifications were prepared by the National Bureau of Standards, in cooperation with the Dental Association and the manufacturers of dental gold materials. See Chapter E of this volume.

that dental wrought gold alloys should contain at least 75% gold-and-platinum-group metals.

The casting gold alloys are also made up in a wide variety of formulas. They differ from the wrought golds primarily in that the gold content is relatively higher—up to 90% and over—and the platinum-group metals are lower. The Association Specifications require for soft casting alloys a minimum of 83% gold and platinum group, and for medium and hard casting alloys a 78% minimum.

The dental technician will have a variety of wastes containing these alloys, including scrap, clippings, old dentures, and the stuff swept from the bench where they are fabricated.

For convenience we shall divide these materials into two grades: first grade, consisting of clean buttons, sprues, dentures, clean scrap, and clean old jewelry; while second grade scrap consists of filings and stuff swept from the bench, which contain considerable dirt such as emery, rouge, carborundum, wax, rubber, plaster of paris, investment compound, charcoal, and what not.

For the present we shall exclude all amalgams and mercury; these will be taken care of in Chapter XVI.

For the present we shall handle material that contains comparatively little silver. Later in this chapter we shall consider the button in which silver is the major element.

EQUIPMENT AND CHEMICALS

These are the same as were employed in Chapter XI. Since in this chapter we dissolve all our metal, we may need some more large vessels, such as a large evaporating dish and one or more large jars or crocks, in addition to those already used.

BEGINNING WORK

For your first refining take a very small quantity, say 40 or 50 dwt., in order to gauge the size of vessels that this method calls for. Briefly, the procedures are as follows, most of them being already familiar.

A. Any preliminary treatment that may be useful.
B. Melting into a button if necessary.
C. Granulating this button, or rolling it thin, as preferred.
D. Dissolving the metal in aqua regia.
E. Recovering the iridium from the silver chloride.

F. Recovering platinum from the aqua regia solution, as usual.
G. Recovering gold from the aqua regia solution, as usual.
H. Recovering silver if worth while.
I. Laying aside the remaining solution—the Stock Pot—for treatment in Chapter XIII.

A. PRELIMINARY TREATMENTS

First grade clean scrap rarely needs any preliminary treatment. But second grade stuff, in which there is much assorted dirt, should be sieved, and probably burned in the frying pan or boiled in caustic, and it may help to take out iron particles with a magnet. Remember that if appreciable quantities of amalgam are present, the material should be treated by methods to be described later—Chapter XVI.

Nitric acid, which we used in Chapters III, V, VI and XI to get rid of base metals, is sometimes employed here, but not always, for a variety of reasons. Thus, high grade wrought or casting golds are not attacked by it; therefore nothing would be accomplished by using it. Sometimes it pays to use it on the second grade (dirty) materials, depending upon the kind of dirt present, but usually it is easier to flux the dirt off in the next procedure. A further consideration is the possible presence of palladium. You will recall that *palladium*, when present in pure form or in certain alloys, is soluble in nitric acid; also a few rare alloys containing *platinum* will go completely into solution when boiled in nitric acid.

Accordingly, take a sample of your material, and boil it in nitric acid for a few minutes, then test the liquid with stannous chloride testing solution. If it shows that platinum or palladium has gone into solution, omit the treatment with nitric acid.

If you find that nitric acid dissolves only base metals, then treat the whole quantity of material with nitric acid as usual. If the solution contains worth while quantities of silver, put it in your Silver Jar and refine according to Chapter VIII.

If you are in doubt, omit the nitric acid treatment.

B. MELTING THE MATERIAL INTO A BUTTON, IF NECESSARY

Second-grade stuff, especially if it contains much carborundum or emery, is generally melted into a button.

Mix it well with a flux such as crushed borax glass and soda ash, using equal weights of flux and material, and melt in a gold-melting furnace, using a sand crucible. The flux serves to liquefy the dirt, while the metallic particles collect into a button at the bottom of the crucible. If the proportion of emery is high, use more flux. The chapter on Low Grade Wastes gives formulas of other fluxes. Do not use litharge. Let the melt cool in the crucible, which is then broken and the button carefully separated from the slag.

First-grade clean stuff, such as old dentures, may or may not need to be melted into a button. It does no harm in any case, and after a little experience you can tell whether it does any good or not; different kinds of metal call for different treatments.

Thus, if your metal—either first-grade or second-grade material—runs more than half platinum, whose melting point is high, ordinary melting will not get it into a homogeneous button; you will want to lower the melting point of the whole mass by adding some brass, or perhaps some copper or zinc. If you have some rolled or filled gold scrap to get rid of, here is a good place to utilize it by melting it in with your second-grade dental wastes.

When breaking the crucible to remove the button, look out for beads or shot metal embedded in the slag; if there are many of these it means that you did not heat long enough, or did not use enough flux, or that your platinum percentage was too high. If properly done, the melting will consolidate all the metallic particles into a button, and all the emery, rouge, plaster-of-paris, etc. will go into the slag which then can be thrown away.

C. GRANULATING THE METAL, OR ROLLING IT THIN

The next task is to get the metal into such form that acids can work upon it easily. Sometimes the lumps or buttons are so soft that they can be rolled thin as paper. Cut the strips into short lengths and twist them so they will not lie flat in the acid, then anneal. Roll very thin; a few minutes spent at the rolls will save hours in the acid.

But often these metals refuse to roll, and it is easier to granulate them. This is done by remelting the metal and pouring it while molten into a big vessel of water. (See Chapter V.)

If your metal is as much as 12% silver, the silver will cause trouble when you try to dissolve the button in aqua regia. In Chapter VII on green gold we discussed this subject and the reader would do well to refer to this chapter now. So, if you know your metal to contain as much as 12% silver, melt some other metal in with it—gold, or copper, or zinc or brass—sufficient to get the silver content down to say 10% or less.

If you do not know what the percentage of silver is, drop a piece of your metal into a little aqua regia, heat to a boil, and see what happens. If the acids are very slow to act the chances are that it would pay you to melt your metal up with brass, gold, or other metal, in proper quantity to reduce the silver to 10% or less.

Usually it is best to add this extra metal when you are about to granulate the material. But some workers like to add it when making the first melt, just described.

D. DISSOLVING THE METAL IN AQUA REGIA

Place the metal, which by now is rolled thin or granulated, in a casserole and cover it with aqua regia. Mix as follows:

Nitric acid, full strength	1 part
Hydrochloric acid, full strength	4 parts
Water	2 parts

Do not add any sulphuric acid yet.

Use 6 or 8 fluid ounces of the mixture to each Troy ounce of metal; with much platinum you may need more.

Sometimes the acids go to work at once; usually you will have to heat. If possible, set the casserole on a steam bath as that does not cause spattering or require continuous attention. Stir often to dislodge the scum of silver chloride. Place an inverted funnel over the dish, to prevent spattering, save acid, and keep out dirt.

Some people like to use an Erlenmeyer flask for this step, because it permits them to see what is going on. The thin Pyrex glass models withstand heat well. The frontispiece shows several Erlenmeyer flasks in operation, and on page 171 the reader will find other illustrations, with catalogue numbers and prices. The refiner may have occasion to use both the narrow-mouthed form and the wide-mouthed; the latter when there is some danger of boiling over. The narrow-mouthed form comes in many sizes, from the tiny 10 cc. size to the 6000 cc. model. The wide-mouthed form is made in three sizes—250, 500, and 1000 cc. Another advantage of these flasks is that the material therein can be stirred easily merely by rotating the flask—not too briskly, of course, or it might froth over.

Do not use an evaporating dish for this procedure, as it permits too much acid to evaporate off wastefully.

The length of time required to dissolve the metals depends upon several factors. You can hasten matters by having the pieces very small and thin, by heating, and by stirring often to loosen the coating of silver chloride. Also, the more platinum and the more silver in the metal, the slower the action of the acids.

Silver, especially, makes the process slow. If it runs as high as 12% the slowness is noticeable; if as high as 25% the metal is practically insoluble.

Sometimes it helps matters to pour the solution off into a pitcher, then dump the whole mass of metal into the mortar and grind it hard with the pestle, to loosen the chloride. Then dump it back into the casserole, washing it back with a little water; then cover it again with the aqua regia solution, which will now go to work again with vigor.

Sometimes individual lumps or strips of metal will be much slower to dissolve than the bulk of the material. It may pay to pick out such lumps and lay them aside until they can be melted up and the silver content reduced to 10% or less.

Finally all the metal will seem to be dissolved, and you will have left only the powdery residue of silver chloride. Here, however, we meet a new consideration—a point that has not come up before. *If your original material contained iridium, the iridium will now remain undissolved as a metallic dark powder, mixed with the silver chloride.*

This fact—that when these alloys are dissolved in aqua regia the iridium remains undissolved—was not appreciated by most early workers, but careful research at the National Bureau of Standards[3] and elsewhere has established the fact that iridium does have this peculiarity. And if the platinum content is high, sometimes some of the platinum also will remain with the silver chloride. This may or may not complicate your task, however, first because dental alloys normally contain little if any iridium, and second because the platinum content is rarely high. The iridium residue has a dark color, and as you become more experienced you can tell by its appearance whether the silver chloride does or does not contain enough value to justify its further treatment. Assuming for the moment that our material might contain a good amount of iridium, we would proceed as follows:

E. RECOVERING IRIDIUM FROM THE SILVER CHLORIDE RESIDUE

When the aqua regia has dissolved all the metal that will dissolve, dilute it with its own volume of hot water, let it stand a little while; then pour or siphon off the solution—do not filter it yet—leaving the residue in the dish. Wash the residue and add the washings to the main solution. This main solution contains the gold, platinum, and palladium, and the base metals. Add a little sulphuric acid to it at this point, an ounce or less to each quart of solution, stirring well and adding the acid slowly. This precipitates any lead that might be present, and also facilitates the removal later of the excess nitric acid. Set the solution aside to settle, while we turn our attention to the residue in the dish.

Take a small sample, say as much as can be taken on the tip of the porcelain spoon, place it in a small beaker or tiny porcelain casserole, and add chemically pure ammonia diluted with hot water. Ammonia dissolves silver chloride, leaving iridium or platinum undissolved as a fine heavy dark residue, so fine that it may be almost

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[3] See William H. Swanger's paper on ANALYSIS OF DENTAL GOLD ALLOYS, Scientific Paper of the Bureau of Standards No. 532, of August 11, 1926. Also see Raleigh Gilchrist's NEW PROCEDURE FOR THE ANALYSIS OF DENTAL GOLD ALLOYS, Journal of Research of the National Bureau of Standards, Vol. 20, June 1938, pages 745-771. These papers, which are devoted primarily to the analysis of these alloys, rather than to their refining, are mentioned again in Chapter E of the Appendix.

invisible. Rotate the little vessel and whirl all the powder into the center, and it will be easier to see.

Frequently there is a light-weight light-colored residue, insoluble in ammonia, that is merely flakes of glass or porcelain scaled off the dishes and acid bottles. This is plainly of no value, and should not deceive a careful observer.

You may find that no precious-metal residue remains; if so your silver chloride is of small value and may be placed in the Silver Jar or with other silver residues. But if the ammonia test reveals appreciable quantities of iridium, then the whole quantity of silver chloride must be dissolved out.

This procedure is similar to procedure 4 in Chapter XI, where you dissolved the silver chloride from the platinum filings, using either cyanide or ammonia. If you are not already familiar with this procedure, go over it again now. Simply cover the material with water to which cyanide or ammonia is added, and heat. Most workers prefer ammonia for this task, rather than cyanide, because it is safer and because the silver may be recovered therefrom more conveniently.

Sometimes this treatment reveals pieces of metal that have not been acted upon sufficiently by the aqua regia, and which must be returned for further treatment, but after you have had a little experience this will not occur.

The residue that remains after all the silver chloride is dissolved will consist of the fine dark iridium powder, which may contain some platinum, and almost always there will be the light flakes of porcelain or glass from the vessels. Wash it well and catch it in a filter paper. The disposal of this powder will depend upon the needs of the worker. If the iridium is to be used in making up new alloys, the flakes of porcelain or glass should be removed with hydrofluoric acid according to the method given in Chapter XVI. If not, let the residue dry and then sell it to a professional refiner who gives credit for iridium.

F. RECOVERING PLATINUM FROM THE AQUA REGIA

Returning now to the aqua regia solution that contains dissolved gold, platinum, palladium, and base metals: we shall recover first the platinum, then the gold, according to methods that were used in Chapter XI. Turn back now to Chapter XI, procedure 6, and proceed exactly as there described.

You will note that the first step is to consider any sediment that may be present; sometimes there is much sediment, sometimes very little, and it can be removed now or later, as desired. The next step is to drive off excess nitric acid, dilute with water, filter if not perfectly clear, and recover platinum with ammonium chloride, exactly as in procedures 6, 7 and 8 in Chapter XI.

G. RECOVERING GOLD

This is accomplished precisely as in procedures 9 and 10, Chapter XI.

H. RECOVERING SILVER IF WORTH WHILE

This is accomplished as in Chapter VIII.

I. THE STOCK POT

Here again we follow the procedure of Chapter XI. The solution from which you recovered the gold and most of the platinum still contains all the palladium, as well as a little platinum. This constitutes what is called the Stock Pot, and it is laid aside for further treatment in Chapter XIII.

* * * *

SUMMARY AND DIAGRAM

The following diagram will summarize this chapter, and will be useful to the worker who is already familiar with the various procedures. It is helpful to compare it with the scheme given at the end of Chapter XI.

Dental Alloys—alloys containing Gold with Platinum-Group metals and Base Metals, possibly mixed with organic Trash such as paper, wax, vulcanite, as well as sand, emery, abrasives, iron from files, etc.

Remove iron with a *magnet.*
Remove organic trash by *burning,* or by means of *caustic,* or by *melting* the material into a button.
Heat with *aqua regia* until all metallic particles are dissolved.

- Residue: Silver Chloride, mixed with dark powder of Iridium, also Sand.
  Treat with *cyanide* or ammonia.
  - Residue: Iridium, Sand. See Chap. XVI.
  - Filtrate: Cyanide or ammonia salt of Silver. See Chap VIII,or discard.
- Filtrate: Gold, Platinum-Group metals (except iridium) and Base Metals, in solution.
  Expel excess nitric, take up with water and *hydrochloric acid,* filter and discard residue, and to the clear solution add *ammonium chloride.* Let settle and filter.
  - Ppt: Orange powder. Reduce to metallic platinum.
  - Filtrate: Gold, traces of Platinum-Group metals, and Base Metals, in solution.
    Add *copperas.* Let settle and filter.
    - Ppt: Fine Gold.
    - Filtrate: contains traces of Platinum-Group metals, especially Palladium, with base metals. To Stock Pot—Chapter XIII.

SILVER-RICH BUTTONS

As we intimated earlier in this chapter, if an alloy containing both gold and platinum-group metals should also contain much silver, it will require somewhat different treatment. If the silver content is as high as 15%, the button will be very difficult to dissolve in aqua regia. The best plan, in such cases, is to add enough gold (or copper or brass or zinc) to reduce the silver content to 10% or less, then to proceed according to the method just given.

However, it occasionally happens that an alloy contains so much silver, and so little gold and platinum-group metals, that the above expedient will be unsuitable. If you can so manipulate your materials as to avoid the formation of buttons of this type, do so, as they are not easy to refine.

You will recall in Chapter X, that when a button containing much silver and only a little platinum is treated with nitric acid, more or less platinum goes into solution. If the platinum content is low, it will all dissolve; if the platinum content is high, part of it will dissolve, and part of the silver will remain in the residue. In other words, nitric acid does not effect a separation. And it is not easy to recover the platinum from the nitric acid solution.

The way out is to dissolve such buttons in sulphuric acid—not full strength acid, but acid containing about one part water to three parts acid. (Pour the acid into the water, slowly, and stir well.) This can be done when the gold-platinum content is not over 25%. The process is similar in principle to the inquartation described in Chapter VI, where a silver-gold alloy was refined by means of sulphuric acid; and the same precautions should be observed.

After the sulphuric acid has acted all it will, pour it off into a large jar of water, leaving the residue in the vessel. The liquid in the large jar will contain sulphate of silver (and sulphates of base metals), and the silver can be recovered as in Chapter VIII. The residue will contain gold, platinum, and possibly some silver that was not reached by the acid. Collect it and wash well, then treat it with aqua regia exactly as you treated the gold-platinum alloys that constitute the main topic of this chapter.

If you should, by inadvertence, dissolve a silver-platinum alloy in nitric acid, and find that a worthwhile quantity of platinum has gone into solution as platinum nitrate, do this: to the nitric solution, which contains platinum, silver, and perhaps other metals, add enough hydrochloric acid to precipitate all the silver as silver chloride. Filter, and handle the silver chloride as described in Chapter VIII. The solution will contain platinum dissolved in a sort of aqua regia in which the proportion of nitric acid is unusually high. Evaporate as usual to expel the nitric acid, then recover the platinum with ammonium chloride, as usual.

QUESTIONS AND ANSWERS

Q. Is it essential to add sulphuric acid to the aqua regia solution? I have a friend who does this work, and he says he never uses it.

A. No, the sulphuric acid is not necessary. Many expert workers never use it at all, even when lead is present, maintaining that it tends to make the solution so strongly acid that the precipitation of gold is hindered. On the other hand, one of the largest and best refiners of dental wastes uses considerably more sulphuric acid than is suggested in this book. See REFINING AND MELTING SOME PLATINUM METALS, by J. O. Whiteley and C. Dietz, of the Dentists' Supply Co. Laboratories, published by Mining and Metallurgy, March, 1928.

* * * *

Q. After precipitating the orange powder, I set the jar aside overnight and next morning there was a crust of green granular stuff all over the orange powder, and some was floating on the liquid. What shall I do?

A. The green crystals are probably a nickel or copper salt, crystallized out when the solution cooled. You may be able to get rid of some of the crystals by fishing them out with the porcelain spoon. Dissolve the rest in a little hot water, stirring well; then before they have time to form again capture your orange powder in a filter paper, and proceed as usual. This happens often when your material contains much nickel or copper.

* * * *

Q. My material contains considerable palladium, but very little platinum, and no indium to my knowledge. When I add the ammonium chloride in Procedure F, I get hardly enough orange powder to show on a filter paper. Can I omit this treatment?

A. Yes. If you know that your solution contains very little platinum you can omit the ammonium chloride, and proceed immediately to take down the gold. Whatever platinum is present will be recovered when you refine the Stock Pot in the next chapter.

* * * *

If you have not already done so, we suggest that you read the group of Questions and Answers at the end of Chapter XI.

CHAPTER XIII

THE STOCK POT

Material handled. Equipment and chemicals. Collecting the precious metals with zinc. Refining the black powder. The iridium residue. The dilute aqua regia solution—platinum, palladium, gold. Burning the red palladium powder. Further treatment. Disposal of the final tailings. Diagram. Questions and answers.

* * * *

MATERIAL HANDLED

This chapter covers the recovery of the precious metals, usually present in small amounts, that remain in the solutions that were left over at the ends of Chapters X, XI and XII.

These solutions should be stored in a large crock of good-quality stoneware. Cheap earthenware sometimes absorbs solution and in time may crumble.

These solutions normally contain only a little platinum. Palladium and iridium will be present in either large or small amount, depending upon the original material; dental scrap usually contains considerable palladium and very little iridium; jewelers' scrap will differ from batch to batch.

If you used enough copperas in Chapters XI and XII there will be no dissolved gold in the Stock Pot; if some should remain through accident, it will be recovered in time. If you filtered properly there will be no silver chloride and no lead sulphate.

Other base metals will be present in considerable quantities. Thus if you used copperas (iron sulphate) to precipitate your gold, there will be much dissolved iron in the Stock Pot; this gives it a brown color. Copper, nickel, zinc, tin, cadmium, and possibly other base metals will be present as well.

The other metals of the platinum group—rhodium, osmium, and ruthenium—are present here only under exceptional circumstances. If present, they will be recovered in time. They will be discussed more fully in Chapter XVII.

The Stock Pot should contain only such solutions as are definitely described as suitable to be added to it. In particular, never let any cyanide get into the Stock Pot, nor the silver nitrate solutions that belong in the Silver Jar, nor any of the other solutions you were told explicitly to throw away.

The Stock Pot should be kept lightly covered to exclude dust. If possible, set it on top of a radiator or steam pipes, that it may slowly concentrate by evaporation.

EQUIPMENT AND CHEMICALS

At the beginning of Chapter XI we mentioned the equipment and chemicals that will be used in this chapter.

COLLECTING THE PRECIOUS METALS WITH ZINC

Some workers wait until they have accumulated several gallons of this solution before going to the next treatment. The man who has very little room will probably want to refine each lot at once, instead of waiting. For your first refining, handle not more than three gallons.

When you are ready to clean out the Stock Pot, add a good quantity of zinc shavings and a little hydrochloric acid. Zinc shavings are much better than granulated zinc or mossy zinc, but these latter forms can be used if you cannot get the shavings. The kind described as “zinc shavings for cyaniding” is the best, and well worth the slight extra cost.

There should be some bubbling when it goes in; if not, slowly add more acid. But be careful, as sometimes it boils over, or it might get hot enough to crack the jar.

You cannot tell beforehand how much acid or how much zinc will be needed; it all depends upon how much precious metal is present, and how much acid. A pound of zinc shavings may be enough for a three gallon lot of solution; or you may need much more.

Let this stand for at least three or four hours. If you stir it often it may be ready sooner.

The zinc reduces or throws down the precious metals (also copper) as a fine black powder. If you have used enough acid and enough zinc, in a few hours your solution will be a pale green, almost colorless.

Sometimes the solution suddenly becomes thick and muddy, with a scum on top. In that case, add hydrochloric acid and stir, until it clears up. Try to avoid this thick mud, by having plenty of acid in your solution.

When the solution becomes a clear pale green, almost colorless, you are usually safe in concluding that all the precious metal has been thrown down, and that the solution contains nothing of value. Test it with stannous chloride (see Chapter IX), which will show if any precious metal is still in solution. (The only exception is iridium, which reacts slowly with zinc and is the last to come down.)

After the black powder is once thrown down, do not leave it for long with the pale green solution standing over it, or it will re-dissolve. In that case you must add more zinc and more hydrochloric acid, just as before, until the black powder comes down again and the liquid again becomes pale green and is proven to be of no value.

Let the black powder settle, dip off the clear solution and throw it away. If the powder is slow to settle, pour in a good quantity of hot water, and it will settle more promptly. Or, if necessary, filter.

Next get the black powder out of the big crock into a casserole or big beaker, washing it out with the big wash-bottle.

Some people like to refine each batch of black powder at once. Some merely wash each batch, and wait until they have accumulated several batches before refining it. But for your first refining of the black powder use a small quantity, not more than enough to fill a 300 cc. beaker.

If you prefer to put it away for a while, wash it into a vessel that can be closed air-tight; a Mason jar is good. Use a wide-mouthed vessel because it is hard to get powder out of a vessel with a narrow mouth. Wash the powder down, so as not to leave any sticking to the sides of the jar, and cover it with water, to stay wet until refined. Stopper the jar firmly.

REFINING THE BLACK POWDER

There are several ways of refining this powder. The following is a general method, and other methods will be given in Chapter XIV.

If your black powder has been left standing and if some of it has re-dissolved and turned the liquid yellow, add a little hydrochloric acid and zinc, until the liquid is colorless again. Next, wash the black powder well to get rid of acid and zinc salts, using plenty of water; then dry it. The usual method is to get it into a clean filter paper, and spread it out to dry in a warm place.

The next step, if possible, is to ignite this black powder—to heat it strongly, but not to melt it. The ideal arrangement is to place it in a quartz evaporating dish and heat it in a muffle furnace. This step is not absolutely necessary, and may be omitted; its purpose is to convert the iridium into a form that is not readily soluble in aqua regia, so if you are not anxious to obtain your iridium separate from the platinum, this ignition may be omitted. If the ignition causes the powder to stick together in clumps, break these up by crushing with a glass rod or grinding in a mortar. Part of the palladium will oxidize, and you will see the blue and green colors that you observed in the acquaintance tests.

The next step is to dissolve platinum, palladium, palladium oxides, gold and base metals, and to leave the iridium (and the other platinum-group metals, if any) undissolved. To do this we first treat the powder with plain hydrochloric acid; then without filtering we add nitric acid and some water to form dilute aqua regia. (Palladium oxides dissolve readily in plain hydrochloric acid, but not in aqua regia; that is why we add the hydrochloric acid first). Since we do not know how much palladium oxide is present, we begin by using only enough hydrochloric acid to cover the powder, then heat gently and watch the effect. Perhaps there will be very little action; perhaps you will have so much palladium oxide that more hydrochloric acid will be needed; the intention is to dissolve everything that will dissolve in hydrochloric acid.

Then, as we said, without filtering, we add dilute aqua regia to dissolve platinum, palladium, and whatever gold and base metals are there. By "dilute" aqua regia we mean a mixture of 1 part nitric acid to 4 parts hydrochloric acid and about 6 parts water. This acts readily upon the finely divided metal particles; heat gently for a few minutes; it may not be necessary to bring it to a boil.

Let the dilute aqua regia act all it will, stirring well so that it can reach all parts of the material. Do not leave the acids on any longer than is necessary to dissolve everything that will dissolve under this gentle treatment. Then filter off the liquid and set it aside for further treatment, leaving the residue in the dish.

THE IRIDIUM RESIDUE

This residue should be washed, the washings being added to the main solution. Possibly there was no iridium, rhodium, or ruthenium in your original material; in such case this residue will be merely light-colored flakes of glass or porcelain that have scaled off the vessels and acid bottles, which naturally may be discarded at once. Iridium, if present, will be in a fine dark powder, very heavy. Normally your residue will consist of both the light flakes and the heavy iridium particles. Wash this into a filter, using plain water at first. Then as you wash add an occasional drop—no more—of hydrochloric acid. When washed in plain water these fine metallic powders sometimes go through the paper; a little acid, or an occasional crystal of table salt, in some odd way lessens this tendency. Add the washings to your main solution.

If your original Stock Pot solution contained any rhodium, ruthenium or osmium, these metals will now be found as heavy metallic powders, mixed with the iridium powder, presenting the same appearance.

The disposal of this residue will depend upon individual circumstances. Often the best thing is to sell it to a professional refiner who gives credit for iridium. Sometimes you can use it to make up new alloys. Unfortunately this separation is never a perfect one, no matter how skilled you may be; that is, some iridium dissolves in the dilute aqua regia, and usually the iridium residue contains a little platinum, and possibly other things. Hence the advisability of subjecting the residue to further purification as in Chapter XV, or of selling it as it is. The flakes of glass and porcelain can usually be dissolved out with hydrofluoric acid, as in Chapter XVI, and with a little experience you can tell by its looks whether the residue is of good quality or not.

THE DILUTE AQUA REGIA SOLUTION—PLATINUM, PALLADIUM, GOLD

This contains all the palladium, a little platinum, any gold that might have gotten into the Stock Pot, and base metals; also considerable water, which we now get rid of by evaporating to a syrup. Use a big evaporating dish and heat on the steam bath. At the same time the excess nitric acid will be driven off. It does no harm here to add a few drops of sulphuric acid, to throw down any lead that might be present and at the same time to facilitate the expulsion of the excess nitric acid.

This is in every way comparable to the evaporations in previous chapters. Take up the syrup with a little hydrochloric acid, as usual, repeating if necessary, to get rid of all nitric acid; then dilute the syrup with several volumes of water, all just as usual. If gold bakes out, dissolve it with a few drops of hot water containing a little sodium chlorate. (This combination of chlorate and acid produces a gas which can be explosive under certain conditions, so work slowly and keep everything hot; if all your solutions are hot there is little danger of this gas accumulating in sufficient quantity to cause damage.)

If any sediment or residue remains, filter it out and put it in your paper storage. It is probably lead sulphate, but may contain something valuable.

PLATINUM

To the solution now add ammonium chloride—either the dry, pure salt, or a concentrated solution. This will precipitate platinum as the familiar orange powder, exactly the same as in Chapter XI or XII. Let it settle, pour or siphon off the solution, catch the orange powder in a filter, wash it well as usual, then dry and burn it, all just as usual. If your original material contained no platinum, nothing will happen here, so proceed at once to the next step. (But even if you should know that platinum is absent, add the ammonium chloride, as it is required for the next step.)

PALLADIUM

The solution from which you have removed the orange powder should now be in a vessel that will stand heating; a tall glass beaker is best, or a casserole. Heat it almost to boiling, and slowly add a few small crystals, one or two at a time, of sodium chlorate. (See Acquaintance Test with Palladium, Chapter X.)

Turn the flame down so that the liquid just boils. It is very apt to boil over. Soon you will see bubbles of chlorine gas, so do this work near the exhaust fan or flue.

For a quart of liquid a teaspoonful of chlorate may be enough; sometimes much less, sometimes more. The amount of chlorate depends upon the amount of palladium present, and upon other factors not easily regulated.

(Potassium chlorate is not as good for this work as sodium chlorate, but it can be used if you cannot get the sodium chlorate.)

Soon you will see a red powder forming on the surface of the liquid and on the sides of the dish. If no red powder forms in five minutes, add some more hydrochloric acid and more chlorate, and scratch the inside of the vessel with the glass rod.

This red powder is palladium-ammonium-chloride.

Use only enough chlorate to bring down all the red powder possible. Keep the solution hot—almost boiling. With a little practice you can tell when you have used enough chlorate, because as the palladium goes into the form of red powder, and settles to the bottom of the beaker, the liquid becomes paler and paler in color.

If you are interrupted while doing this, you may find on your return that some of the red powder has re-dissolved. If so, heat the solution again and add a little more chlorate.

Let this stand on the little flame for perhaps half an hour, adding an occasional crystal of chlorate, and filter within 24 hours. Wash it into the filter as usual, washing the powder down into a lump with a thin stream of ammonium-chloride-water. Drop a crystal of chlorate into the funnel as it runs through. Wash well, the same as you washed the orange powder in Chapter X. Then let it dry.

BURNING THE RED PALLADIUM POWDER

Dump the dry red powder out of the paper into a small porcelain crucible, and ignite it exactly the way that you burned the orange powder of platinum-ammonium-chloride. It shrinks on being burned, so add more powder from time to time. Sand crucibles have been used for this work, but the palladium sticks to them so tightly that there is always loss in getting it out.

The red powder melts and burns down to a crust of palladium sponge. It may be grey, or tinted with red, blue and green oxides. Loosen the crust with a pen-knife and drop it out of the crucible into a casserole.

It pays to reduce the palladium oxides before melting the sponge, thus: moisten the sponge with alcohol and heat it gently until the colors go and the sponge is a clean grey or black. The alcohol will take fire, so work carefully.

Most people make up new alloys with the sponge, without melting it into a button. With careful work you may get sponge pure enough for commercial purposes at the first precipitation, but most workers like to purify it further. (See Chapter XV.) The red powder is more easily purified than the sponge, accordingly, if you intend to repurify, do not ignite the powder, but proceed at once to Chapter XV.

Another method of reducing the red powder, in which formic acid is used, will be described in Chapter XIV.

To melt the palladium sponge, use an oxy-gas torch, as described in Chapter A of the Appendix. The button may swell up and act queerly, because it absorbs large amounts of gases when hot, then gives them off when cooling. After the metal is all molten, move the flame away very slowly, turning the oxygen off slowly so that the button may cool gradually in a yellow flame. Then turn the button over and heat the other side until it just runs smooth. You can get a whiter button by dropping it into water while still very hot.

FURTHER TREATMENT OF THE SOLUTION FROM WHICH PLATINUM AND PALLADIUM HAVE BEEN REMOVED

Returning to the solution from which we filtered off the red powder: it will contain traces of both platinum and palladium, and possibly some gold. (You tried to recover all your gold in Chapters XI and XII, but now and then some finds its way into the Stock Pot.) Test it with the stannous chloride testing solution, as your next treatment will depend upon what it contains.

Normally it contains only *traces* of platinum and palladium, and therefore, will be placed in the Stock Pot again. (Note that this completes a sort of circle, the residues from the Stock Pot going back to become a new Stock Pot.) But sometimes it contains considerable palladium—so much palladium that you feel that further treatment is necessary—in which case you may follow the procedure below. If palladium is present only in small amount, however, proceed to the later section in which gold, if any, is recovered.

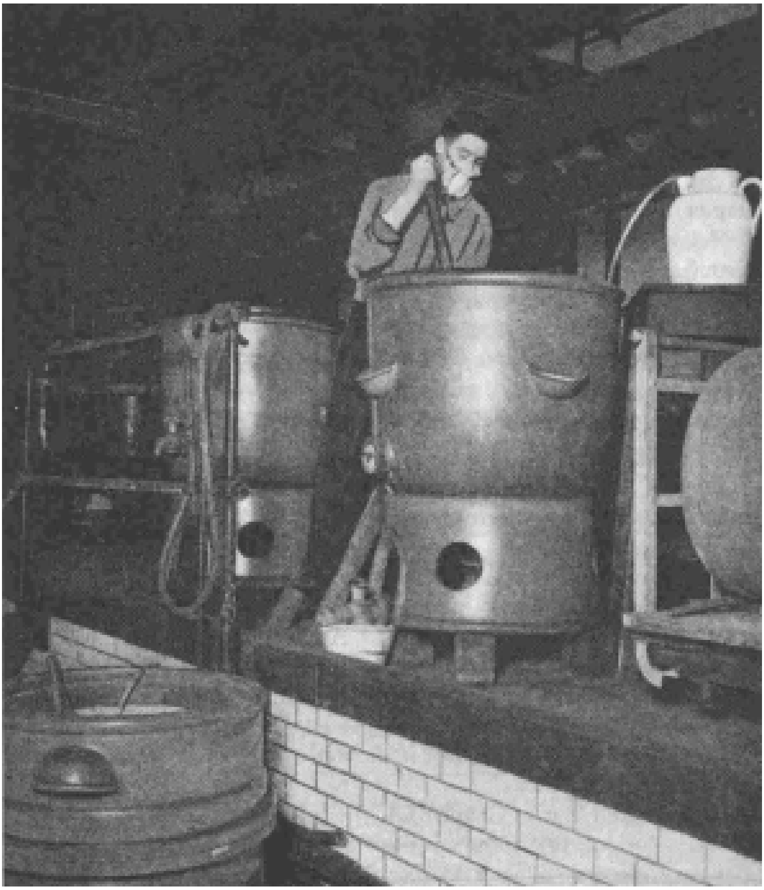
Further treatment to recover palladium, to be used when the chlorate treatment was inadequate and when considerable palladium is present, follows.

First, add ammonia, slowly, and stir all the time. It gets hot and fumes. With the first few drops you will get pasty precipitates of different colors, depending upon what base metals are present. As you add more ammonia, the precipitates may get heavier. Add still more, and most of them will re-dissolve.

The amount of ammonia needed depends largely upon the amount of acids and base metals present. You want to add so much that there is no further change in color, and no more precipitate dissolves. The chemist would say that this is an “excess of ammonia.”

If much copper or nickel is present, the liquid will now be a beautiful sapphire blue. If much iron is present, the precipitate will be a brown jelly in little flakes. Lead and tin give pale precipitates.

After a few minutes filter off this precipitate. Generally it can be thrown away, as it consists of base metal compounds. But if very bulky, put it in the paper storage or the sweeps, as bulky precipitates sometimes take some palladium down with them. Wash the precipitate in the funnel with a little ammonia.



Adding ammonia to a large quantity of palladium solution.

Now take the clear ammonia-palladium solution, and very slowly add just enough hydrochloric acid to it to make it change color again. Make it distinctly acid with the hydrochloric acid. Stir well with a glass rod.

The mixture becomes hot and bubbles appear, of a gas whose odor suggests mice, and a bright yellow powder is soon seen. Let it stand half an hour or so; over-night if desired. This yellow powder is called palladosamine chloride, as well as by other names. It is much like the red palladium powder in its general nature.

Filter off the yellow powder, washing it down into a lump with the ammonium-chloride-water as usual. Wash and dry as usual, and burn it the same as you burned the red powder. The two may be mixed together if desired, or reduced by means of the formic acid method that will be described in the next chapter, or repurified as described in Chapter XV.

(Note: This "Further Treatment" should be avoided when your solution contains very large quantities of copper. The sapphire-blue copper-ammonia compound, observed above, has an unexpected effect upon paper, and when present in large amount will weaken the filter-paper and render filtration difficult.)

DISPOSAL OF THE FINAL TAILINGS

The solution that remains should now contain only a trace of precious metal. It is usually referred to as the final tailings, to distinguish it from the solutions left over from Chapters XI and XII. Frequently it is of such low value that you should throw it away without further ado. Take out small samples and test them, first with copperas to see if gold is present, then with stannous chloride to see if there is enough platinum or palladium to justify further effort. At this point you find use for a thorough familiarity with the color changes described in Chapter IX, especially in comparison with standard solutions containing a known weight of metal.

Normally gold is absent. But if present in paying quantities, recover it as usual with copperas.

You will recall that in Chapter IX, you were told that ammonia added to these solutions, can form amino-compounds from which it is sometimes—not always—difficult to recover platinum and iridium, even by treatment with zinc. When you recall this fact you see why we hesitate to add this particular solution with its high concentration of ammonia salts to the Stock Pot. One alternative is to evaporate it to a crust and put the crust in the sweeps. Another alternative is to keep it in a small jar, separate from your big Stock Pot, but to treat it with zinc in the same way, using extra time and care to insure the recovery of all precious metal.

You will recall, also, that you have been told not to pour acid solutions into the settling barrels or tanks through which your factory wash-waters pass, because they might dissolve solid particles of precious metal. You can get around this dilemma sometimes, however, by neutralizing the acid in your tailings. (This may or may not be feasible.) Take out a pint or so of the tailing solution, and add small lumps of air-slaked lime, for example, until the acid is killed. This point can be recognized by the litmus paper test described in Chapter IX; also by color changes in the solution. Work slowly, as the lime and liquid become hot, and might break the crock. Usually the mixture becomes pasty and many-colored, depending upon the variety of base metals present. This pasty stuff may clog some types of wash-barrel systems so consider this possibility before using this plan on the whole solution.

Other suggestions will be found in Chapter XVIII on Low Grade Wastes. Most jewelers, it might be noted at this point, are inclined to waste time, chemicals and floor space on these low-grade solutions, and workers have been known to spend fifteen or twenty dollars packing up and shipping off a solution that contained about two dollars' worth of metal. The way to avoid such mistakes is to utilize the tests and the Standard Solutions that were described in Chapter IX.

* * * *

The following scheme will be helpful in following the routine of the Stock Pot refining, but should not be used until after one has become familiar with the individual steps.

<table>
<tr><td colspan="4">Black Powder obtained from concentrating the Stock Pot solution with zinc—contains Platinum-Group metals, Base Metals, and possibly some Gold.
Wash, ignite if possible to convert iridium to a less soluble form, treat with <i>dilute aqua regia</i>, applying the hydrochloric acid first to dissolve the palladium oxides. Filter.</td></tr>
<tr><td colspan="3">Filtrate: contains Platinum, Palladium, Gold if any, and Base Metals.
Expel excess nitric acid, dilute, add hydrochloric acid, discard residue, add <i>ammontum chloride</i>. Filter.</td><td rowspan="3">Residue is Iridium with flakes of glass and porcelain from the vessels Possibly ruthenium and other platinum-group metals.</td></tr>
<tr><td rowspan="2">Ppt is orange powder of Platinum Ammonium Chloride.</td><td colspan="2">Filtrate contains Palladium, Gold if any, Base Metals, and traces of the other platinum-group metals.
Add Sodium Chlorate slowly to hot solution. Filter.</td></tr>
<tr><td>Ppt, is red powder of Palladium Ammonium Chloride</td><td>Filtrate contains traces of Platinum-Group metals. Gold, if any, and Base Metals. Consider "Further Treatment" with ammonia, etc.</td></tr>
</table>

When you read this over for the first time you will think that the refining of the Stock Pot is a long and complicated process. But remember that the amount of metal handled is only a small percentage of the original material, and that you may do only one Stock Pot refining to several regular refinings. We might add also that the Stock Pot refining is the most interesting part of the work.

* * * *

QUESTIONS AND ANSWERS

Q. I have run through four Stock Pot refinings, and have recovered very little metal. Doubtless that is because my material contains no palladium, and very little iridium, and I am always careful to recover all my gold the first time. The Stock Pot seems to be a lot of work for a very small return. I did get some platinum out, so I hesitate to throw away the next Stock Pot. Have you any suggestions? My material contains considerable copper and nickel.

A. In Chapter XIV you will find several other methods of refining the Stock Pot solutions, some of which are especially suitable when the copper concentration is high, others of which are advised when palladium is absent, and so on. We suggest that you become familiar with more than one method, then use the one best suited to your needs and equipment.

* * * *

Q. When we refined rolled and filled gold we took special precautions to get rid of tin and lead. Do these metals cause any trouble in the Stock Pot?

A. Occasionally. Small amounts of lead sometimes get into the Stock Pot, in spite of the fact that you tried to get rid of it when, in mixing up your original aqua regia, you added a little sulphuric acid. This sulphuric acid precipitated most of the lead as lead sulphate, which was discarded. Tin is rather more apt to get into the Stock Pot. For one thing, it gets in from the stannous chloride solution that you use in testing—stannous chloride being another name for tin chloride.

You recall that the first treatment of the Stock Pot is to add zinc and hydrochloric acid. This throws down the heavy metals and may carry down some tin. But if plenty of hydrochloric acid is present at the end of this process, the amount of tin that comes down will be very small. That is, if you have more than enough hydrochloric acid to dissolve all the unused zinc, you probably will at the same time dissolve any tin that may have been deposited.

But if your black powder does contain tin or lead, they may show up in one or several places. They may be carried down with the colored powder of palladium or platinum; tin oxide may contaminate the iridium. If so, the repurification methods described in Chapter XV will remove them.

* * * *

Q. It is slow work to filter these big jars of solution. How can I hasten the process?

A. In many cases you can save labor by letting the solution settle overnight, then syphoning off the clear part and filtering only the last fraction. A solution goes through a filter more rapidly when hot, and sometimes this fact can be utilized. Sometimes you can use three or four funnels on the same job. This question comes up again in Chapter XX, in which the Büchner funnel is described, that being a device that is commonly used when handling large quantities of solutions.

CHAPTER XIV

ALTERNATIVE METHODS FOR CHAPTERS XI, XII AND XIII

Part I. An alternative procedure for the aqua regia solution in Chapters XI or XII. Part II. Formic acid method of reducing the colored powders. Part III. An alternative method of precipitating palladium, using dimethyl glyoxime. Part IV. Alternative methods of refining the Stock Pot. Alternative acid method for the black powder (Stock Pot concentrates); recovering palladium from nitric acid solution; the second black powder, platinum and iridium. Diagram of second scheme for Stock Pot concentrates. Questions and answers.

* * * *

In this chapter we shall describe some alternative methods of handling gold and platinum mixtures, gold and platinum alloys, and the Stock Pot solution. It is assumed that the reader is already thoroughly familiar with Chapters XI, XII and XIII.

PART I. AN ALTERNATIVE PROCEDURE FOR THE AQUA REGIA SOLUTION IN CHAPTER XI OR CHAPTER XII

In Chapters XI and XII we precipitated first the platinum, then the gold, from the aqua regia solution. You will recall that platinum comes down more completely in a concentrated solution, while gold comes down more cleanly in a dilute solution. This is one of the considerations that impel us to precipitate the platinum first, the washings that follow the first precipitation serving to dilute the solution and prepare it for the subsequent treatment with copperas. There are other considerations as well, some of which are not easily explained to the non-chemist, and the beginner would do well to follow the regular procedure unless he has excellent reason for doing otherwise.

It is true that some workers, including Whiteley and Dietz,[1] regu-

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[1] REFINING AND MELTING SOME PLATINUM METALS, by J. O. Whiteley and C. Dietz, Technical Publication No. 84 of the American Institute of Mining and Metallurgical Engineers. Published with Mining and Metallurgy, March, 1928. This paper describes the methods employed in the commercial refining of jewelry and dental scrap.

larly precipitate the gold first, using sulphur dioxide gas. They free the aqua regia solution from excess nitric acid as usual, filter it clear of all sediment or cloudiness, then saturate with sulphur dioxide gas until all the gold is precipitated. The gold powder is filtered off, washed thoroughly as usual, first with water, then with hot hydrochloric acid, then with water again, to remove dissolved platinum and base metals. The filtrate from the gold precipitation contains base metals and the platinum-group metals. It is now thoroughly saturated with chlorine gas for some time, in order to counteract the reducing effect of the sulphur dioxide upon the platinum. (This effect is one of the considerations mentioned above, which is not easily explained to the non-chemist and about which we shall say something in the "Questions and Answers" at the end of this chapter.) After that, the solution is placed in an evaporating dish and concentrated somewhat, until there is no longer an odor of chlorine.

If ammonium chloride should be added at this point, it will precipitate platinum as the orange powder, and *most of the palladium and iridium will come down with it*. (The color of the powder will run from pale yellow to deep maroon, depending upon the proportions of the various metals and the temperature of the reacting substances.)

In some cases this is a satisfactory method—that is, some workers are willing to obtain all their platinum-group metals together in this way, and then repurify the powder as required. Other workers, including Whitely and Dietz, vary the procedure thus: just *before* adding ammonium chloride, they stir some alcohol into the hot solution from which the chlorine gas has just been expelled. This reduces the palladium and iridium compounds to the "ous" condition, in which they stay in solution while the platinum salt comes down. The palladium and iridium are recovered later from the Stock Pot, as usual.

As we said above, to the non-chemist this is confusing. We have mentioned certain "considerations" and "effects" that are difficult to explain, and this is one of them. In the Questions and Answers at the end of this chapter we shall discuss these more fully under the heading of "Oxidizing and reducing effects—changes of valence—'ous' and"ic"conditions."

PART II. ALTERNATIVE METHODS OF REDUCING THE COLORED POWDERS OF PLATINUM-AMMONIUM-CHLORIDE, PALLADIUM-AMMONIUM-CHLORIDE, AND PALLADOSAMINE-CHLORIDE TO METALLIC FORM

In previous chapters we reduced the orange, red, and yellow powders to platinum or palladium metal by heating them strongly until they decomposed and the metallic sponge remained. In this chapter we shall refer to these salts simply as the "colored powders," since the method is the same with all three, also with the related dark iridium salt. There are certain disadvantages to that strong heating—the danger of loss of precious metal in the fumes, and the fact that the method does not remove any impurities. In spite of this, the method is widely used. Large plants cut down the losses in two ways; they pass the fumes through special baffles to capture any volatilized metal, and sometimes they play a stream of burning hydrogen or illuminating gas on the colored powder as it is being decomposed. This lessens the tendency to volatilize, but hydrogen and illuminating gas are highly flammable, and can be explosive if not properly handled.

The other method of reducing the colored powders is to boil them with formic acid and ammonia as described below. This formic acid method has several advantages: there is little danger of loss of metal; many impurities are automatically removed during the reduction; no muffle or furnace is needed; the method is quick; and the fumes produced are not highly objectionable. The expense is low. The precious metal is obtained as a finely divided powder, called "platinum black" or "palladium black," not so easily handled as the grey sponge but equally suitable for making up new alloys, and easily susceptible to further purification if such is desired. The method carries no personal hazards, and is destined to become popular.

EQUIPMENT NEEDED: Formic acid, which is a colorless liquid with a strong odor; ammonia; litmus paper; one or more Pyrex beakers, preferably with a lip; the 2-liter size is good. A casserole can be used, but the glass vessel is better since you can see through it and watch the color changes. For large quantities of material, use several 2-liter beakers.

For each ounce of platinum expected, you will need approximately the same weight of formic acid. It is easy to measure out a definite weight of the acid by placing a tared beaker on the scales and pouring in acid until the proper weight is reached. Formic acid loses strength on standing, so you may need more; do not be afraid of using too much, as a moderate excess does no harm. Palladium requires a little more formic acid than platinum.

When using this method the first time, use only a few pennyweight of the colored powder.

Mix the formic acid solution thus: place the proper quantity of formic acid in a big beaker, dilute it with two or three volumes of water, and drop in a piece of litmus paper. Now very slowly add ammonia, stirring constantly. The solution gets hot and will spatter unless you work slowly. The litmus paper will at first be red; use enough ammonia so that, on stirring, the litmus just turns blue. Now, *add more formic acid,* so that the litmus *just turns red* again.

(In other words, you want a mixture of ammonia and formic acid that is slightly acid, and just turns litmus paper red. Fish out the litmus paper with a glass rod and throw it away.)

Next take one of your 2-liter beakers and fill it about one-quarter full with this formic-ammonia solution. Place your colored powder in a casserole or beaker, cover it well with water and bring it to a boil. At the same time the formic-ammonia mixture, in its beaker, is also being brought to a boil.

Now slowly pour the precious metal mixture into the formic-ammonia solution, and if everything is quite hot the reaction will take place at once, the mixture foaming up and turning black. (That is why you were told to use a small quantity and to have your beaker not over one-fourth full—so that your foaming mixture would not overflow the beaker.)

After the reaction once starts, the heat of the reaction will keep the liquid hot, and there will be considerable bubbling and fuming. Sometimes—rarely—you need to bring the mixture to a boil a second time before the reaction will begin.

If your mixture is still yellow or brown after being boiled a few minutes, try adding a little more ammonia. If that does not help, add some more formic acid, slowly, and again bring to a boil.

When the reaction is complete your precious metal will all be in the form of a black powder, which soon settles, leaving the liquid colorless (or possibly pale green from nickel or copper). Let the beaker stand in a warm place for about an hour. If your metal is pure, the heavy black powder settles quickly; if impure, it settles slowly and the mixture looks like ink.

After the black powder has settled, it is easy to wash it by pouring off the clear liquid (filter if necessary), adding hot water and pouring off as often as seems necessary.

Work with clean vessels, free from fingerprints inside. Otherwise, precious metal will deposit as a mirror on the inside of the glass.

For very large quantities, do this: place the colored powder in a big crock, cover it with water and run in steam. While it gets hot, mix the formic acid, water, and ammonia, and pour the mixture into a number of 2-liter beakers, about two inches to a beaker. Place these beakers in a row on a steam bath or hot plate, and start the fan to draw off fumes. When everything is hot, dip up the mixture of colored powder and water, and pour it into the beakers; with a little practice in judging quantities you will be able to use up all the formic acid and still not add too much colored powder.

Let the beakers stand in a warm place till the black powder has "digested," then wash as usual, and dry.

If your original powder is contaminated with small amounts of iron, zinc, or other light metals, this method will separate your precious metal from them. That is, the light metals will remain dissolved in the liquid after the black powder has been thrown down, but if your colored powders are contaminated with heavy metals, such as gold, mercury or iridium, this method will not remove them. They will come down with the black powder, indistinguishable from it.

If nickel, copper, or silver are present in very large amounts, they may come down to some extent, especially if the acid concentration is too low. In such case a single repurification is normally sufficient.

When properly performed, this method converts all precious metals into the metallic powder, and the liquid that remains, and the wash waters, can be discarded as worthless.

* * * *

A final method for reducing the colored powders to metallic form is the familiar one of cementing them out with zinc in the presence of a dilute acid. Weak hydrochloric acid is commonly used.

PART III. AN ALTERNATIVE METHOD OF PRECIPITATING PALLADIUM—WITH DMG

It will be recalled from Chapter IX, on the identifying of precious metals, that palladium reacts with dimethyl glyoxime to produce a bright yellow precipitate. The reaction constitutes a delicate test, a very small amount of palladium in a large amount of solution producing a very conspicuous precipitate.

Dimethyl glyoxime—called DMG for convenience—can also be used to recover palladium from solutions in which the other platinum-group metals are present. In the assay of ores and bullion containing these metals, it is standard practice to precipitate palladium with DMG.

However, the method is rarely used in *refining* these metals; only in their assay. The reasons are: first, the DMG is relatively expensive; second, the precipitate produced is so voluminous as to be difficult to handle. Even a few pennyweight of palladium will produce so copious a precipitate as to demand large vessels—much larger than needed for the formation of the red palladium-ammonium-chloride. The same peculiarity that makes DMG useful in identifying small quantities makes it unhandy in recovering large ones.

There may be occasions however when the method may be useful; for example, to recover palladium from an aqua regia solution containing platinum-group metals, the usual base metals, but no gold, when you are anxious to recover the palladium at once, and are willing to postpone the recovery of the other platinum-group metals to a later day.

For each pennyweight of palladium expected, at least 2½ pennyweight of DMG are required, and a slight excess is advisable. Dissolve the DMG in hot water—a pennyweight of DMG to about 5 fluid ounces hot water (roughly the same as 1 gram of DMG to 100 cc. water). The powder dissolves slowly; if necessary filter out any cloudiness, and let cool. The aqua regia solution, which may contain platinum-group metals, and base metals, but no gold, should contain about 3% to 5% acid; if it is stronger than that, dilute it with water.

Add the DMG solution slowly; do not heat because heating will bring down platinum as well. The voluminous yellow precipitate of palladium-dimethyl-glyoxime appears at once. If your solutions are so concentrated that the mixture becomes thick, dilute it with considerable cool water, and let the yellow precipitate settle, then filter. Wash well with much hot water. The solution and washings are treated with zinc and hydrochloric acid, to cement out the other platinum-group metals.

The yellow precipitate can be reduced to palladium metal by strong heating, or by means of formic acid, as in the case of the other colored powders.

PART IV. ALTERNATIVE METHODS OF REFINING THE STOCK POT

In Chapter XIII the precious metals in the Stock Pot were recovered by a standard method, one that the student should understand thoroughly before attempting other methods. The diagrammatic scheme at the end of Chapter XIII will serve as a reminder of the various steps.

* * * *

Sometimes the Stock Pot is of such slight value that you find it does not pay to refine it. This is especially the case where your original material contained little or no palladium or iridium, and where you succeeded in removing all your gold at the first precipitation with copperas. In such a case the Stock Pot will contain merely a small amount of dissolved platinum, plus much base metal. If your time is valuable, and if your plant is crowded, it may pay you, instead of refining this solution, to follow one or another of these suggestions: (a) evaporate the Stock Pot solution to a crust, and put the crust in with the low grade wastes that will be sold to a professional refiner who gives credit for platinum-group metals; (b) neutralize the acid in the solution by adding lime, then put the thick mixture in with the wash barrel residues; (c) seal it up in a tight barrel and sell it as is.

* * * *

But generally the Stock Pot solution is well worth the time and effort to refine it. Assuming such to be the case, the following are several of the possible methods.

(I) Instead of precipitating the precious metals with zinc or other precipitants, *evaporate* the whole Stock Pot solution down to a crust on a sand bath or steam bath. This takes some time, but can go on without attention from the worker, and if you are equipped with a good steam bath (and you should be) it may pay to use this method. *Melt the crust down* with a *reducing* flux such as soda ash with charcoal, using a sand or graphite crucible and a gold-melting furnace. This gives a metallic button that must be refined by methods to be determined by an examination of the button—probably by the methods given in Chapter XII.

Normally this button contains much iron (from the copperas) plus considerable other base metals. The main disadvantage of this method is the presence of this large amount of iron.

(2) Cement out the heavy metals by means of zinc (or other metallic precipitant) as described in Chapter XIII, then *melt* the black powder into a button, using a *reducing* flux such as soda ash and charcoal. This button may be refined as it is, or melted in with other metallic residues. The main objection to this method is the large quantity of copper that is usually present. Also, if the black powder contains much platinum and iridium, with their high melting points, the melting point of the button may be so high as to be troublesome.

(3) Cement out the heavy metals by means of zinc (or other metallic precipitants), then *melt* the black powder into a button, using an *oxidizing* flux, such as sodium nitrate. When properly done, as described below, this method converts the copper into copper matte, while the precious metals collect as a small and relatively valuable button. Most of the iron and other base metals go into the copper matte. Here are the details of this method, as described by the refiner of one of our finest Eastern bullion plants:

"I take down my Stock Pot solutions with zinc, then wash the precipitate well by decantation, filling the crock up at least four times with hot water. This removes most of the acid. Then I cover the metal with a little water and add considerable sal soda, stir well, and leave overnight. I use about three pounds of sal soda to a five gallon jar of our solutions, which are fairly rich.

"In the morning, add hot water again and decant, and by this time the washings should be alkaline. If not, add more sal soda and let stand again. Finally wash and catch the residue and dry it. I use a suction funnel and wash it well with hot water in the funnel, then dry it slowly on a hot plate.

"We melt about a 600 cc. beakerful of this dry powder at a time. To the 600 cc. of powder, add 600 cc. of *nitrate of soda* and a tablespoonful of ground glass. This goes nicely into a size M Dixon sand crucible.

"If we know that there is much palladium present, or very much platinum, we add a half ounce of cement silver to collect them. We have an iron mould, cup shaped, and when melted we pour into this iron mould; in that way we can use the sand pot several times. When the melt cools, drop it out and you will see that the precious metals form a button in the bottom. This comes off readily with a knock of a hammer. The copper matte contains most of the other base metals. If properly handled, this matte does not contain appreciable quantities of precious metal." The button will then be refined according to the method of Chapter XII.

(4) *The roasting method.* Cement out the precious metals as usual, wash well, and dry. Then *roast* the powder, preferably in a muffle furnace where air can reach it, at red heat, and rake the powder about so that air can reach all parts of it. This converts the copper into copper oxide, a form that will dissolve easily in dilute sulphuric acid. At the same time the platinum, palladium, iridium (and tin) are converted into forms that resist dilute sulphuric acid. Let cool in the presence of air, and break up the lumps.

Treat the roasted material with warm dilute sulphuric acid, made by pouring one quart of acid into five or six quarts of water. (Add the acid to the water, slowly, stirring all the time.) The copper-oxide (or most of it) will dissolve readily, as will most of the other base metals that may be present. The residue will consist of precious metals, tin oxide, and traces of other base metals. Wash it well, then treat it according to one or another of the methods already familiar, preferably according to the scheme given in Chapter XIII, where you dissolve the black powder in aqua regia, adding the hydrochloric acid first to dissolve palladium oxide, then adding nitric acid and water. From that point, follow Chapter XIII.

* * * *

The following methods differ only in detail from the scheme outlined in Chapter XIII.

(5) Instead of concentrating the heavy metals by means of *zinc*, use some other metal precipitant. Thus it is possible to use *aluminum, iron* or *copper* in the first step. Aluminum costs a little more, but works much more rapidly. This rapidity may become a disadvantage unless the aluminum is added very carefully, as it reacts quickly, the liquid becomes hot and may boil out of the vessel, or may cause sudden local heating sufficient to crack an earthenware jar and permit the solution to be lost. If you elect to use aluminum, use foil or wire or sheet, and add them slowly; aluminum powder reacts too quickly for safety.

The black powder obtained should be treated exactly the same as if it had been precipitated by zinc.

Iron is the cheapest of the metals that will serve this purpose. It may be used in the form of rods or plates. It is noticeably slower than zinc, but so cheap as to be very popular. Copper plates and copper wire are also slow, but the black powder obtained is clean and easy to handle. The heavy metals deposit upon the wire, sometimes forming a coating on it. Some workers then take the coated wire and melt it all together into a button, then refine the button. Others refine the coated wire without melting it down, using one or another of the plans with which you are now familiar.

(6) In Chapter XIII when adding zinc, we added a little hydrochloric acid. *Sulphuric acid* can be used instead of hydrochloric. It costs less, and the action is practically the same. Add it slowly, a little at a time, stirring well to prevent local overheating.

* * * *

Assuming that we have concentrated our heavy metals as a black powder by any one of the methods just mentioned, we are now ready to consider another acid method by which this black powder can be refined. It differs in only a few steps from the scheme used in Chapter XIII.

ALTERNATIVE ACID METHOD FOR THE BLACK POWDER (STOCK POT CONCENTRATE)

First wash the black powder with unusual care to get rid of every trace of hydrochloric acid. Wash until the washings have no effect upon blue litmus paper. Do not let the powder dry. The washings should be of no value and should be discarded. (If possible, after you have once started this washing, try to proceed without interruption until you have completed the next process and the nitric acid solution described below is filtered off and the filter washed down well.)

The washed black powder should now be in a casserole or beaker. Cover it with nitric acid diluted with about two volumes of water. It begins to act in a few seconds, dissolving the palladium and base metals, and leaving undissolved the platinum, iridium, and any gold that might be present. There will be the usual brown fumes. Warm gently, and stir well. Do not leave the acid on any longer than is necessary—less than half an hour is generally enough even for a large lot.

As soon as all is dissolved that will dissolve under this gentle treatment, filter the liquid through a small filter, washing the remaining powder well so as to free it of solution. Sometimes this remaining powder is so heavy that it will stay in the vessel while the clear solution is being poured off; but usually it is so fine that the use of filter paper is essential. While washing the powder into the filter paper, drop in one or two crystals of sodium nitrate. (If washed with plain water, this very fine powder will run through the paper; we add the sodium nitrate and in some way it coagulates the fine powder and keeps it from running through.)

Your palladium is now in the nitric acid solution. This can be left standing as long as you wish. Methods of recovery are given below.

If your original material contained no palladium, this nitric acid solution should be of no value, and should be thrown away. (Do not put it in the Stock Pot.) If it contains much nickel or copper, it will be green. Palladium in solution is brown.

Your platinum and iridium are now in the form of this second black powder. For its further treatment, see later paragraphs in this chapter. If any gold, rhodium, ruthenium, or osmium were present in the Stock Pot, they also will be concentrated in this second black powder.

(Note: The six metals of the platinum-group are like each other in many respects. As a result, these separations are never perfectly complete. That is, a little platinum may dissolve with the palladium even under the gentle treatment just described. Also, some of your palladium may remain with the residue of platinum and iridium. This is unavoidable.)

RECOVERING PALLADIUM FROM THE NITRIC ACID SOLUTION

This solution contains the bulk of the palladium, perhaps all of it, with base metals. Place it in an evaporating dish and evaporate to a syrup, preferably on a steam bath. Add a little hydrochloric acid slowly, and again evaporate to a syrup. This is similar to previous evaporations, and the purpose is the same—to get rid of the unused nitric acid, and replace it with hydrochloric acid.

Finally thin with water, and if any sediment appears, filter it out and put it in the paper storage.

The solution should now be in a beaker or casserole, not more than two-thirds full.

From here on, the recovery of the palladium is exactly the same process as that used in Chapter XIII. You add ammonium chloride, as much as will dissolve. Sometimes a slight orange precipitate of platinum-ammonium-chloride appears here; if so, filter it out and add to your other platinum powders. Next, heat the solution to boiling and slowly add sodium chlorate, a crystal at a time, stirring well and scratching the sides of the beaker with the glass rod. The familiar red powder of palladium-ammonium-chloride will form and settle as before.

This red powder will be collected, washed, and reduced to metallic form exactly as before—either by igniting as in Chapter XIII, or by means of formic acid and ammonia, as described in this chapter.

The solution from which you filtered off the red powder should be tested with stannous chloride Testing Solution A. Usually it contains only a trace of precious metal, mixed with a considerable quantity of base metals, and may often be discarded immediately. Sometimes it is of sufficient value to be put into the Stock Pot. Sometimes, however, you find that your treatment with the sodium chlorate was so unsuccessful that considerable palladium is still present; if so you may wish to go through with the so-called “further treatment” in Chapter XIII, in which you obtained the yellow powder.

THE SECOND BLACK POWDER—PLATINUM AND IRIDIUM

Let us return now to the second black powder, insoluble in nitric acid, which we left in a filter on page 166 of this chapter. The metals in this form are called “platinum black” and “iridium black.” Under ideal working conditions this residue will consist solely of the platinum and iridium that were not previously recovered in Chapters XI and XII, plus little flakes of glass and porcelain from the vessels and reagent bottles. (These flakes can be removed by hydrofluoric acid—see Chapter XVI.)

Jewelers usually do not need to separate the platinum from the iridium —indeed, they prefer to keep these two metals together—so their next step is to melt this black powder, using the oxygen-gas flame as described in the Appendix. Usually one can tell by its appearance whether this powder is clean enough to melt or not, or a small test melt can be made first. If the original material contained much iridium, the button will be rather hard, and some soft platinum must be added to bring the alloy to the desired composition.

However, ideal working conditions do not occur every day, and this black powder is often too impure to be melted up at this stage. For instance, gold sometimes gets into the Stock Pot, and will show up in this powder, giving it a brown color. Sometimes for other reasons the powder is unattractive. Sometimes your original material contained rhodium, ruthenium, or osmium, which would be accumulated here.

Accordingly this powder generally receives some further treatment before being melted. Thus, suppose you suspect gold and base metals to be present; you would proceed as follows: Dry the powder and heat it to redness (do not melt) to convert the iridium to a less soluble form. Then boil in concentrated aqua regia, adding the hydrochloric acid first. This dissolves palladium, gold, platinum, and most base metals. Iridium dissolves very slowly, if at all. Rhodium would remain with the iridium; also undissolved are the flakes of glass and porcelain, and perhaps a little silver chloride that had escaped previous treatments.

Dilute this aqua regia solution with two volumes of water and filter. If the undissolved residue is whitish, it is of no value and can be thrown away. If the residue is dark it probably is of value, and should be treated according to the methods described in Chapter XV under the repurification of iridium, or—if known to contain ruthenium, osmium or rhodium—sold to a refiner who purchases such metals.

The aqua regia solution just obtained should be treated as usual for the recovery of platinum and gold.

SECOND SCHEME FOR REFINING STOCK POT CONCENTRATES

<table>
<tr><td colspan="7">Black Powder obtained from Stock Pot solution. Contains Platinum, Palladium, Iridium, Base Metals, possibly Gold possibly other Platinum-Group metals.
Wash with great care to remove all hydrochloric acid. Do not ignite. Treat with warm <i>dilute nitric acid</i>. Filter.</td></tr>
<tr><td colspan="3">Filtrate contains Palladium,with base metals, possibly traces of other platinum group metals.
Convert to chloride, add <i>ammonium chloride</i>. Filter if necessary.</td><td colspan="4">Residue consists of Platinum, Iridium, possibly Gold, flakes of glass and porcelain possibly other platinum group metals.
<i>Ignite</i>. Treat with <i>aqua regia</i>, applying the hydrochloric acid first. Filter.</td></tr>
<tr><td rowspan="3">Ppt is orange Platinum salt.</td><td colspan="2">Filtrate contains Palladium and base metals.
Add sodium chlorate slowly to hot solution. Filter.</td><td colspan="3">Filtrate contains Platinum, Gold, Base Metals, possibly traces of other platinum-group metals.
Expel nitric acid, add <i>ammonium chloride</i>. Filter.</td><td rowspan="3">Residue is Iridium, glass, possibly other platinum-group metals.</td></tr>
<tr><td rowspan="2">Ppt is red Palladium salt.</td><td rowspan="2">Filtrate may contain enough palladium to justify further treatment, to obtain the yellow salt. Or, place in Stock Pot or sweeps.</td><td rowspan="2">Ppt is orange Platinum salt.</td><td colspan="2">Filtrate contains Gold, base metals, traces of others. Add <i>copperas</i>.</td></tr>
<tr><td>Ppt is Gold.</td><td>Filtrate to Stock Pot.</td></tr>
</table>

* * * *

In Chapter XXI still more alternative methods—methods suitable primarily for the very large plant—will be described. And in Chapter E of the Appendix the searcher for still further alternative methods will be shown the way to find them.

* * * *

To the beginner, this wealth of alternative methods will be confusing, possibly baffling. The only safeguard is to confine oneself to a single, well-recommended method until it is truly familiar, remembering that the other man's method, like the grass on the other side of the fence that always looks so green, may really be no better than one's own.

QUESTIONS AND ANSWERS

Q. Please tell us more about the use of chlorine gas.

A. Chlorine gas is dispensed in steel cylinders, similar to those used with sulphur dioxide or ammonia. Chlorine under pressure is a liquid;

when released it forms a gas. The gas is most unpleasant and corrosive, attacking metals and fabrics as well as human lungs and eyes. It is widely used in industry as a bleaching agent, and in sanitation to purify water supplies and sewage. In the refining of precious metals it has several uses, notably in the Miller process for refining gold—see Chapters XXI and XXII—in one method of extracting gold from low grade ore, and for oxidizing platinum and palladium salts in solution to their higher valences.

* * * *

Q. Please explain the following phrases, which I have found in articles on the platinum metals: “Oxidizing with chlorine”—“reducing with alcohol”—“changing the valence”—“higher and lower valences”—“the *ous* condition”—“the *ic* condition.”

A. A full explanation of these phrases, all of which refer to the same group of chemical relationships, is beyond the range of this book. It is well known that metals exist in various forms; thus we know iron as a metal, also as an element in a pale green compound called copperas, whose chemical name is ferrous sulphate. This ferrous sulphate, after reacting with dissolved gold (or being exposed a long time to air) turns yellow, and is then known as ferric sulphate. Thus there are two kinds of iron salts, the ferrous and the ferric.

There are also two kinds of platinum salts—the platinous and the platinic. In fact, most metals occur in both the *ous* and the *ic* conditions. Chemists have another way of saying the same thing; they say that most metals have at least two valences, the salts of the higher valence being called the *ic* form, and the lower valence being called the *ous* form. The change from a lower to a higher valence is described as an oxidation, though frequently no oxygen is present. The change from the higher to the lower form is called a reduction. These changes can be brought about in many ways. Some oxidations are accomplished by mere exposure to oxygen, some reductions by heating the substance in the presence of charcoal. The electric current used in a gilding bath is said to *reduce* the dissolved gold when it deposits it upon the article that is being plated, while at the same time it *oxidizes* the anode and carries it into solution. An electric current can also change a salt in solution from the *ous* to the *ic* condition, or vice versa.

This discussion is in no sense a satisfactory explanation. However, this book attempts to describe the procedures of refining so that the reader may perform them, even though unaware of their underlying chemical principles. For an adequate discussion of oxidation and reduction phenomena, valences, the differences between *ous* and *ic* salts, the reader is referred to any text book of general chemistry.

CHAPTER XV

REPURIFICATION OF GOLD, PLATINUM, PALLADIUM, SILVER, IRIDIUM

Part I. Repurifying gold: by reprecipitation; the use of oxalic acid; by fire; by chlorine gas; by electrolysis. Part II. Repurifying platinum. Part III. Repurifying palladium: the colored powders; buttons, bars, and palladium black; palladium sponge. Part IV. Silver. Part V. Iridium.

* * * *

The precious metals that are recovered in the earlier chapters of this book are not always as pure as your needs require. Small amounts of tin, lead, iron or other metals may contaminate your "fine" gold. Your platinum may contain some silver chloride or palladium; your palladium may contain platinum; and so on. The amount and nature of these impurities will depend partly upon your skill and patience, but primarily upon the character of the original material, and in most cases it is no reflection upon you or your method that repurification should be necessary.[1] Indeed, in many plants at least one repurification is routine, except where the original material was already of high quality.

You are advised to make a test melt of *every* batch of recovered metal. Melt up a few grains of the gold powder, or the cleaned platinum filings of Chapter XI, and if the sample button is unsatisfactory, do not melt up the bulk of the metal—it is easier to repurify powders or filings than to repurify buttons or bars.

With a little experience you can quickly judge the quality of your metal, especially by its appearance when molten and its behavior when hammered or drawn. As we suggested at the end of Chapter VI, it is wise to obtain samples of gold, platinum, palladium, and silver of unimpeachable purity, then melt, roll and hammer them, noting their characteristics carefully. Pure platinum, under the oxy-gas flame, melts and rounds up into a thick almost globular button, with a mirror-like

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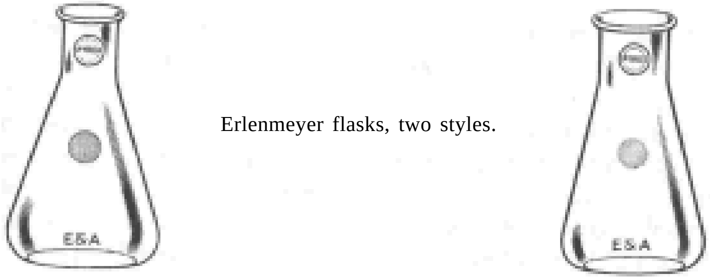
[1] The serious student is referred to the 29-page paper PURIFICATION OF THE SIX PLATINUM METALS, by Edward Wichers, Raleigh Gilchrist and William H. Swanger, published in Mining and Metallurgy, March, 1928.

surface, while impure platinum flattens out into a thin button with a skin or film on the surface. Pure platinum or gold can be drawn into extremely fine wire, while impure metals cannot. And so on—the “feel” of the metal under the saw, file, or hammer, conveys much information to the experienced user.

The commonest process of repurification, and the one to be described first, is simply to dissolve the metal in acid and to precipitate it again. With the colored powders of palladium, a slightly different plan is possible.

In all cases—gold, platinum,or palladium—if your metal is already in the form of a button or bar, roll it out as thin as possible, and cut the strip into short lengths, twisting them a little. If too brittle to be rolled, the metal may be granulated, or broken up with a hammer.



Erlenmeyer flasks, two styles.

When redissolving the metal, use a casserole or flask. A Pyrex glass flask, Erlenmeyer style, is the most popular vessel. Eimer & Amend No. 23382 with the narrow mouth, and No. 23386 with the wide mouth, are good. The liter size, thin glass, either model, costs 38¢. (See also page 136.)

PART I. REPURIFYING GOLD

By Reprecipitation

If your gold is in the form of a powder, and if you believe it to be contaminated with *tin*, begin by heating it gently almost to redness in an open shallow crucible. Do not let it melt. This converts any tin into tin oxide, a substance that does not easily dissolve in acid. If your gold is in a button or bar, roll it out thin, or break it up, as mentioned above, and cover it with aqua regia.

For each Troy ounce of gold use about one-half fluid ounce of nitric acid, two ounces hydrochloric acid, a little water, and several drops of sulphuric acid. Add slowly, as it may bubble over, especially if your gold is in the form of a powder. Warm gently if necessary.

When all the gold is dissolved, place the solution in an evaporating dish and expel nitric acid, as usual, taking up the syrup in hydrochloric acid, and evaporating again, as usual. When you are sure all the brown fumes have been expelled, add considerable water—say ten volumes or more—and set aside for several days to settle.

Silver chloride, lead sulphate and other salts will deposit out slowly as a fine mud. So will the tin oxide that was formed when the powder was heated almost to redness. The liquid must be perfectly clear and free from sediment before you go to the next step, so use particular care in getting rid of this deposit. If time permits, let it settle well, then siphon off the clear liquid, filtering only the last part. This filtering is not always easy, as the fine powder sometimes goes through the paper. One plan is to use filter paper specially made for fine precipitates. Another plan is as follows: tear up a filter paper into small scraps and drop them into the liquid to be filtered, stir until the paper has disintegrated into shreds, then filter as usual into a clean filter paper. The tiny particles of tin oxide, silver chloride, and lead salts will cling to these shreds and the filtrate will run clear.

You are now ready to precipitate the gold again. As in Chapter VI, you have a choice of several precipitants, but sulphur dioxide, oxalic acid, and sodium nitrite are the best. Sulphur dioxide is especially suitable when tin is present. Use it exactly as described in Chapter VI, then collect and wash the gold powder as usual—first in hot water, then in hydrochloric acid, then in hot water again—after which it is ready to be dried and melted. Test a few drops of the remaining solution with stannous chloride Testing Solution A, and if it contains appreciable quantities of precious metals, put it in the Stock Pot.

If you have no sulphur dioxide gas, use sodium nitrite as described in Chapter VI, or oxalic acid, as described below. Some people use pure copperas for this work, but it is not as good as oxalic acid or sodium nitrite.

In general, do not use the same precipitant for your repurification that you used in the first recovery. Thus: sulphur dioxide tends to carry down traces of the platinum group metals with the gold; oxalic acid does not. But oxalic acid does tend to carry down tin and copper; sulphur dioxide does not. Therefore, if you use sulphur dioxide for your first precipitation, use oxalic acid for the repurification, and vice versa.

The Use of Oxalic Acid

This method was mentioned briefly in Chapter VI as being especially suitable for the recovery of gold from solutions that contain relatively few impurities. Its disadvantage is that it will work only when all the solutions are hot—preferably boiling—which means that the precipitation must be carried out in vessels that will withstand considerable heat. It costs more than copperas or sulphur dioxide, about the same as sodium nitrite. Under most conditions the gold recovered is of high purity.

For each Troy ounce of gold you will need at least a Troy ounce of oxalic acid crystals. If you failed to expel all the excess nitric acid, you will need more.

Dissolve the oxalic acid in hot water. Add a little ammonia, say a teaspoonful or less to an ounce of oxalic acid; add slowly to avoid spattering.

Do not use too much ammonia—the mixture should not smell of ammonia after being stirred. If it does, add enough additional oxalic acid to kill the ammonia smell. If you have litmus paper, use it here, and let the mixture show a slight acid reaction. Have the mixture in a big beaker or jar that will withstand heat.

Next, heat your aqua regia solution to boiling. Also have the oxalic solution hot—boiling if possible. Pour the gold solution slowly into the oxalic acid solution. Gold comes down at once with hot oxalic acid, but takes hours or even days if it is cold.

Some people pour the *oxalic* into the gold; we think it is better to pour the gold into the oxalic.

There will be bubbles and fumes, so work slowly or the liquids may boil over when they come together. If you failed to expel all the excess nitric acid, brown fumes will appear here; if this happens you may have to add much more oxalic acid in order to kill all the nitric acid.

Let the mixture stand for some time, keeping it hot if possible. The gold comes down as bright clean crystals, often very beautiful, which usually settle promptly.

Finally pour or filter off the liquid, after testing some of it with the stannous chloride testing solution to be sure you used enough oxalic acid. If worthless throw it away at once. In rare cases it may show enough palladium or platinum to be put in the Stock Pot.

The brown powder of gold should now be washed well with much hot water, to remove all traces of hydrochloric acid, then boiled with a little nitric acid, to remove traces of palladium or base metals. Finally wash with plenty of hot water again, and dry and melt as usual. This normally gives gold of high quality.

By Fire

Sometimes a batch of brittle gold can be purified by one or more remeltings with the addition of suitable fluxes. The commonest (and one of the oldest) method is to add a little nitre (potassium nitrate) or sodium nitrate to burn out the impurities. The gold is heated in a clay crucible, and the nitre is added cautiously just before the gold melts. Considerable bubbling occurs immediately, and the oxygen in the nitre unites with the base metals. It is customary to protect the crucible by a ring of bone ash, which absorbs the base metal oxides, or to use a flux of borax glass. Iron and zinc can be removed readily in this way. Lead is more difficult to remove. Platinum-group metals are removed by prolonged nitre treatment and will go off with the fumes and be lost.

Instead of nitre, ammonium chloride can be added to the molten gold, and it is especially useful in removing lead. When considerable lead is present, alternate additions of nitre and ammonium chloride are employed.

By Chlorine Gas

This method, called the Miller method, is described in detail in Chapters XXI and XXII. It will not remove the platinum-group metals, and has other disadvantages, including the formation of extremely dangerous fumes. It seems to be used only by large plants, but there is no inherent reason why it should not be used by the small plant as well, and the serious student is advised to consider its merits.

By Electrolysis

Electrolytic methods, suitable to the large plant only, are described in detail in Chapters XXI and XXII. Gold that is already about 860 fine or finer, and which contains platinum-group metals, is carried to a high degree of purity by these electrolytic processes, which are standard in the Mints, in the large copper and nickel refineries, and in several of the refineries that specialize in dental gold. Electrolytic methods are not adaptable to the needs of the average small plant.

* * * *

PART II. REPURIFYING PLATINUM

The commonest impurity in precipitated platinum is silver chloride, which makes it brittle and dark in color. Iridium and palladium, which do not make it brittle, are also apt to be present, especially if your original material is high in these metals, because they are so similar to platinum in chemical characteristics that it is not easy to separate them. Gold and tin appear often enough to be troublesome. Usually one precipitation is sufficient to remove most of the silver chloride, gold and base metals. Complete freedom from palladium and iridium is rarely required by the jeweler, which is fortunate, for as we say, these metals are so much alike that the task of separating them is difficult. The usual method of purification is simply to dissolve the metal in aqua regia, and then to precipitate it again with ammonium chloride, and when greater purity is desired, this may be repeated several times.

For each Troy ounce of platinum, mix up about 1 fluid ounce of nitric acid and 4 of hydrochloric acid, with 1 ounce of water and a few drops of sulphuric acid. You may need more aqua regia than this, especially if the metal is in the form of shot or thick foil. Sponge dissolves promptly. Stir often, by rotating the flask, and heat gently, preferably on the steam bath, raising the temperature slowly to avoid too vigorous action.

After the metal has all gone into solution, the next step is to drive off the unused nitric acid, as usual. This may be done without previous filtering. Heat almost to a syrup, and when a little water is added there will be an evolution of brown fumes. Add some hydrochloric acid also, and evaporate again, repeating as often as necessary. After the last evaporation, add water only, adding sufficient to bring the platinum concentration to about three ounces to each quart of liquid. Let settle overnight or longer.

Silver chloride, tin oxide and lead sulphate will settle out as a whitish mud. After it has settled well, filter off the clear liquid into a clean jar or big beaker, and catch the residue, using the shredded filter paper that was described in the purification of gold, and throw it away.

When your solution is perfectly free from cloudiness, reprecipitate the orange powder, using about a Troy ounce of pure ammonium chloride to each ounce of platinum. Some workers advise having both solutions quite hot at the time of adding them together. The bright orange powder will come down at once. If much iridium is present, the dark iridium-ammonium-chloride will slowly come down too. The longer it stands, the more platinum will be precipitated out, but impurities will come down too, therefore for highest purity, filter immediately.

Wash the orange powder before it dries, getting it into a beaker and covering it with a good quantity of ammonium-chloride water and stirring well. Let settle, and pour off the liquid. Repeat, stirring well to wash out all impurities. These washings always contain some platinum, and possibly gold and palladium as well, so put them in the Stock Pot. Finally catch the washed orange powder in a clean filter paper, reduce to metallic form, make a test button, and if pure melt as usual. This precipitation can be repeated if desired.

This method of repeated precipitations with ammonium chloride will readily remove gold, silver chloride, lead, tin, and many other contaminants. But it does not immediately remove the sister metals of the platinum group. In their paper on the PURIFICATION OF THE SIX PLATINUM METALS, Wichers and his co-workers say: “With the possible exception of iridium, . . . one might expect to eliminate the metals of the platinum group about as rapidly as gold and the base metals, by the repeated precipitation of ammonium chloro-platinate. This is not the case. Rhodium, iridium, and palladium display remarkable persistence in contaminating the platinum salt.” These writers then give an alternative and quite different scheme, described as the “collective precipitation of impurities,” which however should not be attempted by the non-chemist. As we said above, the jeweler fortunately does not often demand that his platinum be completely free of its sister metals, and accordingly the method of reprecipitation with ammonium chloride normally suits his requirements.

Platinum, unlike gold, should not be repurified by fire. Attempts to remove impurities by repeated remelts cause a loss of metal, without compensating improvement in the quality of the platinum.

* * * *

PART III. REPURIFYING PALLADIUM

Palladium recovered from dental and jewelry wastes is usually contaminated with platinum, copper and other base metals, and perhaps with iridium as well. The following cases will be considered: the red palladium ammonium chloride and the yellow palladosamine chloride; the sponge obtained by burning either of these colored salts; the palladium "black" obtained by reducing the colored salts with formic acid; and palladium metal in the form of button, bar, or foil.

The Colored Powders

This process utilizes the reactions employed in Chapter XIII under the heading "Further Treatment for Palladium." You will recall that you took a solution containing palladium, added ammonia to form a flesh-colored precipitate which redissolved in an excess of ammonia, filtered out base-metal impurities, then re-acidified to obtain the yellow precipitate. The same chemical reactions will be utilized again here, as follows:

Place the colored powder—either the red or the yellow—in a good sized flask or beaker and add cold concentrated ammonia (ammonium hydroxide, C. P.) slowly, stirring well. The palladium salts dissolve to give a solution that is almost colorless. Copper and nickel salts dissolve to form sapphire-blue compounds. Iron forms pasty rust-colored flakes, lead and tin form pale gelatinous flakes. Platinum and iridium remain as orange or dark red powders. Use just enough ammonia to dissolve everything that will dissolve, add a volume or more of water and set aside an hour or two for the pasty precipitates to coagulate. If too much ammonia was added by mistake, some of it can be removed by warming the dish on the steam bath. Let settle, then filter clear. The stuff in the filter will consist of salts of platinum and iridium, plus the pasty hydroxides of iron, tin, etc., and should be placed in the paper storage.

Next, add hydrochloric acid, a few drops at a time, to the strongly ammoniacal solution. It will become hot and fume and bubble, so work slowly and stir well. Add enough hydrochloric acid to acidify the whole solution, as determined by the change in color, and until no more yellow salt forms. The yellow salt settles readily, and should be captured in a filter paper, washed in cold water, dried, and a sample should be reduced to metal and melted into a small test button. The solution that remains should be tested with stannous chloride Testing Solution A, and disposed of as suggested in Chapter XIII, according to its contents.

If the yellow powder just obtained is not yet of the desired purity, repeat the above process.

Repurifying Palladium Buttons, Bars, and "Black"

Palladium metal in the form of buttons or bars should be rolled thin or granulated. Palladium "black," the fine powder obtained by reducing the colored salts with formic acid, is already in a form that will react almost instantly with acids.

The first step, in either case, is to get the palladium into solution. You are already familiar with two ways of doing this. In Chapter XIII you dissolved palladium in aqua regia, and in Chapter XIV you dissolved it in nitric acid. Either solvent can be used here, after which the solution is filtered well and the palladium reprecipitated exactly as in Chapter XIII or Chapter XIV.

If you decide to use nitric acid, dilute it with at least two parts water to one of acid. Action is very rapid with "black" or thin foil, but thick lumps may require some heat. Gold, tin oxide, silver chloride, and a few other impurities will remain undissolved. If platinum is present in the black powder, most of it will remain undissolved. Platinum present as an alloy with the palladium in massive form, however, will probably go into solution with it. Filter the solution clear and put the residue in the paper storage, as it may be of some value. You are now ready to precipitate the red powder again, exactly as in Chapter XIV.

If you decide to use aqua regia as a solvent, dilute it also with some water. Aqua regia will dissolve all the gold and probably all the platinum group metals that are present, leaving as a residue any silver, lead, or tin oxide. From here on, proceed exactly as in Chapter XIII.

Repurifying Palladium Sponge

The sponge obtained by burning the colored powders usually shows blue and green shades due to palladium oxides. These oxides, as we remarked before, do not dissolve readily in nitric acid nor in aqua regia. They do dissolve in hydrochloric acid, however. This fact must be borne in mind. Sometimes the best plan is to reduce these oxides at once to metallic form, by heating them with alcohol as in Chapter XIII. The alcohol usually catches fire, so work carefully to avoid burns on the hands or face. Another plan is to boil the sponge with a little formic acid to which some ammonia has been added, as in Chapter XIV.

A third way is the way mentioned in Chapter XIII—when you dissolved the black powder in aqua regia you applied plain hydrochloric acid first, to dissolve the oxides, then without filtering added the proper quantity of nitric acid to form aqua regia.

Whichever plan is used, the procedure from this step on will be according to methods with which you are already familiar.

PART IV. REPURIFYING SILVER

In general it does not pay the small organization to rework silver. It is better practice to sell it or exchange it for pure metal. However, a worker occasionally wants to purify some silver for special reasons, perhaps merely to satisfy his curiosity, and so a description of one method, suitable for handling small lots, will be given.

Roll the metal thin or break it up, and dissolve it in hot concentrated sulphuric acid. (See Chapter VI) When the silver has dissolved, dilute the solution by pouring it slowly into a considerable quantity of water, and set it aside for the undissolved particles to settle. Capture these as they may contain gold, possibly platinum group metals as well, and put them in with your next batch of filings.

When the dilute sulphate solution is perfectly clear, add to it enough hydrochloric acid to precipitate all the silver as silver chloride. Let this settle, pour off the liquid, and wash the chloride well with much hot water. Finally reduce it to metallic silver by one of the methods given in Chapter VIII, using high grade reagents. (Thus, if you elect to reduce it with zinc, use chemically pure zinc, free from arsenic or other impurity.)

Test the liquid from which you recovered the chloride, and if it contains a worth while quantity of palladium or platinum, add it to the Stock Pot, first evaporating off as much of the water as you conveniently can.

Large plants handling silver in quantity, use the electrolytic methods that will be described in Chapters XXI and XXII.

PART V. REPURIFYING IRIDIUM

In some cases the iridium black obtained from the Stock Pot in Chapters XIII and XIV may contain ruthenium, rhodium, or osmium. The non-chemist is advised to sell such powder to a professional refiner who gives credit for these rarer elements. In Chapter XVII these metals will be discussed again, and the difficulties attendant upon refining them will be described.

It has been pointed out that this iridium black is often contaminated with porcelain or glass that has flaked from the reagent bottles and vessels. Earthenware is especially apt to scale under strong acids or alkalies. A way to get rid of these flakes is given in the next chapter—Chapter XVI—and the task is easy and inexpensive to perform.

The melting point of iridium is very high, and the attempt to melt the clean black powder obtained from the Stock Pot may be discouraging, even when the powder is of good quality. Normally it contains more or less platinum, and to most users this is not objectionable; indeed, many workers try to keep the two metals together. Accordingly the usual fate of this clean black powder is to be melted up with sufficient soft platinum to give an alloy suitable to the manufacture of new goods.

If the refining has been carried on successfully, the result will be a button of good quality and hardness. If too hard, remelt it with a little more soft platinum. (Methods of melting platinum are described in Chapter A of the Appendix.)

But sometimes this button is not of good quality, even when there is no ruthenium, osmium, or rhodium, and even when the flakes of porcelain have been removed. For the beginner the best procedure may be to sell such a button to a dealer who gives credit for iridium. But the worker who has had a little experience, especially if he has the inclination to study these metals, will sooner or later elect to repurify such a button, in the same way that he has repurified his gold or platinum. There are two or three ways of doing this, but none is really satisfactory.

Suppose your purpose is not to separate the indium from the platinum, but merely to obtain a good-quality iridio-platinum alloy. In that case, add enough soft platinum to reduce the iridium content to about five percent, making an alloy that is soluble in aqua regia. Roll the metal very thin, cut it up, and dissolve it in full strength aqua regia, as in Part II of this chapter, and precipitate the orange powder of platinum-ammonium-chloride as usual. Do not filter immediately—let it stand overnight and the dark iridio-ammonium-chloride will come down too. Filter, wash, and burn as usual, and the resulting sponge should when melted produce a button of good quality, containing most of the platinum and a large part of the iridium. The precious metals remaining in the solution should be precipitated by zinc, and recovered as described in Chapter XIII.

Suppose, on the other hand, your purpose is to separate the platinum from the iridium. One way is to proceed as above, obtaining the mixed colored powders as above. Then (instead of burning them) reduce these powders with formic acid as in Chapter XIV. This gives you a mixture of platinum black and iridium black, not unlike mixtures you have already encountered in Chapters XIII and XIV. Wash well, dry, and ignite.

Your iridium black is now in the less soluble form. Treat the ignited powder with dilute aqua regia, which dissolves platinum, leaving the iridium black undissolved. As noted before, this separation is not a perfect one, but it serves many purposes.

For a more complete separation, see the section on Electric Contact Points, in Chapter XVI, where the iridio-platinum alloy is melted up with a quantity of zinc, then treated with acids as there described.

The classic separation of iridium and platinum, as used by assayers, requires the alloy to be fused with six or more times its weight of lead, at a temperature about that of melting gold. The iridio-platinum-lead alloy is next treated with nitric acid to dispose of excess lead, the residue then being boiled in aqua regia. This leaves the iridium unattacked, in the form of small bright crystals. This method is laborious, and not suited to the amateur refiner's abilities. Full details of this procedure will be found in the publications of the National Bureau of Standards, as listed at the end of Chapter XVII.

CHAPTER XVI

SOME MORE SPECIAL CASES

Sand, glass, porcelain and enamel. Emery and carborundum. Chromium plate. The peculiar case of 18-k green gold with platinum; stripping with the current; equipment; the current; recovering gold and silver from cathode and cyanide bath. Mercury and amalgams. Dental pins. Gold pen points with osmiridium tips. Gold leaf. Contact points. Chemical ware.

* * * *

SAND, GLASS, PORCELAIN AND ENAMEL

These substances, often found in jewelers' and dentists' bench wastes, are not removed by ordinary solvents. They can be gotten rid of by melting the metal into a button, using a flux, but sometimes this is not desirable. Fortunately they dissolve readily in hydrofluoric acid.

Hydrofluoric acid is dispensed in wax bottles, and must not be used with china or glass vessels, as it quickly attacks the surface and would in time dissolve the whole vessel. Plastics such as Bakelite are not attacked by it, nor is platinum or gold. Lead is attacked very slowly.

To remove sand, enamel, porcelain, and glass from your platinum filings or from the iridium powder recovered from the Stock Pot, simply place them in a suitable dish and cover them with hydrofluoric acid, and warm gently. Do this after they have been through all the other regular treatments with nitric acid, aqua regia, or the like, and have been washed well.

Lead dishes are inexpensive, and can be bought from almost any supply store, or shaped up out of a piece of sheet lead. Eimer and Amend No. 22026, four inches in diameter, costs 28¢. Do not heat it strongly or it will melt. The best vessel for this job is a dish of platinum or gold, shaped about like a shallow evaporating dish. It will last indefinitely.

The fumes are bad for the lungs and skin, and will frost your window glass if allowed to touch it, so work carefully, outdoors if possible.

Leave the filings in the acid until the foreign matter is dissolved, stirring with a piece of platinum wire or strip of Bakelite or hard rubber. If you use a platinum or gold dish, it is easy to apply heat, but a lead dish must be heated with caution, preferably on a sand bath.

Lead dish.

Sometimes you can use the same hydrofluoric acid on two or more lots of filings, saving it in a wax bottle. Finally ~~pour the spent acid down the drain~~, washing it down with much water.

Wash the filings very clean, then dry and melt as usual.

EMERY AND CARBORUNDUM

These are not soluble in ordinary acids, nor in hydrofluoric acid. Some kinds of emery used as a polishing material can be removed from platinum filings by boiling them in water to which has been added caustic soda.

Carborundum, and most other kinds of emery, are not readily removed by any of the solvents in ordinary use, and when present in sufficient quantity to be troublesome, are best gotten rid of by melting the filings into a button, when possible, or by dissolving all the metal in aqua regia.

CHROMIUM PLATE

White gold jewelry, especially the cheaper kind, is sometimes finished with a thin coating of electro-deposited chromium. Chromium differs from most base metals in that it does not dissolve easily in nitric acid, and accordingly is sometimes mistaken for white gold or platinum. It does dissolve readily in plain hydrochloric acid or dilute sulphuric acid, if hot, and can be removed by either.

If chromium should get into your aqua regia solution, it probably will cause no difficulty. It behaves a little like nickel in some respects, like iron in other respects.

THE PECULIAR CASE OF l8-K GREEN GOLD WITH PLATINUM—STRIPPING WITH THE CURRENT

You will recall (see Chapter VII) that 18-k green gold, which consists of 75 parts gold and about 25 parts silver, is practically insoluble in acids, as it contains so much gold that nitric acid will not affect it, and so much silver that aqua regia will not affect it. When mixed with platinum, as in jewelry with a green gold base and a platinum top, it presents a real problem to the refiner. Sometimes it is convenient to mix such scrap in with considerable other metal, such as yellow gold or brass, to produce a button that will yield to aqua regia; but here is another method, differing fundamentally from those previously suggested, that is peculiarly suited to this problem.

This method is being used occasionally with yellow or red gold-and-platinum combinations as well. It consists of dissolving the gold away from the platinum, using a cyanide solution and a “reversed” electric current. If you have had experience in electroplating, this method will be easy to understand and carry out.

The method is designed for *mixtures* of green gold and platinum, not for buttons or alloys. This distinction is the same one that was mentioned so often at the beginning of Chapter XI, and is based on similar considerations, as will soon be clear.

Equipment. Use an earthenware jar or glass cylinder such as is used in electroplating. It must be heated, preferably by a steam bath. Use the same direct electric current that you use for gilding, electro-stripping, or the like. Your clippings are wired directly to the anode rod. Filings are placed in a platinum-lined dish, which is wired to the anode rod. Take a china bowl and line it with thin platinum foil, reaching not quite to the edge, using a dish large enough to hold the filings comfortably, spread out thin, so they can be stirred without spilling. All wires under the water line are of platinum. This wire can be used for years without loss, so use wire of generous size, as thin wire wastes current.

A sheet of lead or copper, called the cathode, is attached to the work rod by means of stout copper wire. Use a small cathode for small jobs, and a larger one for larger jobs. Thus for 300 or 600 dwt. of clippings, use a cathode 6 X 6 inches or larger. Filings can take a larger cathode than the same weight of clippings, since they present more surface to the current.

Make up a cyanide bath, with 4 to 8 ounces commercially pure sodium cyanide or cyanide mixture to each gallon of water.

Large scrap should be rolled extremely thin. Filings should be treated by the preliminary treatments mentioned in Chapters III, V and XI—burn out the grease, use a magnet, and remove as much base metal as possible with the usual nitric acid treatment, and wash with much hot water.

As soon as your metal is thoroughly washed, place it in the cyanide bath, which should be heated to about 140° F., and turn on the current.

Gold, silver, and copper will dissolve, and finally will be deposited (more or less completely) upon the cathode. Platinum will not be affected at all. The gold dissolves slowly, the time depending upon how thick the gold is, and how strong the current is. The hotter the bath and the better the connections, the shorter the time, but the more cyanide will be used up. Let it run all night if you wish. You can tell when all the gold is gone by the looks of the remaining platinum. Rinse it, and melt it as usual, with the oxy-gas torch.

The Current. Use a stronger current, if possible, than what you are using for coloring or stripping. Have a generous “action,” with perhaps 6 to 10 volts, and as much as 15 amperes or more. Use as much current as you wish, as long as your wires and rods do not get hot.

Watch out for clippings that sometimes drop off the wire, particularly those on which the platinum is not continuous. Look out for short circuits. But have the cathode and metal as close together as convenient.

Remember also that the current will take the shortest path from the anode rod to the work rod. You want it to go through your clippings. Some workers slip a small piece of rubber tubing over the wires that are used for wiring on the clippings, so as to force the current down into and through the clippings themselves.

It takes longer to refine filings than strips. If you can fix up some method for stirring the bath all the time, the work will go more rapidly, and a higher current can be employed.

Be sure that the current goes THROUGH your filings. That is why you use a platinum-lined dish, instead of an all-platinum dish; if the dish were all metal the current would go from the outside of the dish to the cathode and skip the filings.

Another plan is to put the dish on the bottom of the earthenware vessel, and hang the cathode over it, so that the current goes straight up and down. In this case, you must do something to keep flakes of gold from the cathode from dropping back into the dish, where they will have to be dissolved again.

One way to keep these flakes from dropping back is this; buy at a department store a pair of wooden rings used for stretching embroidery. Stretch a piece of thin cotton cloth over these rings. Lay this on your dish of filings to catch the loose gold.

If a dark cloud forms in the solution, around your metal, and remains after you stir, add more cyanide. Some workers simply add a little cyanide to the bath each time they use it. Now and then scrape any loose flakes off the cathode, and save them for later purification.

You can usually judge by the color of the metal when all the gold has been removed from the platinum. Look for large pieces; the small ones dissolve first. When all the gold has been removed, wash the platinum well with hot water, adding the washings to the cyanide solution. If you did not go through the filings with a magnet at first, do so now, as the current does not remove iron. Your platinum should now be clean and free from gold and base metals, ready to be dried and melted.

When you turn off the current for any reason, lift the cathode out of the bath, to keep it from dissolving in the cyanide.

Recovering Gold and Silver from Cathode and Bath. The cathode by this time is coated with a spongy layer of gold, silver, and probably other metals. Scrape off the loose deposit, and use the cathode over and over as often as desired, finally rolling it thin and refining it as below.

When the cyanide bath becomes foul, cement out the gold and silver by means of zinc—see Chapter VIII on Cyanide Solutions. Collect the deposited powder and wash it well.

All of these materials are refined by essentially the same process—the loose flakes that dropped or were scraped from the cathode, the cathode itself after it has been rolled thin, and the cement gold and silver that were deposited out by zinc. Remove silver and base metals by means of nitric acid; the powder that remains will be high quality gold, possibly fine enough for your needs. If not, repurify it according to the methods of Chapter XV.

This plan of stripping gold from platinum by means of the reversed current requires little labor, and its cost will depend upon that of cyanide and electric energy. The consumption of cyanide can be controlled by regulating the temperature of the bath, and by occasional additions of caustic soda, sufficient to keep the concentration of the latter at about 2 to 4 grams per liter (about 3 to 6 dwt. per quart). The cyanide does not decompose appreciably below 113 deg. F. As the temperature rises the decomposition increases, with the formation of ammonia and sodium formate. Above 149 deg. F. cyanide decomposes rapidly, and when nearly at the boiling point the whole bath can be destroyed within a few hours. For most economical results, keep the bath at about 140 deg. F. Unfortunately, the bath works faster when hot; the worker must therefore make a compromise between speed and cyanide conservation.

This method has been described as an electrolytic method. However, it differs in many ways from the better-known electrolytic methods used in large-scale refining (see Chapters XXI and XXII) and should not be confused with them.

* * * *

MERCURY AND AMALGAMS

In earlier chapters you were advised to keep mercury and its alloys (known as amalgams) separate from your ordinary wastes. In some ways mercury acts like silver, being soluble in nitric acid, and being precipitated by hydrochloric acid as a white chloride. It can cause confusion in other ways as well, contaminating the gold and interfering with the stannous chloride tests.

The amalgams used in dentistry are made by mixing mercury with alloys of tin, silver, zinc, and other base metals. Normally they are of low value and inconvenient to refine. Now and then, accidental bits of gold or even of gold-platinum alloys, get mixed in with a lot of old amalgam, but this mixing should be avoided as far as possible.

In shops that handle gold leaf, gold amalgams are sometimes encountered. They are normally of more value than dental amalgams. The process of refining is essentially the same for both kinds of amalgams.

The material is first heated strongly in an iron retort to drive off the larger part of the mercury, which is caught in water and should be redistilled before being used again.

A crust of metal remains in the retort; it always contains some mercury. It is melted into a button. This second melting, of the crust, is the most dangerous part of the work, as the heavy mercury fumes can seep out into the building and make the workmen sick.

The button that is obtained from dental amalgams is difficult and expensive to refine on a small scale, largely because of the large proportion of tin it contains, and we do not encourage you to refine it yourself.

The button obtained from gold amalgams may be of high quality and easy to work with, and usually may be refined by methods that are already familiar.

* * * *

Now for the details of the method of retorting off the mercury. A very small amount of amalgam can be retorted in a glass tube, sealed at one end and bent into a V. A tube of ¾ inch diameter is best. The amalgam is broken into small pieces and dropped into the closed end, where it is heated, and the fumes condense in the long open end of the tube.

In another method for small amounts of amalgam, a potato is used as a condenser. This is a device popular with prospectors because it is very simple, and saves a part of the mercury. A large potato is cut smoothly in half, and in the flat surface of one half a recess is hollowed which should be considerably larger than the amount of amalgam to be treated. The amalgam is placed on a clean sheet-iron surface (a frying pan or clean shovel), the half potato is placed over it, and the whole is set over a hot fire. Some mercury vapor will escape under the edges of the potato, and, as before, these fumes must be avoided. After fifteen or twenty minutes of strong heating the potato may be lifted off for inspection. If all the mercury is gone from the gold the potato may be crushed and panned, and a considerable part of the mercury will be recovered.

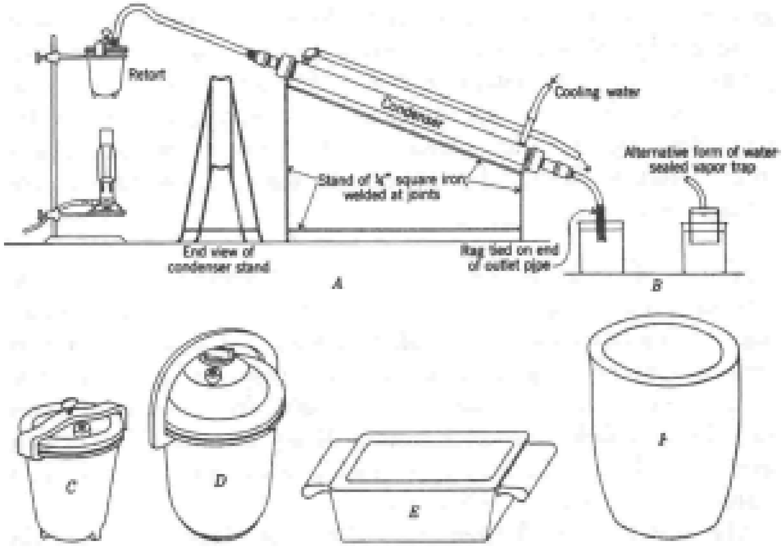
However, it is much better to use a regular cast-iron retort or still. Eimer and Amend list an iron retort for this purpose, their number 30574. Pint size $4.50; two-pint size $5.00.

The material is put in and the lid clamped down very carefully, and a long iron pipe is connected with it. The retort should be coated on the inside with chalk, or painted with a thin paste of clay, and dried, to keep the gold from sticking to the iron. A lining of paper serves the same purpose, but forms an objectionable deposit in the condenser tube.

Do not fill the retort too full; pile the lumps of amalgam loosely in the retort, to not over $^{2}/_{3}$ of its volume. (When retorting liquid mercury, $^{1}/_{3}$ to ½ full is enough.) Clamp the cover on tightly, being sure that the condenser pipe is free from obstructions. The joints should be luted with some sealing compound, such as a cement of ground asbestos with litharge and glycerine.

Retort for mercury.

Set the exit tube so that the mercury will run downward, and place a vessel of water under the open end. Wrap a piece of cloth around the open end of the exit tube, like a cuff, and let it dip into the water. The idea is to conduct the mercury into the water as it con-



Apparatus for retorting amalgams. A, set up of small retort with condenser; B, water sealed vapor trap; C, one style of retort; D, Nevada type retort; E, bullion mold; F, graphite crucible.

Reprinted from U. S. Bureau of Mines Information Circular 6787 denses, the wet cloth helping to cool any fumes that have not already been condensed.

DO NOT let the IRON tube dip into the water—only the bottom edge of the cloth cuff. Remember that when the retort cools, water may suck back into the hot iron pipe and cause it to explode. The cloth cuff tends to prevent this sucking-back, since it is not airtight. But, after you once start to heat, keep the heat going steadily, and remove the water *before* stopping the heat. This is important.

The retort may be heated by a Bunsen burner, blow torch, or other means. Old-timers say a wood fire is better than a coal fire. Apply a low heat at first, then after ten or fifteen minutes increase it gradually, just enough to maintain a small steady trickle of condensed mercury.[1]

Mercury boils at about 675 deg. F., which is halfway between the boiling point of water and the first visible red heat of iron. However, mercury begins to *volatilize* at the boiling point of water, and gives off fumes that are dangerous to the worker even when heated quite gently. When no more mercury appears, increase the temperature for a few minutes to red heat. Do not go much above this or you will drive over the zinc, which may clog the pipe. Remove the water, then let the retort cool. Some vapor may remain in the retort, so be careful not to breathe the fumes when you take off the cover.

A crust of metal remains in the retort. Sometimes it is sold or refined as it is, but generally it is melted first, in a gold-melting furnace, with a flux such as borax glass. As we said above, this second melting may be dangerous, as the fumes may not go up the flue unless the draft is better than average. Aside from this hazard, this step does not differ markedly from ordinary melting. The molten metal may be cast into an ingot mold, or possibly granulated in water, as circumstances will dictate.

The metal obtained from most dental amalgams will contain much silver and tin, and is usually of low value. It is possible to refine it by acid methods, of course, but the process is made tedious by the tin, and the amount of acid and labor required is usually enough to make the job unprofitable. In most cases the best disposal of such metal is to a silver buyer.

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[1] Parts of this section are adapted from United States Bureau of Mines Information Circular 6787, of October 1934, PLACER MINING IN THE WESTERN UNITED STATES, Part II, by E. D. Gardner and C. H. Johnson.

As we said at the beginning, there is always a possibility that accidental admixtures of gold, or gold and platinum, can get into collections of low-grade dental amalgams. Accordingly a test for these elements is always in order. Take a scrap of the metal and treat it first with nitric acid to dissolve silver, then add hydrochloric acid (forming aqua regia) to dissolve gold and platinum; add a little water and let the copious white silver-chloride settle; if gold or platinum is present it will now be in solution in the liquid, which should be tested with stannous chloride Testing Solution A.

The final task is to repurify the distilled mercury. Sometimes a single re-distillation is the best method. A clean retort and clean condenser pipe, free from rust, should be used, and it is not necessary to heat as strongly as before. This re-distillation is not as simple as it would seem, because when the mercury boils it “bumps” violently, and sometimes shakes the condenser pipe loose. Accordingly in some plants that do this work on a large scale, the distillation is carried out in a vacuum, at a relatively low temperature.

Or, the mercury can be purified by washing with chemicals. Place very dilute nitric acid in a tall narrow vessel, such as a length of wide glass tubing; let the mercury trickle down it a drop at a time. One plan is to place the mercury in a bag of chamois and squeeze it through, into a funnel that rests in the top of the wide glass tubing. The acid dissolves tin, zinc, silver, etc. After that, wash the mercury first with water to remove the acid; then with sodium hydroxide to remove any residual traces of acid; then water again to remove sodium hydroxide; then finally with ether to remove the water. The mercury should be bright and free from scum, ready to be used again, or sold to a mercury dealer.

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DENTAL PINS

High grade dental restorations, especially those made several years ago, often contains substantial iridio-platinum pins to anchor the porcelain teeth to a metallic plate. When the price of platinum became high, many substitutes were devised. Some were of base metal with platinum ends or coatings. Others were made of alloys of platinum with gold, palladium, nickel, and whatnot. Others contained no precious metals at all.

When handling dentures, first get rid of the porcelain and vulcanite by hammering and pinching with pliers. Then heat the metal parts with nitric acid. Base metals will be attacked and some kinds will disappear in a few minutes. Test the nitric acid, as it may contain palladium; if not, throw it away.

Platinum pins, and pins that consist of high grade platinum-gold alloys, will not be attacked by the nitric acid. It may be worth while to get pins of this type out of the metal in which they are embedded, heating them in a gas flame until the solder softens and they can be pulled out. This is slow work, but sometimes it pays. (The alternative is to melt up everything and treat it according to Chapter XII.)

The metal from which the pins were pulled may consist of high grade gold. Generally it contains neither platinum nor palladium and should be refined as a simple gold job.

Next, place the pins in nitric acid again, and heat, to remove any remaining base metal, then treat with aqua regia. Iridio-platinum pins will show almost no action, indeed they can be boiled in aqua regia for hours before dissolving completely.

The cheaper pins will dissolve more readily in aqua regia, depending upon their composition. If any silver is present it will form the familiar grey scum of silver chloride.

Most people pick out the high-quality iridio-platinum pins and melt them without further refining. The cheaper alloys should be allowed to dissolve, and the precious elements will be recovered according to methods with which you are already familiar.

* * * *

GOLD PEN POINTS

Some gold pen points are tipped with grains of native osmiridium—a naturally-occurring alloy of osmium and iridium. Synthetic alloys of the platinum-group metals are also used, as well as a few base-metal combinations. Good fountain-pen points must be very hard, and most of them are also difficult to dissolve or melt.

The refiner’s normal procedure is to clip off the points with shears, and to handle the gold part of the pen as a simple high grade gold job. The points should then be treated with aqua regia to remove remaining gold. The grains that survive this treatment may or may not be valuable.

Some of the inexpensive base-metal grains contain tungsten, and will behave so much like osmiridium as to confuse the worker. Exposing the washed grains for a second or two to an oxy-gas flame may reveal the base-metal particles, as tungsten forms colored oxides and may take fire, while osmiridium remains unchanged. This test should be used with care, however, as longer exposure to the flame may volatilize osmium, as well as the ruthenium that is used in some of the better-grade synthetic alloys, occasioning a loss of valuable elements as well as danger to the worker, the fumes being poisonous.

When all these facts are considered, it is not surprising that many professional refiners do not buy these grains, even when presented in sufficient quantity to justify an assay. (The complete assay of these grains can be a laborious task.)

In Chapter XVII more will be said about methods of handling the rarer elements of the platinum group. Meanwhile, for most workers the best program is to recover all the gold, and to accept whatever price is offered for such grains as remain after the treatment outlined above.

Now and then a worker makes the mistake of melting up a lot of gold pens without first clipping off the points. The osmiridium does not alloy with the gold, merely remains as lumps that appear when the metal is rolled. To overcome this, remelt the gold in a tall narrow crucible, and let it cool slowly in the crucible. The heavy osmiridium will settle to the lowest part, which can be sawed off and treated separately. T. K. Rose[2] points out that osmiridium grains settle better from an alloy that is mainly silver, so the rich bottom portion should be remelted several times with silver, the lowest part being clipped off each time. Finally granulate the metal, which by that time is mainly silver, and part it with sulphuric acid (see Chapter VI) which dissolves silver and leaves a residue of gold and osmiridium grains. Treat this with aqua regia to dissolve the gold, and clean grains of osmiridium will remain.

GOLD LEAF

Gold leaf is thinly-beaten fine gold, or, more generally, an alloy containing a very little copper or silver. The manufacture of gold leaf is simple in theory—sheets of high-karat gold are rolled and hammered to extreme thinness—but the actual operation is an art that demands much deftness and close attention to many details, as well as muscular prowess. (See Encyclopedia Britannica on Goldbeating.) Accordingly the user is not apt to make his own leaf, and so has little incentive to refine the scrap. The usual procedure

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[2] THE METALLURGY OF GOLD. Seventh Edition, page 463.

is to return scrap to a professional refiner, who burns out the trash and refines the residue as a simple gold job, such as would be handled according to Chapter V or XV.

ELECTRICAL CONTACT POINTS

These are made in many sizes and shapes, of many materials, both precious and non-precious. Silver is widely used because of its low electrical resistance, but to the refiner the most interesting contact points are those made of platinum and its alloys

For highest grade equipment, where price is no object, the lridio-platinum alloys are preferred, from ten to twenty-five percent iridium. The requirements[3] to be met by contact points differ widely, and for many purposes cheaper materials are adequate. Economy is effected in various ways, notably by making the bulk of the article of brass or other base metal, and coating only the exposed area with precious metal.

In the catalogue of a single manufacturer[4] of contact points we find the following metals and alloys mentioned fine silver; Sterling silver; coin silver; silver overlaid or inlaid on monel metal, brass or copper; silver welded to steel; platinum; lridio-platinum; platinum group alloys welded to nickel, steel and bronze; platinum overlaid on bronze; tungsten; tungsten carbide; special alloys of platinum, iridium, gold, silver, palladium, and other precious metals. Other sources mention gold-silver, platinum-ruthenium, gold-silver-nickel, gold-nickel, silver-copper-tin, and many other alloys.

In the face of so extended a list, it is clear that the refining of old contact points may reasonably be deferred until the worker has acquired some familiarity with metals and their reactions.

Sometimes he is fortunate enough to know the composition of the materials he is handling, and his task should not be difficult. Other times his first, and perhaps his most difficult step, will be to identify the materials. A few acquaintance tests on contact points of known composition will save much time in later operations.

Points usually reach the refiner still attached to the brass, steel, or other parts to which they were welded or screwed while in use

Tungsten and tungsten carbide should be gotten rid of promptly,

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[3] For a discussion of these requirements, see USE OF THE NOBLE METALS FOR ELECTRICAL CONTACTS, by E. F. Kingsbury. Mining and Metallurgy, New York, March, 1928.

[4] The H. A. Wilson Company, Newark, N. J.

as they are of small intrinsic value and can cause trouble if melted in with precious metals. A few seconds' exposure to the oxy-gas flame, as mentioned in the section on fountain pen points, may reveal them, as tungsten forms colored oxides and presents a characteristic reaction to the flame.

The magnet will locate steel parts, and hot dilute sulphuric or hydrochloric acids will dissolve them away without affecting the precious metals. If the articles are not too small, it helps to roll them as thin as the rolls will take them, but this is hard on the rolls. Nitric acid will remove brass, monel metal, bronze, and other base metal parts, but will also dissolve silver and palladium, so should be used only when provision is made for the recovery of those metals.

After as much base metal has been disposed of as seems expedient—and the worker must exercise judgment as to the amount of effort to expend on each step—a treatment with aqua regia is indicated. It may dissolve all the precious metal parts, and tests given in Chapter IX will suggest proper methods of recovery.

Some of the higher grade contacts will not dissolve in aqua regia, even after prolonged boiling. This includes the valuable iridio-platinum alloys, the iridio-platinum-rhodium alloys, and the iridio-ruthenium complexes. Possibly the simple isolation of these high grade bits of metal will serve the refiner's need and his work will be done. But if he wants to separate the elements, the following procedure[5] is suggested: Melt the contact points—high grade platinum-group alloys insoluble in aqua regia—with considerable zinc, in a gold melting furnace. Granulate the resulting alloy and treat it with hydrochloric acid, which removes zinc and leaves the heavy metals as a granular powder. Wash this residue and heat it to redness to convert iridium to a less soluble form. Treat it with aqua regia and the platinum will dissolve, the iridium and ruthenium remaining as a dark residue. Recover the dissolved platinum as usual, with ammonium chloride. (Do not use this plan on alloys containing osmium.)

Professional refiners handling these contacts in quantities are not apt to have the patience to examine each contact with care, and may melt everything together, obtaining a button that would be treated

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[5] Adapted from ASSAYING PLATINUM METALS, by Martin Schwitter. Metal and Mineral Markets, Jan. 21, 1932, pp. 6-10; Feb. 18, pp. 6-7; March 17, pp. 6-11.

according to the scheme of Chapter XII or some modification thereof. The assay of these points is laborious, and unless the composition is known the price paid is correspondingly low.

CHEMICAL WARE

The chemical industry is the second largest consumer of platinum, using the metal as a catalyzer in the manufacture of sulphuric and other acids, as electrode metal in a variety of electrochemical processes, and as laboratory equipment in the form of dishes, crucibles and other apparatus. For most purposes pure platinum, or platinum alloyed with a small amount of some sister metal, is preferred. Special purposes may employ special alloys; the thermo-couple, for example, consists of two wires, one a platinum-rhodium alloy, the other pure platinum.

Manufacturers of platinum laboratory ware are generous in providing instructions on the care and handling of such equipment. They also make reasonable allowances for the return of damaged articles. Accordingly only a small amount of chemical platinum will find its way to the jeweler or small refiner. In some cases, such as old electrodes and dishes, the refiner's job is easy. The bulk of the metal may be of high quality, ready to be remelted after a little treatment with nitric acid to remove surface impurities, the remainder being refined according to the procedures in Chapter XII. Other types of waste such as old contact masses are much more difficult, and should be sold to a professional refiner.

Chemical apparatus is made of other precious metals too. Pure gold, pure silver, and gold-palladium alloys are popular. To the student who has followed the suggestions in this volume, the identification and refining of such ware will be easy.

Platinum-clad nickel and platinum-clad copper are recent developments that may became of considerable commercial importance. Sheets of platinum are welded to sheets of the base metal and rolled down after the fashion of rolled-gold plate. The resulting platinum-clad plate is then fabricated into vessels of all sizes and shapes, highly suitable to many chemical and industrial processes. When properly made the platinum layer is thick enough to protect the inner layer from corrosion, but thin enough to reduce the cost of the whole to an attractive figure.

The refining of such dual metals should not offer undue difficulty to the student of this book.

CHAPTER XVII

RHODIUM, RUTHENIUM, OSMIUM

Their rarity. Rhodium. Ruthenium. Osmium. Refining rhodium, ruthenium and osmium, the “mysterious” metals. Some schemes of separation: I. The classic system. 2. The method of Gilchrist and Wichers. A list of books and papers referring to the three rarer metals.

* * * *

THEIR RARITY

According to the Minerals Yearbook, published annually by the United States Bureau of Mines, platinum is by far the most widely used metal of its group. In 1938 it accounted for 68.8 percent of the total of platinum group metals sold by domestic refiners. The jewelry industry was the largest purchaser, the chemical industry second, dentistry third, and the electrical industry fourth. Next to platinum, palladium is the most widely used metal, constituting 27.5 percent of the total sold by domestic refiners in 1938, of which over half went into dentistry. Iridium sales came next, but amount to only 2.6 percent of the total. Osmium, rhodium, and ruthenium together amount to only 1.1 percent of the total consumption of the group.

From these figures it will be seen that osmium, rhodium and ruthenium, however interesting they may be from the chemical viewpoint, are of secondary importance commercially. All six metals of the group are normally found in crude platinum ores, but osmium and ruthenium are (except in a few exceptional cases) not used in either dentistry or jewelry. Rhodium is occasionally used in small amount. Accordingly the jeweler or dental technician who refines his own scrap has little occasion to consider these three less familiar elements.

This is fortunate, for their separation from their sister metals is tedious and unsatisfactory, even in the hands of experienced chemists. In general, if a non-chemist believes that his residues contain appreciable quantities of these metals, his best procedure is to find a refiner equipped to separate them (many professional refiners are not so equipped) and when selling such stuff, always to mention the fact that these elements are present. Because of the difficulty of refining and assaying the purchase, the financial return may be disappointingly low.

Full descriptions of these metals, their histories, natural occurrence, physical characteristics such as melting points, electrical conductivity, and so on, will be found in the publications mentioned at the end of this chapter and in Chapter E of the Appendix. For our immediate purposes, their most interesting characteristics are their insolubility and the fact that two of them—osmium and ruthenium—form volatile oxides when heated.

RHODIUM

This metal received its name from the characteristic rose color of several of its compounds. When in compact form it does not dissolve in any single acid, and is attacked very slowly by aqua regia except when alloyed with considerable platinum or other metal; rhodium "black" dissolves slowly in hot concentrated sulphuric acid. Rhodium can be plated electrolytically to give a handsome silvery finish to jewelry, silverware, or optical instruments. Since it is almost totally insoluble in acids, the finish once applied is not easily removed. Grinding is the method usually employed, and the deposit is so hard that even this is difficult.[1]

Rhodium plate is perfectly non-tarnishing, and when properly applied can protect the underlying metal against corrosion. The amount of metal needed to give a serviceable deposit is minute, and the refiner need not expect to recover much rhodium from his wastes, even when handling stuff that is known to be rhodium plated.

The solutions used for rhodium plating are sold by certain of the precious metal dealers. When they become exhausted or foul, do not add such solutions to your other platinum wastes—their separation would be unduly expensive and troublesome. Instead, evaporate

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[1] Atkinson and Raper mention a method of stripping rhodium plate from silver, the article being immersed in a molten mixture of cyanides of potassium and sodium; if it is made anode and a current passed, the removal of rhodium is hastened. The method should be operated only by experts. For details see British Patent No. 419,819. There is obvious need for a simpler and more adaptable method.

them down a bit to get rid of excess water, then return them for credit to the dealer from whom they were purchased, shipping by express (not mail) and using the same acid-proof container in which they came. It is possible, of course, to precipitate the rhodium with zinc, but the task of making it up into a new bath is beyond the skill of most non-chemists.

A second use for rhodium is in scientific apparatus, especially the so-called Le Chatelier thermo-couple, mentioned in Chapter XVI, whose essential part is two wires, one pure platinum, the other an alloy of 10 percent rhodium with 90 percent platinum. Rhodium-platinum alloys resist high temperatures extremely well.

RUTHENIUM

Ruthenium is the lightest of the platinum group. Its name comes from "Ruthenia," an old name for Russia, where it is found. Like rhodium, it is insoluble in any single acid, and difficult to get into solution by any means. It is occasionally used as a stiffener and hardener for platinum, the alloy containing 8 percent ruthenium being almost as hard as the one containing 20 percent iridium. This fact has been utilized at times when the price of ruthenium was low enough to compete with iridium.

Alloys of palladium stiffened with a little ruthenium and rhodium have been recommended for jewelry. Their working qualities are good, and because of their low specific gravity an ounce of such alloys goes almost twice as far—makes up almost twice as many articles of a given size—as an ounce of iridio-platinum. A typical formula is 95 parts palladium, 2 to 4 parts ruthenium, and the remainder rhodium. The sale of these alloys for jewelry has been hampered in this country for three reasons: first, our stamping laws are so worded that it is difficult to stamp them in a way that will appeal to the buyer; second, the refining of the mixed filings is complex; and third, the melting of the scrap metal calls for some extra care.

Ruthenium, when heated to about 600 degrees C., forms a volatile oxide. When alloyed with other metals this tendency is lessened, but it can occur nonetheless. The fumes are poisonous and the loss of metal may be appreciable, especially when the ruthenium content is high.

OSMIUM

Osmium is the heaviest of the platinum group, and has the highest melting point. Like ruthenium, it has been used as a stiffener and hardener of platinum when its price compared favorably with that of iridium. Its employment in fountain pen points is mentioned in Chapter XVI, and one of its compounds is used as a stain in microscopy. When heated in air or oxygen, osmium also forms a volatile and very poisonous oxide, and is even more dangerous to the operator than ruthenium, the fumes appearing at a lower temperature. Partly because of this volatility its alloys have found limited usefulness, in spite of the fact that it is more efficient than iridium as a hardener of platinum.

Any operation involving the heating of osmium should be conducted in a hood with a good draft, and a mask should be worn to protect the face, eyes and throat of the operator. The fumes have a garlicky odor and act as a poison to the lungs. The vapor is reduced to the metallic state when in contact with the eye tissues, and if deposited upon them in sufficient quantity can produce permanent blindness. The word osmium is derived from a Greek word meaning stench.

Osmium and ruthenium and most of their alloys are dissolved in acids only with difficulty, even when in the finely divided form, and in most systems of separation the volatility of these oxides is utilized.

REFINING RHODIUM, RUTHENIUM, AND OSMIUM, THE “MYSTERIOUS” METALS

As we said before, it is fortunate that jewelers and dental technicians have little occasion to accumulate these metals. Until the last few years there was little in print on their refining, and an aura of mystery, partly justified by the facts, surrounds them. The intelligent layman naturally resents this situation, and we shall now mention the several reasons that have, in combination, brought it about.

First, these three metals have so few industrial applications that only a few people are interested in their technology, which means that publishers are not tempted to print books about them. A second reason is that some companies that sell these metals have deliberately shrouded their laboratories in secrecy. During the last few years, however, the free publication of research by other firms, and especially by our National Bureau of Standards, has made much information available to all, and the tendency now is toward greater frankness, as is proven by the list of publications at the end of this chapter.

A third reason, and the main one, is directly related to their chemical characteristics. With the discovery of new reactions and better procedures, their separation will undoubtedly become easier and more dependable, and the cloud of mystery will blow away. Active research is going on in several famous laboratories, some of it directed at precisely this problem. At present, however, the refining of these rarer elements is not for the laymen, mainly for chemical reasons such as will now be described.

The reader has met several procedures described as “good” separations. For example, the precipitation of gold from acid solution by copperas is normally a “good” or “clean” separation; when properly conducted it brings down the gold—all the gold and nothing but the gold—cleanly and completely. There are thousands of such separations known to chemistry, many being used by non-chemists. But when the reader precipitated platinum as the orange platinum-ammonium-chloride he did not bring down *all* the platinum, and he did bring down *some* of the sister metals, notably iridium and rhodium if they were present. This precipitation therefore is not a “clean” one, and affords only partial separation.

Again, the reader recalls that when he separated platinum from iridium by boiling the mixed blacks in dilute aqua regia, some of *both* metals dissolved, and some of *both* metals remained in the residue. This is another incomplete separation, highly characteristic of the group. It is chemical characteristics such as these which are the real reason for the apparent mystery that surrounds these metals.

Nor is that all. The reader must have been struck by the number of alternative methods that are possible in the refining of even the simpler gold-silver mixtures; and when several elements are present, as in the Stock Pot, the possible variations become even more numerous. Now, there are six platinum-group metals, and wastes containing them normally have other metals in addition—gold, silver, copper, nickel, tin, iron, and what not. A listing of all the combinations and permutations in which this baker’s dozen of elements might associate themselves, with sometimes one, sometimes another as the main constituent, would run into the thousands. And with every change there might be a modification of the procedure.

It should now be clear why even the skilled chemist finds this refining a laborious task, and why he must be prepared to vary his procedure from batch to batch if necessary. Whiteley and Dietz begin their paper[2] with the words: "It is difficult to give a refining outline that may be followed for any and all combinations of the platinum metals; different combinations require different. methods of attack." The same point is brought out in the paper[3] in which Johnson and Atkinson describe the processes used in the Acton (England) refinery of the Mond Nickel Company, Ltd. They say: "In precious metal refining, the order of operation depends upon the ratio in which the precious metals are present. The order described here is followed because it has been found to be the most suitable for these by-product concentrates, although it is realized that other sequences of operations might be more suitable for other types of material."

We shall therefore make no attempt to give full directions for the refining and separation of these three rarer metals. We shall instead give a brief outline of the general principles used, and, for the reader with a knowledge of chemistry, a list of publications wherein he can find detailed procedures.

SOME SCHEMES OF SEPARATION

I. *The Classic System*

The classic system of separation of the platinum group was worked out over sixty years ago. Sainte-Claire Deville and J. S. Stas published a paper[4] in which they described the refining of the metals used to make the standard bar of iridio-platinum on which the international metric system is based. Even then the shortcomings of the ammonium chloride separation were recognized. The following quotation from the book THE PLATINUM METALS, by E. A. Smith, published in London in 1924 by Sir Isaac Pitman & Sons, Ltd., is an outline of a

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[2] REFINING AND MELTING SOME PLATINUM METALS, by J. O. Whiteley & C. Dietz, Mining and Metallurgy, March 1928.

[3] REFINING METALS OF THE PLATINUM GROUP, by C. Johnson and R. H. Atkinson, The Industrial Chemist, (London), June 1937.

[4] DE L'ANALYSE DU PLATINE IRIDIÉ EMPLOYÉ PAR LA SECTION FRANÇAISE DE LA COMMISSION INTERNATIONALE DU MÈTRE À LA CONFERENCE DES PROTOTYPES, Procès-Vcrbaux, Comité International des Poids et Mesures (1878), Annexe No II. By E. H. Sainte-Claire Deville and J. S. Stas.

modern adaptation of the classic system, as used in many modern refineries for the treatment of crude platinum; it is summarized from Louis Duparc's method as given in his LE PLATINE DU MONDE, Geneva, 1920. This scheme is susceptible of dozens of variations as to details and order of procedure. We quote:

"The process involves ten main operations, as follows:

"1. The treatment of the mineral with aqua regia with the separation of the insoluble osm-iridium and sand, etc.

"2. The precipitation of the platinum as the orange ammonium chloroplatinate and subsequent calcination of the precipitate to produce platinum sponge.

"3. The separation of the iridium as ammonium chloro-iridiate from the mother liquor by long standing, and calcination of the precipitate to obtain metallic iridium.

"4. The treatment of the mother liquor (after removal of the platinum and iridium as above) with iron or zinc, to separate in the metallic state other metals of the platinum group (together with any small quantities of platinum not previously separated) which are deposited as a fine black precipitate called *first blacks*. Drying and roasting of the blacks and treatment with dilute sulphuric acid to remove copper and other base metals.

"5. Treatment of the cleaned blacks with dilute aqua regia to obtain a solution containing palladium (with traces of platinum, rhodium, and iridium) and an insoluble residue containing rhodium.

"6. After separating the traces of platinum, rhodium and iridium from the solution from 5 with ammonium chloride, the palladium is separated by means of metallic iron as a black mass which is purified and the metal sold as palladium sponge.

"7. The insoluble residue from 5 is fused with barium dioxide, and the fused mass treated with aqua regia to effect solution of the rhodium and iridium. These metals are then precipitated with ammonium chloride and finally converted into metallic sponge.

"8. The insoluble residue of osm-iridium remaining after the first treatment of the ore with acid, is fused with zinc to effect its decomposition. The fused product is treated with aqua regia, and the acid liquor so obtained is submitted to distillation.

"9. The acid liquor is distilled in the presence of steam whereby osmium distills over as osmic acid, and is collected in water, and the osmium subsequently separated as metal.

"10. The acid liquor retains the iridium and ruthenium which are separated with ammonium chloride, and finally converted into sponge."

The last four processes, involving fusion with barium dioxide, fusion with zinc, and the distillation of the volatile oxides, have not been discussed in this book. As we said above, they are subject to many modifications. Thus, potassium pyrosulphate or sodium peroxide may be used instead of the barium peroxide. Sometimes the distillation is carried out in an atmosphere of chlorine. And so on and so on.

2. The Method of Gilchrist and Wichers

Recognizing the importance of the platinum metals, our Bureau of Standards has been studying them for some years. The first task was to make sure that each metal could be determined, once it had been separated from its sisters. The second was to find good methods for the separation of any pair of the metals. The third was to provide a method of analysis for the entire group, on which could be based practical schemes of assaying and of refining.

On March 9, 1939, two of the Bureau's workers, Dr. Raleigh Gilchrist and Dr. Edward Wichers, were awarded the Hillebrand Prize of the Chemical Society of Washington, for their paper entitled A NEW SYSTEM OF ANALYTICAL CHEMISTRY FOR THE PLATINUM METALS, which had been presented before the Ninth International Congress of Pure and Applied Chemistry at Madrid, Spain, in 1934. In reporting this award the magazine *Science*, in its issue of March 3, 1939, says:

"The work represents the first general advance in the analytical chemistry of the platinum group since Deville and Stas devised methods for the analysis of the platinum alloys used in fabricating the international prototype meter and kilogram, over sixty years ago. The new system enables the chemist to separate and determine these six closely related metals with a degree of accuracy equal to that of the more exact procedures used for the common metals. Related procedures applied to refining have resulted in the preparation of the platinum metals in an exceptionally high degree of purity."

Gilchrist and Wichers have since prepared a second paper that details the procedures of the prize paper. This latter paper, entitled A PROCEDURE FOR THE SEPARATION OF THE SIX PLATINUM METALS FROM ONE ANOTHER AND FOR THEIR GRAVIMETRIC DETERMINATION, was published by the Journal of the American Chemical Society (volume 57, 1935, pages 2565 to 2573), a periodical that can be found in a majority of American public libraries.

This new procedure is not suited to the needs of the non-chemist refiner, but serious students of the platinum group are urged to consult it, as it seems destined to serve as the foundation for improved methods in many fields.

In this new system, in the words of the authors, "Precipitation with ammonium chloride, fusion with pyrosulfate and extraction of metallic residues with acids are avoided entirely. The separation of platinum from palladium, rhodium and iridium is accomplished by controlled hydrolytic precipitation. When a boiling solution containing these four metals as chlorides, and in addition sodium bromate, is neutralized to approximately pH 7, the hydrated dioxides of palladium, rhodium, and iridium precipitate quantitatively, leaving platinum in solution. A second precipitation of the dioxides suffices to effect complete removal of platinum. . . Palladium is separated from iridium and rhodium, in chloride solution, by precipitation with dimethyl glyoxime. . . Rhodium is separated from iridium by reducing it to metal with titanous chloride in a boiling solution of the sulfates in diluted sulfuric acid. The metallic rhodium is dissolved in hot sulfuric acid and precipitated a second time, to remove iridium completely.

"When this new procedure is applied to the separation of all six of the platinum metals from one another, osmium is the first metal to be isolated. This is accomplished by distilling its volatile tetroxide from a nitric acid solution. Ruthenium is next isolated by distilling its tetroxide from a solution of the sulfates in diluted sulfuric acid to which sodium bromate is added. A very suitable reagent for the absorption of osmium tetroxide, and also of ruthenium tetroxide, is 6N hydrochloric acid saturated with sulfur dioxide. . .

"In the recovery and determination of each of the six metals, the new features of the procedure consist in the precipitation of osmium, of ruthenium, and of iridium, as hydrated oxides, with final ignition to metal. Rhodium, and also platinum, are recovered as sulfides, and ignited to metal. Palladium is recovered as the glyoxime compound, in which form it may be weighed, or it may be determined as metal after ignition of the glyoxime precipitate. . . The procedure is designed for the analysis of the platinum group, in the absence of other metals."

The last phrase of the above quotation is important—"in the absence of other metals." That means that the procedure as there outlined does not take care of gold or base metals. However, the Bureau of Standards expects to give consideration to these elements in subsequent work, and the student is urged to keep in touch with current literature.

One piece of further research has already been published, A NEW PROCEDURE FOR THE ANALYSIS OF DENTAL GOLD ALLOYS, by Raleigh Gilchrist, printed as Research Paper RP 1103, in the Journal of Research of the National Bureau of Standards, Volume 20, June 1938. It provides for the separation and gravimetric determination of silver, iridium, tin, gold, indium, copper, zinc, nickel, palladium, rhodium, and platinum. Note that osmium and ruthenium are not included. The procedure can also be adapted to the refining of crude materials containing gold and the platinum metals. This paper can be obtained from the Superintendent of Documents, Washington, D. C., for ten cents. The non-chemist will find it difficult to understand, but the chemist working in this field will find it invaluable.

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(The frontispiece of this book shows Drs. Wichers and Gilchrist at work. Dr. Gilchrist, on the right, is manipulating a series of flasks arranged for the distillation of osmium and ruthenium. Dr. Wichers is pouring something—possibly a solution to which ammonium chloride has been added to precipitate the orange powder—from a big evaporating dish into a Büchner filtering funnel of a type that will be described in Chapter XX.)

A LIST OF BOOKS AND PAPERS REFERRING TO THE THREE RARER METALS

The reader should be familiar with the publications mentioned in Chapter X, and should also refer to the more extended bibliography in Chapter E of the Appendix. The Encyclopedia Britannica, and all text and reference books of advanced chemistry, give interesting and useful facts under the headings Platinum Group; Rhodium; Ruthenium; Osmium.

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NEW PROCEDURE FOR THE ANALYSIS OF DENTAL GOLD ALLOYS. By Raleigh Gilchrist. Research Paper RP 1103, part of the Journal of Research of the National Bureau of Standards, vol. 20, pages 745-771, June 1938.

PLATINUM AND ALLIED METALS. SOME POINTS OF INTEREST TO THE CHEMICAL ENGINEER. By C. Johnson and R. H. Atkinson. Trans. Institute of Chemical Engineers, London, vol. 15, pages 131-144, 1937. This describes the operations

at the Acton (England) refinery of the Mond Nickel Co., Ltd., where all six of the platinum metals are recovered. An abstract of this article was printed in The Industrial Chemist (London), pages 223-233, June 1937. A shorter abstract was printed in The Chemical Age (London), pages 459-462, May, 1937. Extended quotations will be found in Chapter XXII of this book.

METALS OF THE PLATINUM GROUP. ORES, RECOVERY AND REFINING, FABRICATION AND USES, AND PROPERTIES. By R. H. Atkinson and A. R. Raper. Journal of the Institute of Metals (London), vol. 59, No. 2, pages 179-210, 1936. An abstract of this paper appears in The Metal Industry (London), June 15, 1937.

A PROCEDURE FOR THE SEPARATION OF THE SIX PLATINUM METALS FROM ONE ANOTHER AND FOR THEIR GRAVIMETRIC DETERMINATION. By Raleigh Gilchrist and Edward Wichers. Journal of the American Chemical Society, vol. 57, pages 2565-2573, 1935.

A NEW SYSTEM OF ANALYTICAL CHEMISTRY FOR THE PLATINUM METALS. By Raleigh Gilchrist and Edward Wichers. Publicaso en: Trabajos del IX Congreso Internacional de Química Pura y Aplicado, Tomo VI, Química Analítica. Madrid, Spain, 1934.

A METHOD FOR THE SEPARATION OF RUTHENIUM FROM PLATINUM, PALLADIUM, RHODIUM AND IRIDIUM. By Raleigh Gilchrist. Research Paper 654, Bureau of Standards Journal of Research, vol. 12, pages 283-290, March 1934.

ASSAYING PLATINUM METALS. By Martin Schwitter. Metal and Mineral Markets, Jan. 21, 1932, pages 6-10; Feb. 18, 1932, pages 6, 7; Mar. 17, 1932, pages 6-11. A reprint of this article, under the heading REFINING PLATINUM METALS, will be found in The Brass World, issues of Sept., Oct., Nov. and Dec., 1932. It describes the methods used in a plant that refines jewelers' and dentists' scrap.

A METHOD FOR THE SEPARATION AND GRAVIMETRIC DETERMINATION OF OSMIUM. By Raleigh Gilchrist. Research Paper 286, Bureau of Standards Journal of Research, vol. 6, pages 421-448, March 1931.

FABRICATION OF THE PLATINUM METALS. By C. S. Sivil. Transactions of the American Institute of Mining and Metallurgical Engineers, Institute of Metals Division, pages 246-261, 1931.

A GRAVIMETRIC METHOD FOR THE DETERMINATION OF RUTHENIUM. By Raleigh Gilchrist. Research Paper 125, Bureau of Standards Journal of Research, vol. 3, pages 993-1004, December 1929.

MELTING, MECHANICAL WORKING AND SOME PHYSICAL PROPERTIES OF RHODIUM. By Wm. H. Swanger. Research Paper 127, Bureau of Standards Journal of Research, vol. 3, pages 1029-1040, December 1929.

PURIFICATION OF THE SIX PLATINUM METALS. By Edward Wichers, Raleigh Gilchrist and Wm. H. Swanger. Technical Publication No. 87 of the American Institute of Mining and Metallurgical Engineers; 29 pages; issued with Mining and Metallurgy, New York, March 1928.

THE PLATINUM METALS AND THEIR ALLOYS. By Frederick E. Carter. This paper contains in tabular form many of the physical characteristics of the six metals. Technical Publication No. 70 of the American Institute of Mining and Metallurgical Engineers; 24 pages; issued with Mining and Metallurgy, New York, February 1928.

REFINING AND MELTING SOME PLATINUM METALS. By J. O. Whiteley and C. Dietz. Osmium is not included. This paper describes methods of refining dental and jewelry scrap and laboratory ware, in 100 ounce lots. Technical Publication No. 84 of the American Institute of Mining and Metallurgical Engineers; 9 pages; issued with Mining and Metallurgy, New York, March 1928.

THE PLATINUM METALS. By Ernest A. Smith. A book, published by Sir Isaac Pitman & Sons, London. 120 pages. 1924.

THE METALLURGY OF PLATINUM. By Louis duParc, translated by Allen C. Redding and Geo. M. Nelson, with Frank Sanborn. A translation of Chapter XV of duParc's "Le Platine du Monde." Issued in "Mining in California," a publication of the California State Mining Bureau, San Francisco. Vol. 18, April 1922, pages 158-172.

DE L'ANALYSE DU PLATINE IRIDIÉ EMPLOYE PAR LA SECTION FRANÇAISE DE LA COMMISSION INTERNATIONALE DU MÈTRE À LA CONFERENCES DES PROTOTYPES By E. H. Sainte-Claire DeVille and J. S. Stas. Procès-verbeaux, Comité International des Poids et Mesures. 1878, Annexe No. II.

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For a discussion of the dangers connected with the heating of osmium, see *The Keystone*, Philadelphia, issue of January, 1924, page 92. Also *Chemical and Metallurgical Engineering*, New York, November 10, 1924, page 743. Also *The Brass World*, vol. 20, page 242, 1924.

CHAPTER XVIII

LOW GRADE WASTES

Materials discussed. Determining the method of disposal. Two extreme cases. *Part I—The shop of moderate size*. Suggested procedure for floor sweeps. Equipment for dressing floor sweeps. Procedure for wash-barrel residues. For old crucibles. Flue dust. Paper storage—old filter papers. Polishings, grindings, old aprons, carpets, floors, etc. Old solutions. Fluxes for use with low grade wastes. Litharge. Lead buttons. Cupellation. If platinum is the only precious metal. *Part II—The large plant*. Amalgamation not profitable. Disposal of the final fine dust. Sampling. Questions and answers.

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In this chapter we shall discuss materials in which the proportion of precious metal is low, such as the sweepings from the floor of a jewelry factory.[1]

The literature contains frequent accounts of savings that have been made by burning up old jewelry-shop floors, door mats, aprons, and the like, and it is true that even lowlier materials, such as the settlings of the water in which the jewelers wash their hands, will yield up value under proper treatment.

However, there have been many occasions when these low-grade materials have proven a loss, rather than a profit, through improper handling. The literature does not go so fully into this aspect of the case. This chapter, therefore, will attempt to help the owner to decide whether a given material is worth salvaging or not, and what methods to employ.

DETERMINING THE BEST METHOD OF DISPOSAL

It is not easy to draw the line between goods that it pays to refine in your own shop, goods that should be sold to a professional refiner and smelter, and goods which (like sea-water) should best be let alone.

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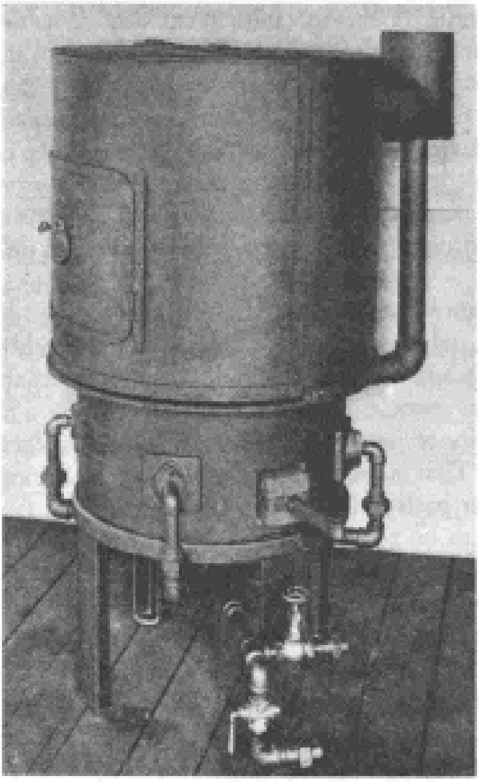
[1] Parts of this chapter arc based on the article JEWELERS' LOW GRADE WASTES: AN ASSET OR A LIABILITY? by C. M. Hoke. The Metal Industry, New York, November, 1934.

The bases of determination are: How much metal is present, and how much will it cost to recover it? The latter depends in turn partly upon the amount of dirt present, but mostly on the character of the dirt, as well as upon the facilities for refining that your establishment maintains. All three factors must be considered.

TWO EXTREME CASES

Suppose one has a dollar's worth of gold, finely divided, and mixed with a quantity of wood, as in the case of old flooring, with gold embedded in the wood fibre, or in an old cocoa door-mat. Simple burning (so long as care is taken to keep gold from going up the flue) will almost solve the problem; pick out any nails with a



Sweep reducer.
Courtesy of the American Gas Furnace Co.

magnet, then flux off the few ashes with a little borax, and your metal is in almost salable form. Expense: perhaps 25¢ or so for the crucible, three or four cents for fluxes and fuel, plus a little for labor.

On the other hand, suppose one starts with a dollar’s worth of gold, silver and platinum mixed with a similar bulk of old crucibles, instead of wood. It would be necessary to (1) break up the crucibles, picking out and discarding the obviously worthless lumps; then (2) grind and sieve the rest, recovering the good-sized metallic shot; (3) mix the remaining fine dust with a large amount of flux and treat it for a considerable time at a high heat; (4) refine the resulting metal and the metallics from process 2 to separate the gold, silver, and platinum from each other and from the base metals present. The labor will be considerably more than in the first instance, the fuel expense will be higher, more flux will be needed, as well as a larger and more expensive crucible, and chemicals will be needed for the separation of the pure metals. Possibly the process will pay; but many a worker has found similar tasks unprofitable.

In other words, the presence of precious metal is only part of the story.

These instances are extreme cases—wood is easy to burn, while old crucibles, whose materials were chosen precisely because they do resist heat and fluxing, are very difficult to separate from the precious metal particles.

The majority of jobs will fall somewhere between these two extreme cases. That is, part of the material can be removed by simple burning, other parts will be less easy to handle.

The point to be remembered, then, is that the *character* of the dirt with which your precious metal particles are mixed, as well as its quantity, must be considered.

If daily care is taken in the collection of the low grade wastes, it is possible to exercise control over both the character and the quantity of dirt that must be worked over before the precious metals can be recovered. For example: the porter in a jewelry shop had been told to collect and burn all papers. He obeyed literally, and collected and burned not only the tissues used in the factory, but also the unopened magazines and newspapers from the office waste baskets—the office in question being used only by clerical workers. This meant an obvious waste of the porter’s time, and in addition the ashes from the coated magazine paper made the task of refining difficult.

PART I. THE SHOP OF MODERATE SIZE

The reader of this book has observed that there are often several alternative methods of refining a given type of waste. Low grade wastes are no exception; hardly any two shops will follow exactly the same routine, even though they may be governed by the same principles. To describe all the possible alternatives would be exhausting. The following paragraphs, then, describe typical procedures, but by no means all possible ones.

SUGGESTED PROCEDURE FOR FLOOR SWEEPS

It normally pays the average shop, having the average amount of space and facilities, to burn, grind, and sieve its sweeps, and to refine the metallic particles that are sieved out. It does not pay to refine the low-grade fine dust that passes through the sieve; this should be sold to a professional refiner and smelter. This statement covers a large majority of cases, and every word should be noted carefully.

The following routine is suggested: Do not let large amounts of floor sweeps accumulate. Handle each day's lot as it comes in, collecting it in a wire basket that rests in a metal box. This permits fine stuff such as filings, small stones, etc., to sift through into the box below.

Sometimes it pays to pan this stuff that goes through the wire basket, the way miners pan earth when looking for gold dust. If there is a possibility of the stuff containing small pearls or other objects that can be harmed by heat, pan it without burning it; otherwise burn it first to get rid of the grease. (See page 51.) Also pass a magnet through it to take out iron and steel.

It takes only a little practice to get the trick of panning—shifting the pan round and round, with water, letting the water and the lighter particles slip over the edge. Finally the bright metal will collect on the bottom. It may be possible to pan the stuff so well that the metallic particles can be treated the same as filings. But usually they will be melted up with a flux, as will be described later.

The papers, etc., in the wire basket, should be burned, and the ashes ground and sifted to say 20 to 40 mesh. The grains that will not pass the sieve should be examined; sometimes they should be treated as clippings; in some cases they are plainly of no value and should be discarded. Usually it is desirable to melt them down into a button, using a flux.

In some cases the sifted material is then ground further, until the bulk of it will pass the 80-mesh screen, the metallics being again collected and united with those previously obtained, and the resulting button being refined by acid methods with which you are now familiar.

The fine dust is dampened lightly to prevent scattering, and is then packed in barrels and sold to a refiner. The sampling process by which its value is determined will be described shortly. The purchaser should always be informed of the kind of material he purchases. Tell him which precious metals are present, and so on. This makes it easier for him to make an assay and appraisal, and may make your net return higher.

There is some question as to the exact size or fineness to which this material should be ground before being passed along to the professional refiner. The process of grinding is noisy; also it calls for considerable energy—either hand power or electric current. Therefore in a small shop the process is not apt to be carried far because of the noise; on the other hand if power is readily available, it is well to carry the process along further. The refiner's first task, after receiving and weighing and drying the stuff, is to grind it—a process for which he makes a charge; therefore if the owner can do this grinding cheaply himself, it is to his advantage to do it.

EQUIPMENT FOR DRESSING FLOOR SWEEPS

The choice of equipment is governed largely by the size of the lots to be handled. Thus, the small shop will burn its sweepings in a big frying pan, ~~pouring on gasoline and~~ burning until the stuff will burn no more. It will grind the residue in a hand mortar, and sieve by hand. A small gold-melting furnace will take care of the melting of the metallics.

A somewhat larger shop will burn its sweeps in a stove made for the purpose—a simple affair, not unlike the old-fashioned wood-burning heater. It will grind the ashes in a small tumbling barrel, using iron balls, and will sieve by hand. The gold melting furnace will take care of the metallics.

The larger plant, as will shortly be described, will have automatic machinery for grinding, sieving, and mixing, and extensive equipment for sampling and bagging.

The final smelting—the smelting down of the fine dust at the plant of the professional refiner—will take place in huge furnaces of special design.

PROCEDURE FOR WASH-BARREL RESIDUES

In the past, a jewelry factory was inclined to estimate its activity and importance by the number of barrels in which its wash-water was settling. Now, however, many shops, especially where rents are high, are using only one or two small barrels, plus a filter press. The advantages and disadvantages of the two methods will be discussed in Chapter XX.

In general wash-barrel residues are handled nearly the same as floor sweeps; that is, dried, burned, sieved, ground, sieved again, the metallics collected, and the fine dust that passes the last sieve should be sold to a professional refiner. The grease that is present tends to float off the fine particles of precious metals; for that reason panning is not advised.

Whether you use a filter press or settling tanks, the residue collected will contain soap, grease, washing compounds, rouge, pumice, and sometimes lime, alum, excelsior or other substances added to agglutinate and hold the flocculent particles.

PROCEDURE FOR OLD CRUCIBLES

As suggested above, these are difficult to handle, because crucible materials are difficult to flux and resistant to heat treatment. Dropping old crucibles into water while still hot, will make them easy to crush, and sometimes permit the immediate recovery of embedded lumps of metal. When breaking them up, if any lumps are plainly of no value, they should be discarded promptly; a little time spent at this task will pay for itself later. The remainder should be crushed and passed through a series of sieves, in order to recover the metallics, which sometimes are of good size and appreciable value.

It probably will pay to pan the dust; it pans much more cleanly than floor sweeps. If small lots are handled at regular intervals, the task is not tiresome. After panning, the remaining low-grade dust can be put in with other sifted dust from the floor sweeps or wash-barrel residue, to be sold.

The metallics, as usual, should be melted into a button; because of the admixture with sand and other highly refractory particles, this will require more flux than ordinary to obtain a clean button.

FLUE DUST

The flue or stack that carries off the fumes from the gold-melting furnace should be cleaned out at intervals. The stuff collected is quite fine, and may be sifted and sold with the fine dust obtained from the final sifting of floor sweeps.

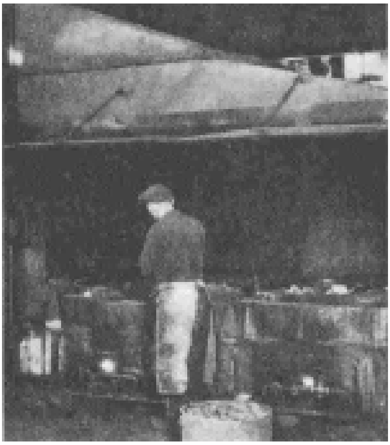
PAPER STORAGE—OLD FILTER PAPERS

The paper towels used when handling precious metal solutions, and the sawdust used to soak up solutions that have spilled, are generally put in with the old filter papers. Many people do not like to class these with the low grade wastes, as they sometimes are of high value. It is difficult to say whether it pays to refine them separately or not, since individual workers differ so greatly in the amount of metal they permit to collect in filter papers or towels. The following suggestions, however, may be helpful.

Tear off all paper that contains no valuable material, and spread the rest out to dry. When you have several papers, burn them in a frying pan, ~~pouring on gasoline~~. Some workers divide filter papers into three kinds: those whose main content is trash such as the cinders flushed out of filings; those whose main content is silver chloride; those that are high in platinum. Those containing much trash should go to the sweeps. Those containing platinum can sometimes, after burning, go in with the next lot of filings. Those containing silver chloride should, after burning, be melted down with soda ash to give a silver button see—Chapter VIII—to be refined by methods already familiar.

POLISHINGS AND GRINDINGS; OLD APRONS, CARPETS, FLOORS, ETC.

The ashes obtained from this group frequently contain much more precious metal per pound than those obtained from floor sweeps. The cotton waste, old buffs, thread, rags, and so on, are sometimes difficult to burn because the fluffy particles are carried up the flue. The procedure is practically the same as for floor sweeps—the material is burned, sifted to about 20 mesh, iron particles may be taken out with a magnet, the metallics are collected, and if facilities permit, the ashes are ground again to pass an 80 to 100 mesh.



Ovens for eliminating water from wet materials or solutions.

Courtesy of Handy & Harman

The metallics are melted into a button as usual, using one or another of the fluxes that will shortly be described, and refined by acid methods. The final fine dust is, as was said above, normally much richer than the final dust from floor sweeps, and some well equipped shops find that it pays them to refine it, melting it down in a sand crucible, as below, to obtain a button for acid treatment. Most shops, however, add it to the collected sweeps and sell it to a professional refiner.

OLD SOLUTIONS

Give attention to any residue or sediment. Sometimes it is the only valuable part. Wash it and examine the particles with a hand lens. Utilize the tests described in Chapter IX. If the residue seems to be of value, capture it in a filter, dry and melt it into a button, for treatment to be determined by its nature.

FLUXES FOR USE WITH LOW GRADE WASTES

In most of the procedures just described, the metallics that fail to pass through the various sieves are collected and melted into a button. Normally this is done in a sand crucible in a gold-melting furnace, with the addition of a suitable flux. The button obtained will be refined according to methods already familiar; if platinum group metals are present, see Chapter XII. If gold and silver are the only precious metals, see Chapters V, VI, and VII.

Slow burning to obtain a concentrated ash.
Courtesy of Handy & Harman.

The word "flux" means to flow. You want to make the sand, dirt, emery, etc., become liquid and literally flow, so that the particles of metal (which also have become liquid because of the heat applied) can collect freely into a button. This is the most important duty of a flux. Sometimes other purposes are accomplished at the same time, as will be seen later. The choice of fluxing material will depend upon the nature of the material that is being handled, and the objects to be obtained. The quantity to be used will depend upon the proportion of dirt that is present and may run from one-half to three times the weight of the material.

Thus, if the metallics are fairly clean, consisting mostly of metal, they can be melted down with a little calcined borax (also called borax glass) without difficulty or great expense. The greater the proportion of dirt, sand and the like, the more flux will be needed.

Many shops will make up a “stock flux” in quantities; then when occasion demands they can add other ingredients to it. A popular stock flux consists of:

Soda ash (or preferably a mixture of soda ash and pearl ash)	About 5 parts
Calcined borax, powdered	3 or 4 parts
Broken glass, crushed	1 or 2 parts

These should be mixed well and kept very dry. The broken glass is not easy to prepare, and some people do not use it.

If the melt tends to boil up and foam unduly, add some common salt.

If the material is almost wholly sand, as from old crucibles, use considerable stock flux, possibly two pounds of flux for each pound of material, and add an ounce of fluorite for each pound of material. Fluorite is especially good for fluxing sand; that means it will be correspondingly hard on the crucible in which the operation takes place.

This does not in the least exhaust the list of possible fluxes. Some workers add a little flour to the stock flux. Some workers say that ordinary lye makes a good flux, the kind sold in cans being mixed with materials such as we have been discussing. In addition there are several prepared fluxes on the market, which if used according to the maker’s instructions, will give good results.

LITHARGE. LEAD BUTTONS

If much carbonaceous matter is present (that includes graphite) use a good quantity of stock flux, perhaps two pounds to each pound of material, and add about one to three ounces of litharge for each pound of material. Litharge is a lead oxide; when heated it gives off oxygen which helps to burn the carbon. The metallic lead that is released will collect and wash down the metallic particles into a compact button.

The charge is then poured into a mold. The lead-bearing metal sinks to the bottom, and when cool can easily be broken from the slag. Under proper working conditions this slag will show no metallic particles. If it should, that may mean you did not use enough flux, or perhaps did not leave the charge in the furnace long enough.

Litharge is also advised for dust that contains very little metallic content, or in which the particles are extremely small in size. For that reason it is regularly used by the refiners and smelters when running down the low-grade dust that has been ground and sieved according to the procedure described in this article.

The formation of lead buttons is a very common procedure in some refineries, as well as in the assay laboratory. This book has generally recommended alternative procedures wherever possible, because most small establishments are not equipped to handle lead buttons by cupellation, and acid treatment is generally tedious.

CUPELLATION

Cupellation is the process of melting an alloy containing lead with precious metals, in the presence of air. The lead is oxidized to litharge, which liquefies and dissolves the oxides of the base metals and carries them into a liquid layer that can be poured or bailed off, leaving behind a precious metal alloy of much higher value than that with which the cupellation started. This method of concentrating the valuable metals will be mentioned again in later chapters.

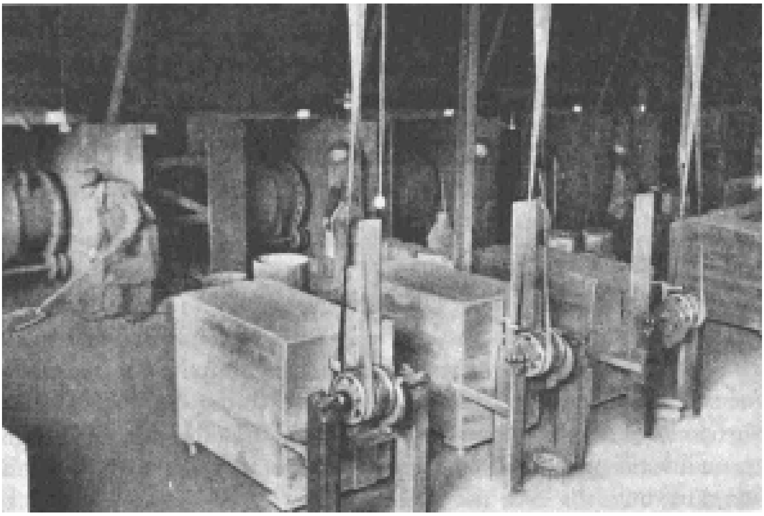
The production of lead fumes involves unusual hazards to the worker without proper equipment, and for that and other reasons, cupellation is rarely used by those to whom this book is dedicated—the jeweler, the dental technician, and the small refiner.

IF PLATINUM IS YOUR ONLY PRECIOUS METAL

If the only precious metal present in the dust or metallics is platinum (as in the case of the factory that handles platinum goods only) some other metal must be added to the melt to collect the platinum particles. The heat of a gas-air furnace will not melt platinum; even though the heat be adequate to flux the sand into a liquid, the platinum particles will not flow together unless some other metal, of lower melting point, is added to dissolve and collect them. Litharge is often used for this purpose. Or, if one has on hand some rolled-gold or gold-plated scrap, or even brass or copper, this can be used instead. This helps to avoid the use of lead, whose fumes are dangerous, and offers an easy way to salvage the gold. The resulting buttons will be refined by acid methods.

PART II. THE LARGE PLANT

In Part I the problem of the average establishment was discussed, and a procedure was suggested for handling the ordinary quantity of floor sweeps, wash barrel wastes, old crucibles and the like. As a matter of interest we shall now describe the procedure followed by one of the largest bullion houses in the United States, where gold is handled literally by the ton, and platinum by the hundredweight.[2] It is unusually well equipped, and has singularly excellent facilities for cost accounting; for that reason alone it is interesting in that it has checked the economics of various methods and has reported on its conclusions.



Pulverizing mills and screens.

Courtesy of Handy & Harman.

Briefly, it burns, grinds, and sieves its floor sweeps, collects and refines the metallics, and sells the remaining fine low-grade dust to a smelter. This in principle is the procedure recommended for the much smaller establishment, and differs from it only in details.

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[2] The United States Assay Office at New York City.

The sweepings are first burned in a large furnace. In this plant, incidentally, there is a Cottrell precipitator for the fumes and dust from the several flues. The ashes are reduced in a jaw crusher to about ½ to 1 inch size, then go through crushing rolls onto a vibrating screen, the larger particles being sent back for further crushing, while bits of iron are caught by a magnet. The metallics that fail to pass a 20-mesh screen are melted with a flux and refined.

AMALGAMATION NOT PROFITABLE

When this plant was first built, it used a mercury-amalgamation process as the next step. The material was mixed with water and passed over huge trays containing mercury; baffle-plates forced all the mud to come in contact with the mercury, which picked up most of the gold and silver, forming an amalgam.

This amalgam was collected and refined, the mercury being used again and again. However, it was found that this mercury treatment did not pay, and this step has been abandoned. (Mercury does not pick up platinum.)

DISPOSAL OF THE FINAL FINE DUST

After the material has passed the 20-mesh screen, the first step of the sampling process is taken. Every third shovelful is placed to one side and saved for sampling. The rest of the dust is placed in bags to be sold. It is interesting to note that this plant, though unusually rich and well equipped, does not attempt to refine this fine dust, but sells it to the highest bidder.

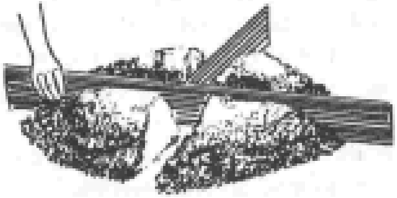
(There are only a few firms in the whole world that can economically refine this fine dust. The job calls for furnaces of huge dimensions, measuring ten to twenty feet or more on a side, and a single melt will run two or three days and involve tons of material.)

SAMPLING

Sampling is a long and painstaking process. A large plant, such as the above, will have the necessary equipment for this task; the average shop probably cannot afford it. But there is another reason why the small shop does not attempt to sample—the big refiner would not accept his figure. The refiner will in effect say this: “We have perfect confidence in your good faith; however we know from long experience that the job of sampling calls for skill, patience, and suitable equipment, and we shall therefore courteously insist upon doing the sampling ourselves."

As a result, the sampling is usually done in the presence of representatives of both buyer and seller, and usually at the plant of the buyer. The large plant we have been discussing is unusual in having space and equipment under its own roof for this process; therefore does its own sampling, but always has representatives of one or several buyers present while the work is being done.

The material (every third shovelful of the ground and sifted sweeps) is carefully mixed and piled in symmetrical cones, then quartered by means of a straight-edge. One quarter will be set aside, the rest added to the stuff already bagged. The fourth cone is combined with the fourth cone from other piles, and is again ground to pass a finer sieve—say 80-mesh. The process of piling and quartering is repeated until the bulk has been greatly reduced—in this case to about forty pounds.



The dried material is piled in cones and quartered.

This is divided into four final lots; one goes to an outside chemist for assay, another is set aside as a reserve to use in case of dispute; the rest is distributed to the refiners who wish to bid on the lot. The one offering the highest bid will receive the entire lot, though if two bids are very close it is customary to divide the lot between the two, handing alternate bags to each. If the stuff is to be shipped any distance, it is packed in air-tight drums, to prevent loss.

This process of coning and quartering is only one of the methods that may be used. Sometimes a borer, an instrument suggesting an enormous apple-corer, is plunged into the pile and samples extracted. When very small quantities of material are to be refined, this laborious sampling is sometimes omitted, the entire lot being melted up and itself serving as the sample.[3]

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[3] For a description of methods of sampling this and other materials, see SAMPLING AND EVALUATING SECONDARY NON-FERROUS METALS, by T. A. Wright. Mining and Metallurgy, New York, February, 1928.

REFINING THE FINAL SIFTED DUST

This material consists of a large number of finely divided particles of worthless material, through which are scattered a few particles of precious metals. The large refineries that do this work use the same principles that have been outlined in this chapter, but handle enormous quantities of material at a time, the mixture being charged into a large furnace and the process of refining going on without interruption for several days. The dust is mixed with a stock flux, plus fluorite and litharge. The fluorite (also called fluorspar, or calcium fluoride) liquefies the sandy stuff, the litharge (lead oxide) furnishes oxygen to burn up combustible materials, and lead in which the precious metals may dissolve. Base metal oxides, and the fluxed sandy materials, form a slag that is bailed off at intervals. The lead in which the precious metals are collected, is finally cast into bars or pigs for further treatment.

The slag just mentioned still contains some valuable material, and is smelted again in a cupola furnace, to give another metallic layer and a final slag that may now be discarded.

This process of smelting with litharge will concentrate the precious metals considerably, the metal in a ton of sweeps now being collected into about a hundredweight of lead.

The next step is to get rid of the lead. This is done in a cupel furnace, the molten metal being exposed to a blast of air which changes the lead back into litharge, while the gold, silver and platinum remain as an alloy. The molten litharge layer will dissolve the oxides of copper and other base metals, and will be bailed off and used again.

The alloy of precious metals, now practically free from lead and other base metals, is cast into slabs or granulated for further purification. Efforts are made to arrange the materials in the original charge so that this alloy will contain at least three parts of silver to one part of combined gold and platinum-group metals. The slabs or granular metal now obtained may be refined by several different methods. Sometimes they are boiled with concentrated sulphuric acid according to the routine suggested in Chapter XII for silver-rich alloys. Usually, especially when the silver content is high enough, they are cast into anodes and refined by the electrolytic methods to be described in Chapter XXII. When the final process is completed, and the purified metals are cast into bars or bricks ready to return again to art or industry, the circle will have been completed.

* * * *

The present United States Treasury regulations make it inconvenient to export gold-bearing materials. But some years ago, before these regulations came into effect, many jewelers, and indeed many small refiners, sent their sweeps to England, and the returns from certain of the English refineries were such as to justify the extra shipping expense. This should not be interpreted as a criticism of American skill; rather it reflects differences in labor and monetary conditions.

* * * *

QUESTIONS AND ANSWERS

Q. It is well known that gold ores carrying only a few pennyweight of gold per ton, are being worked at a profit. Why not use mining methods, such as cyaniding, on floor sweeps and other low grade wastes, which usually contain several ounces of gold per hundredweight?

A. The reason is that floor sweeps contain large quantities of materials that use up or destroy cyanide. In the effort to dissolve out the gold in the sweeps, enormous quantities of cyanide would be needed. It is cheaper to get the gold out by smelting the sweeps with litharge and other fluxes. United States Bureau of Mines Report of Investigations Number 3275, dated June, 1935, entitled STUDIES IN THE RECOVERY OF GOLD AND SILVER, says: “Certain substances in ores are harmful to cyanidation; chief among these are those that combine with cyanide, forming cyanides, and carbon, which precipitates gold from solution.” Floor sweeps contain large quantities of carbonaceous materials, also considerable copper, brass, and other substances that form cyanides.

Certain other methods used in mining are being used in the refining of secondary metals, for example the devices for crushing and sieving. Amalgamation is another mining method occasionally utilized in the recovery of secondary gold.

* * * *

Q. Why is it necessary to grind the sweeps so fine? If the stuff is going to be smelted down anyway, why not leave it as it is after passing the 20 mesh?

A. Fine grinding has been proven necessary for accurate sampling. In cases where sampling is not important, there is no reason for fine grinding.

CHAPTER XIX

LOSSES

Metal losses in the refining room; in the shop; in the furnace room. How much loss is permissible? Figures on losses in melting gold; in melting and reworking platinum; in polishing. Losses due to dishonesty. Losses of money, rather than metal, due to mismanagement. Difficulty of estimating the value of wastes. Assaying. Questions and answers.

* * * *

Losses in precious metal refining are of two kinds—losses of actual metal, and losses of money through mishandling or bad management. This chapter will discuss both kinds. The first kind is easier to trace, being revealed merely by the comparison of the weight of new metal with that of the finished article plus recovered scrap. Losses through mishandling are more difficult to recognize, but should be easier to overcome.

METAL LOSSES IN THE REFINING ROOM

The obvious losses due to splashed or spilled solutions, or broken vessels, are common only with the beginner. But the beginner can expect them, which is another of the reasons why he is urged to handle small quantities at first. If he has a good supply of paper towels, and plenty of sawdust to soak up any spilled solution, the loss will not be considerable.

A few hours after handling solutions containing gold, the beginner will notice deep purple stains on his fingers. The amount of actual gold involved is small, but even so such stains represent a loss of metal, and the more skilled the operator, the fewer the stains. Silver and platinum in solution produce black stains on skin and clothing.

Spattering of hot solutions is a cause of metal loss. Using dishes of generous size, so that the liquid does not reach too near the top, will reduce this. In many processes flasks should be used instead of evaporating dishes or casseroles. A funnel inverted over a casserole in which a solution is being boiled, will save much spattering. For evaporation, use a steam bath or sand bath as much as possible, and maintain the solution just below the boiling point.

Readers often ask if the precious metals boil out when solutions containing them are heated. They do not boil out in the way that water or alcohol does, but if the solution spatters, the loss may be considerable. The table on which the burner stands should be easily cleaned; soapstone and heavy linoleum are better than rough brick. The flue should not have too strong a draft, or droplets may be carried away.

Clean platinum filings are very heavy, and when a mixture containing them is poured from one vessel to another, they cling with great tenacity, and because of their neutral color may escape attention. Gold filings are just as heavy, but their yellow color makes them less apt to be ignored.

Old filter papers often contain more metal than is evident; the heavy valuable filings collect in the point of the filter cone and are concealed by the lighter and less valuable stuff on top.

Waste of reagents is as expensive as any other waste. Thus, the careless refiner when precipitating gold, will dissolve a large quantity of copperas in considerable hot water and dump it in, even though the amount of gold may be very small. This means more than the waste of copperas; it also means loss of time in handling and filtering the extra bulk of liquid. Frequent use of the tests described in Chapter IX will minimize losses of this kind.

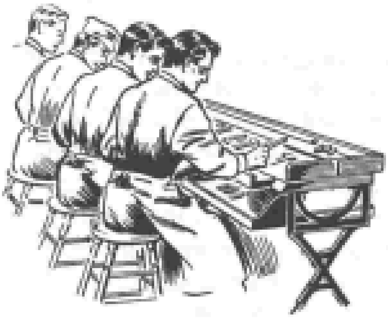
METAL LOSSES IN THE SHOP

These are of many kinds, some more easily controlled than others. It has long been known that shop losses are greater in summer than in winter, because the men’s hands are damp and the filings cling and are carried away, also because windows are open and fans are blowing. Modern methods of air conditioning promise much to the jewelry factory, as they circulate fresh air through windowless rooms, filtering out not only the dust, but also particles of precious metal.

Losses are greater with intricate jewelry designs than with simple ones, and with hand work than with machine work.

Smooth hard-surfaced floors, free from cracks, reduce losses. Gratings or cocoa mats, especially on concrete floors, will keep filings from being ground into shoes and carried away. A vacuum cleaner is a necessity. Good lighting pays for itself in preventing the accumulation of sweeps in dark corners. Thought in the arrangement of benches and heavy equipment, to permit the nozzle of the vacuum cleaner to reach behind them, will be repaid.

So much has been said during the last generation regarding proper suction devices for use in polishing, that it seems superfluous to mention them again. Most health regulations require them.



Some factories employ a laundress to wash the workmen's aprons, towels, scrub rags, etc., and all water must pass through the wash-barrel system. Wash-barrels can be a big source of loss. Mere settling is never enough—an adequate filtering device (see Chapter XX) is imperative, because soap scum will float filings through a whole train of barrels. Keep oil and grease out of the wash waters, as oil is a very efficient flotation agent. When discarding old acid solutions, do not pass them through the wash-barrels as they might dissolve metallic particles therein.

LOSSES IN THE FURNACE ROOM

Platinum filings and clippings must be thoroughly clean before being remelted. Do not attempt to burn out the dirt. You may succeed in burning out certain kinds of trash, but platinum will be scattered, possibly volatilized, at the same time, and the expense of gas and oxygen will be quadrupled. Clean platinum melts quickly, and with little tendency to leave particles of metal embedded in the crucible.

Flue loss in the melting of gold can be appreciable, and the presence of volatile impurities such as zinc may increase it. It is not due to true volatilization of metal, according to T. K. Rose,[1] but rather to the spurting of tiny globules which are carried away by the flue draft. Such globules are so small, some being even less than 0.001 mm. in diameter, that they stay suspended like dust motes even in a still atmosphere. This should be kept in mind when the flue is being built. One plan is to pass the gases through a chamber (lined with smooth tilework) where their velocity can be so reduced that most of the metallic droplets will settle. Very large plants such as Mints use the Cottrell system, described in Chapter XX, and make a nearly complete recovery of this flue dust. A similar loss by spurting may occur when the molten metal is poured.

HOW MUCH LOSS IS PERMISSIBLE?

Exact figures on the percentage of loss in various factories are not always helpful because of the many factors, differing from shop to shop, that are involved. However, such figures are interesting, and we shall accordingly provide a few.

FIGURES ON LOSSES IN MELTING GOLD

T. K. Rose, in the chapter just mentioned, reports that it is the common experience in Mints that the gross loss in melting gold-copper coinage alloys is usually from 0.2 to 0.25 part per 1,000, and after allowing for the amounts recovered from condensation chambers and flues, and from the ground-up crucibles, sweeps, etc., the net loss amounts to 0.1 to 0.15 part per 1,000. This is with gas-fired and coke-fired furnaces. With an electric resistance furnace the crucible loss was only 0.03 part per 1,000, flue loss being eliminated. Rose also reports (page 459) that with a Cottrell precipitator, the flue losses occurring in the refining of bullion (which are presumably greater than in the melting of clean alloys) can be reduced by 97 to 99 per cent.

ON LOSSES IN MELTING AND REWORKING PLATINUM

The United States Bureau of Standards reports that in the handling of $16,000 worth of platinum, involving various kinds of reworking, repurifying, and remelting, there was a loss of only

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[1] THE METALLURGY OF GOLD. Seventh edition, page 66.

$200 worth of metal. These figures would be more helpful if accompanied by more information as to the nature of the reworking.

ON LOSSES IN POLISHING

Ernest A. Smith[2] has made an extensive study of the nature of polishing processes, and quotes figures on several kinds of articles, the effect of different abrasives, different designs, and so on. He finds it difficult to state what percentage of loss can be called legitimate. He says that in the Sterling silver trade it is usually considered reasonable to have a net or unrecoverable loss from all sources—polishing, refining, smelting, etc.,—of about 1 or 2 per cent, part of which is the refiner's fee. He concludes: "The net losses sustained in working gold and platinum are so variable that no general statement can be made regarding them."

The exhaust system for removing buffing dust, lint, and so on, should be carefully designed to avoid pockets, and ample facilities for cleaning should be provided. John S. Isdale[3] describes his experience with a section of an exhaust system which, because of its position, was left uncleaned for four years. The section in question consisted of about sixty feet of 24" galvanized pipe. It was taken down carefully and the dust was collected and refined. The charges for cleaning, transportation and refining came to $33, and the factory received a credit of $900. In other words, $933 worth of metal accumulated in that pipe in four years.

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[2] JUST HOW MUCH PRECIOUS METAL IS LOST IN POLISHING IS AN IMPORTANT QUESTION, by Ernest A. Smith. The Manufacturing Jeweler, Providence, R. I., October 15, 1936.

[3] THE RECOVERY OF PRECIOUS METALS FROM FACTORY WASTE, by John S. Isdale. The Brass World, New York, pp. 138-9, July, 1922.

ON LOSSES IN THE REFINING OF CRUDE PLATINUM ORE CONCENTRATES

The Acton (England) refinery of the Mond Nickel Co., Ltd., subsidiary of the International Nickel Co. of Canada, Ltd., handles concentrates from the company's mines and plants all over the world. They report[4] that not more than 0.25 percent of the platinum metals contained in their concentrates is lost, another 1.25 percent being tied up temporarily in furnace slags that go back for retreatment. This figure is impressive, especially as the concentrates are very complex, but it must be recalled that the processes involve very little contact between metals and hands, as many steps as possible being automatic. This plant will be referred to again in Chapter XXII.

LOSSES DUE TO DISHONESTY

So far nothing has been said regarding the obvious factor of employee dishonesty. The practice of refining individual workmen's filings in separate dishes is a potent incentive to honesty. To carry through each man's return, from start to finish, as a separate job, occasions considerable overhead, and there are ways of reducing this without reducing the effectiveness of individual treatment. In some shops, the following plan is used: All filings, except those of one man, are thrown together; the refiner then has two lots to handle, a large one and a small one, and he keeps the two separate from start to finish. Next week, all filings are combined except those of a second man. And so on, no man knowing when his turn will come. Or if a shop uses much platinum and very little gold, each lot may be kept separate until the platinum filings are cleaned and weighed, while all the dissolved gold is placed in one big jar and precipitated at the same operation.

In this connection an odd psychologic fact might be mentioned. A supply house observed that on visitors' day the general losses were slightly larger than usual. It was not suggested that the guests had pilfered bits of metal; rather it seemed that the workmen, diverted by visitors, and feeling subconsciously that their responsibility was somehow subtly divided, were less scrupulous in making

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[4] PLATINUM AND ALLIED METALS, SOME POINTS OF INTEREST TO THE CHEMICAL ENGINEER. The Chemical Age, (England.) Page 459-62, May 22, 1937.

their returns. Whatever the explanation, the firm finally refused to admit visitors at any time.

MONEY LOSSES DUE TO MISMANAGEMENT IN REFINING

We shall mention only a few instances of money loss, as different from metal loss, our object being to suggest the principle that should be followed in minimizing them. This principle may perhaps be compressed into this one sentence: *The truly skilled refiner knows how to refine, what to refine, and when to refine it.*

For example: one loss, more serious than apparent, comes from letting scrap metal lie idle. Back in Chapter II it was pointed out that when scrap is sold to a professional refiner, there may be a long interval during which the metal is earning nothing, while it accumulates in the shop or in transit. The operator who does his own refining can work with a smaller capital investment because he keeps substantially all his metal in use. Thus the platinum filings in Chapter III need stay in the refining room for only an hour or two. In Chapter XI the bulk of the platinum is back at the bench within twenty-four hours, often less; the gold within two days. The process given in Chapter XII takes longer, but it is unusual for the bulk of the metal to be tied up for as long as a week.

On the other hand, too frequent refining, involving the handling of many small lots, runs the labor costs up. A proper balancing of these factors characterizes the refiner of good judgment—the refiner who knows *when* to refine.

Another common piece of mismanagement is to spend more in labor and chemicals than a batch is worth—to spend five dollars to recover four dollars' worth of metal. The ability to make proper decisions in borderline cases admittedly comes only with experience. The higher the grade of waste, the easier it is to figure its value and to estimate the cost of refining it, which is another reason why the student is advised to begin on high grade materials. After he has completed three or four refinings, and has a good conception of the procedure, he must establish the habit of careful weighing. He must weigh his filings as received, weigh them after the different steps of the refining, making permanent records of the impurities removed, the metals recovered, and so on.

As his skill increases, less and less metal will be tied up in old filter papers, the percentage of metal recovered will be higher, the time and chemicals consumed will be greatly reduced, and his refining profits will grow accordingly. He will steadily become able to handle lower grade or more difficult materials, in less time, as well as the simpler high grade ones.

DIFFICULTY OF ESTIMATING THE VALUE OF MATERIALS

If there were some magic whereby we could know the value of a dish of filings simply by looking at it, and could foretell the exact cost of refining it, our work would be easier and our profits much higher. Fortunately the man who refines only the wastes generated in his own shop does not need precise figures, however much he might enjoy having them. He knows what metals are present, and he soon will know approximately how much dirt can be expected in each workman’s filings, how much metal to look for in each pound of wash-barrel waste, and by using the tests in Chapter IX he should make excellent appraisals of all solutions.

ASSAYING

The situation of the professional refiner who buys from many sources is quite different. He needs an assay for every purchase. An assay is a different thing from the estimates mentioned above, being an exact determination of the precious metal content of a very small, carefully segregated sample of the material. The task of taking the sample is often difficult, and the determination of the contents, while utilizing many of the chemical reactions with which the refiner is familiar, requires a very different technique. In the questions and answers at the end of this chapter, assaying will be discussed again. As we said, the man to whom this book is directed, who refines only the wastes generated in his own shop, has no need for formal assays, since his task is not to buy metals, but to take impure metals and convert them into pure ones.

* * * *

QUESTIONS AND ANSWERS

Q. I want to learn to assay. I have had considerable experience in refining. What equipment shall I need besides the things I already have? How long will it take me to become a good assayer?

A. The ideal way to learn assaying is to attend a qualified institution that teaches it. This takes time. There are some excellent assayers who never attended a college, but learned through working in a good assay laboratory under a good supervisor. This second method usually takes much longer than the first one, and at the end the worker may be able to handle only such materials as happened to come into the laboratory during the period of his apprenticeship—unless, of course, he has the extraordinary luck to have a supervisor who is at the same time a teacher, able and willing to impart the principles of the science as well as its procedures. Such good fortune is rare, and many a young man has spent months in a commercial laboratory, blindly following a monotonous routine, and emerging almost as ignorant as when he entered.

You, however, have had some experience in refining, which means that you know the reactions of some of the metals and chemicals. Presumably you also have acquired some finger skill. With this background you can learn to assay in a shorter time than otherwise, whether you travel the academic road or the route of apprenticeship.

The assayer needs more than a mere knowledge of the procedures, which can be picked up from any textbook. He needs steady hands that can manipulate minute quantities without fumbling; he needs a knowledge of the chemistry of the materials and fluxes; and he also needs a high degree of integrity, a rare mental honesty that will never permit him to “doctor” a weighing no matter how unimportant, or to color a result even when such hypocrisy will deceive only himself.

As to equipment: this is described fully in the catalogues of the chemical supply houses, some of whom maintain special assay departments. A good assay balance is the first essential, and one of the most expensive. The choice of furnace and other equipment will be governed by the metals you plan to determine and the number of determinations you plan to run at the same time.

Assaying jewelers’ and dentists’ wastes for gold and silver is not difficult. The presence of metals of the platinum group complicates the assay, each additional element increasing the complexity sharply.

Your own immediate needs probably could best be solved (and most economically), if you would engage an assayer to tutor you, preferably in your own shop, in the technique of assaying your kind of materials. Write to the head of the chemistry department of the college near you, explaining your problem fully. With your experience you may well find that a few hours of tutoring, spread over a few weeks, will give you a valuable accomplishment at a moderate expense.

We suggest that you go to a college or university, rather than try to hire some “practical” man from another jewelry shop, because the “practical" man is often unable to impart his knowledge, while the university man's business is to do just that. The university man may seem to take longer in getting to the point, but he can teach you the underlying principles that will enable you to go further. If possible, visit the university laboratory and inspect the equipment. Also, go to the library and look over the books on this subject.

CHAPTER XX

MORE ABOUT EQUIPMENT

Where to buy equipment. How to order. When handling large quantities. The Büchner funnel. Equipment used by the professional refinery. New ideas in chemical apparatus. More about ventilation. Crucibles. Cleanliness in the refinery. Wash-barrels and filter-presses. The Cottrell precipitator.

* * * *

Any effort to describe too strictly the equipment for refining precious metal wastes is foredoomed to failure. First, because no two establishments have exactly the same problem. Second, because no two operators choose exactly the same apparatus, even when handling similar materials. In earlier chapters, therefore, our lists were suggestive, not restrictive. Fortunately the dealers provide good catalogues, well illustrated, that are freely available to all users.

WHERE TO BUY EQUIPMENT

In Chapter D of the Appendix will be found a short list of dealers in equipment, furnishings, and supplies. Other names will be found in the telephone classified directories of all cities, as well as in the trade registers such as the Chemical Engineering Catalogue, Sweet’s Catalogue, Thomas’ Register, and MacRae’s Blue Book, which are found in nearly all public libraries. Your trade papers also offer suggestions. There are several jewelry magazines, and many magazines devoted to dentistry. The advertising managers of these magazines will gladly assist you to get in touch with manufacturers.

HOW TO ORDER

When asking for prices or catalogues, and especially when placing orders, be as specific as possible. Thus, do not say “Send me price list of your furnaces” to a dealer who sells several dozen models, some burning oil, others using coke, coal, city gas, natural gas, liquefied tank gas, or electricity; some being small enough to be lifted in one hand, others being as big as a bungalow. Instead, say "Please send me descriptions and prices of furnaces that will melt about 50 ounces of gold, and that will burn natural gas of 600 B.T.U."—or whatever your needs are. When enquiring for equipment that uses electric current, say whether yours is A.C. or D.C., and mention the voltage and cycle. Or, if the equipment is something with which you are not familiar, do not hesitate to tell the dealer frankly that you are not sure which type of fan, or filter-pump, or furnace (for example) will do your work, then describe your situation as completely as possible, and ask his advice. This will save you considerable time in the end, and probably money and annoyance as well.

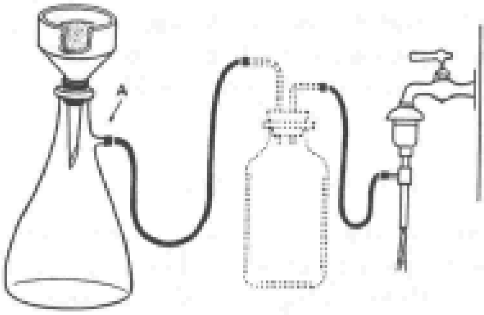
WHEN HANDLING LARGE QUANTITIES

The equipment described in earlier chapters was designed primarily for the beginner. When large quantities of solution are handled, larger vessels and more of them are required. Where a small shop uses one or two casseroles, the big shop will use six or a dozen; where the small shop has a 5-gallon Stock Pot, the big shop will need a 20-gallon jar. As the quantity of solution increases, the task of pouring and filtering it becomes more tedious. Syphons of rubber or of bent glass are helpful, but care must be used in starting them. One way is to use the pump that will be described shortly. Another way is to fill the syphon with plain water, closing one end with the finger, the other end with a little clamp that can be released when you are ready for the syphon to flow.

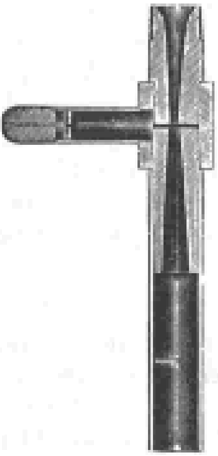
THE BÜCHNER FUNNEL

For rapid filtering there is no more popular device than the Büchner funnel. The sketch shows the arrangement. The Büchner funnel contains a flat perforated plate, on which a filter paper is laid. The paper should not be larger than the plate, and must lie flat. The flask is of heavy glass, strong enough to withstand atmospheric pressure when the pump has produced a partial vacuum within it. Suction may be produced by a vacuum pump of any type, but the little device that screws onto any faucet is the most popular one. Most workers put in an empty "safety" bottle (shown in dotted outline) to keep water from the faucet from being accidentally sucked back into the main solution.

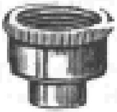
The flask shown, Eimer & Amend No. 23072, costs $2.40 in the 2000 cc. size. The Büchner funnel, No. 23082, five inches across, costs $3.60; the six-inch size is $4.20. A rubber stopper with a large hole makes a tight seal between flask and funnel. The pump, No. 30130, with coupling No. 30138, ¼ inch pipe size, together cost $1.55. Rubber tubing with extra heavy wall, Eimer & Amend No. 30710, ¼ inch I.D., costs about $1.00.



Arrangement for rapid filtering.



Longitudinal section of one type of vacuum pump.



Coupling to attach pump to faucet.

Filter papers are made in many qualities and thicknesses, as well as in many sizes. Ask your dealer for samples of the different qualities, telling him that you are precipitating gold, platinum-ammonium-chloride, silver chloride, and the like. He will help you select a paper whose texture is close enough to capture your precipitates, without being so thick as to make filtration unduly slow.

Dampen the filter paper, start the pump and make sure it is pulling well, and practice first with a little plain water containing a handful of sand or sawdust. Notice that the mixture must be poured steadily. You will soon acquire the knack of pouring at the right speed. As the last drop of liquid goes through, disconnect at point A. Too strong a suction may break the filter paper, especially if it is not properly fitted.

The heavy-walled flask must not be heated strongly or it will crack. When handled skillfully, this set-up is quick and satisfactory. When badly handled the paper breaks, or the water from the faucet will gush back into the flask. That is why the beginner is urged to practice first with some valueless mixture before working with a valuable solution.

The frontispiece of this book shows a Büchner funnel and large filter flask, in operation.

EQUIPMENT USED BY THE PROFESSIONAL REFINERY

In Chapter XXII of this book, the methods and the equipment used by the very large professional refineries are described in detail.

NEW IDEAS IN CHEMICAL APPARATUS

The manufacturers of scientific supplies are just as progressive as the makers of automobiles, jewelry, or any other line, and new designs, new materials, and improvements of all kinds are being developed every season. Most of the supply houses publish periodical catalogues of new articles, and the wise refiner will adapt whatever fits his needs and cuts down his operating expenses. For example, within recent years the glass and ceramics industries—to mention only two—have made great strides. Glass and stoneware are now being fabricated into forms that were literally impossible a generation ago. Glass cylinders of large size, so well annealed as to be highly resistant to thermal extremes or mechanical shock, are now available at low prices. Stoneware,[1] vats, jars, cells used in electrolytic work, and the like, can be bought in shapes weighing up to a ton, and when special resistance to acids, or to alkalies, or to thermal change, or to abrasion, is desired, it can be obtained.

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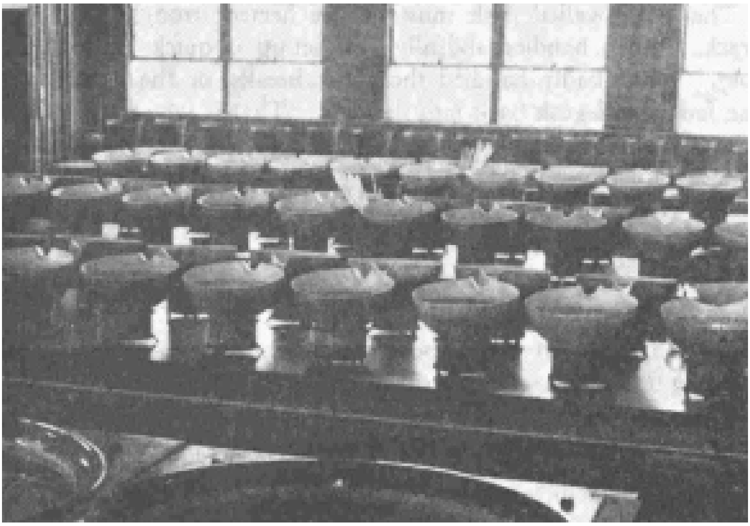
[1] NEW STONEWARE IN THE ELECTROCHEMICAL FIELD. By Percy C. Kingsbury. Transactions of the Electrochemical Society, pages 303-310, 1939.

Fused quartz vessels can serve several purposes in the refinery. Fused quartz differs from porcelain in several respects, notably in its extraordinary resistance to thermal changes. That is, a quartz dish can be heated to redness, then plunged into cold water, without danger of cracking. Accordingly when valuable solutions are being heated, quartz vessels are preferred in spite of their high cost. Quartz crucibles are used when burning the colored powders of platinum or palladium, and quartz dishes or bowls are advised when aqua regia solutions are to be boiled or evaporated.



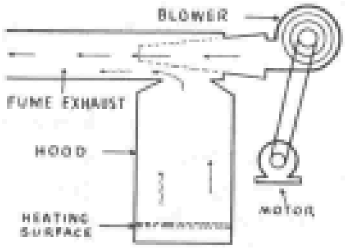
Purifying radium, the most precious of all metals. A battery of 12-inch Vitreosil (fused quartz) evaporating dishes, in use at the Port Hope, Ontario, refinery of the Eldorado Gold Mines, Ltd. Solutions containing radium-barium chloride are being concentrated.

Courtesy of The Thermal Syndicate, Ltd.

Within the last dozen years we have seen an impressive array of new paints and paint-like materials, many of them of synthetic compounds undreamed of in the past. Some of these are excellent for finishing the refinery walls, tables, floors, hoods and fume ducts. They come in several colors and can be applied in a variety of ways. They are described in the chemical engineering magazines and catalogues, and are sold by the chemical supply houses, as well as by some paint stores. The lacquers and cements used in a chromium-plating plant will resist strong acids and are useful to the metals refiner; these are described in magazines that cater to the electroplating industry.

MORE ABOUT VENTILATION

With the development of the chemical industry during the last two decades there has been parallel development of means of handling chemical fumes. No matter how corrosive a gas may be—and the precious-metal refiner handles some of the worst ones—there is a ventilating system that will take care of it. Sometimes the fan-blades are made of wood or laminated acid-resisting plastics, the motor being so housed that fumes cannot reach it. Sometimes a Venturi duct is used—that is, a strong current of air is directed into a duct with a narrowed throat, to produce a partial vacuum that carries off the fumes. Sometimes, indeed, the fumes are salvaged and converted into by-products of value. The Chemical Engineering Catalogue describes systems suitable for use by the refiner.



Venturi or injector duct.

The ducts must be made of an acid-resisting material, or coated with an acid-proof paint. Wood coated with asphalt or rubber-base paint is economical, light in weight, and lasts surprisingly well. Ordinary sheet iron is worthless, but some of the new special irons, made for the purpose, have shown excellent resistance. Lead, so useful with some acids, is worthless with nitric fumes. Earthenware pipe (sewer pipe) when properly luted at the joints is good. Within recent years we have seen glass made up into tubing of large diameter—ideal material for fume ducts as soon as its price reaches competitive levels.

One of the inconveniences of an exhaust system in winter is that, while drawing out the fumes it also draws out the warm air in the room, causing drafts and attendant discomfort to the workers. This must be avoided by care in designing and by the maintenance of a generous warm-air supply.

Chemical laboratories in which many Kjeldahl determinations are being made face much the same problem as the refinery, which might do well to adopt some of their ideas. (A Kjeldahl determination—pronounced Kelldoll—is a method of determining the nitrogen content of materials such as wheat, fertilizer, etc., and involves heavy and dangerous sulphur trioxide fumes.) Sometimes several dozen flasks will be boiling at a time, each flask emitting stifling fumes. In one plan of fume disposal, manufactured by the Laboratory Construction Company of Kansas City, Mo., a stoneware duct of some five or six inches diameter, with a series of small openings down its side, is supported over the row of fuming flasks, each flask close to its individual opening. The fumes are carried through the duct by gentle suction. The same idea could be used with aqua regia or other fumes.

In Chapter D of the Appendix will be found the names of several additional organizations that manufacture fume hoods and will give helpful advice on the planning of a disposal system. Details of design that seem unimportant to the layman may spell the difference between an expensive failure and an inexpensive success. Thus, ducts must be large enough but not too large, of smooth bore and free from sharp bends; provision must be made for condensed steam; the fan must be large enough but not too large; and so on. A frank discussion with a firm of this type will cost nothing and pay well.

CRUCIBLES

Reasonable care in the storing, handling, and use of crucibles is essential, both for economy and safety. Believing that it would be of advantage to their customers, the principal crucible manufacturers of the country have pooled their information and ideas and published a pamphlet that is available freely to all users. The pamphlet is entitled HOW TO CUT CRUCIBLE COSTS, and may be obtained from the Crucible Manufacturers Association (a non-profit group), at 90 West Street, New York City.

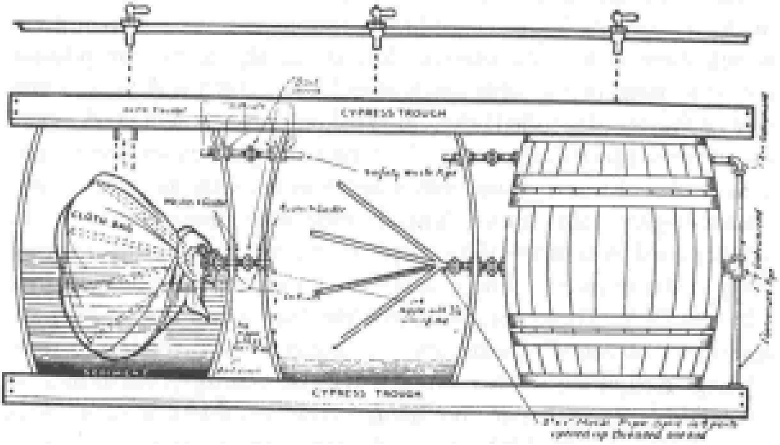
CLEANLINESS IN THE REFINERY

There are several reasons why the precious-metal refinery should he kept “hospital” clean. When solutions are left to dry on a vessel, there is first the obvious loss of metal, second the possible contamination of the next batch of solution, and third (if the outside of the vessel is soiled) there is the danger that it will crack when next exposed to strong heat. The well-managed refinery will show a rack of flasks and dishes that sparkle as brightly as those in any bacteriological laboratory. This is especially important with the articles used in testing—the spot-plate and test tubes used in identifying the metals and establishing their presence or absence. (See Chapter IX.) These tests will show the presence of extremely small quantities of metal. Naturally the spot-plate and test tubes must be kept scrupulously clean, or you will be getting positive tests in everything you examine, no matter how worthless it may be in truth. Vessels should be washed immediately after being used, and stored in a dust-free cabinet. It will be recalled that finger-prints inside a vessel will leave an oily film that will make precipitated gold float on the surface of the liquid, in little shining flakes.

If you cannot spare time to wash the vessels immediately after use, leave them completely immersed in plain water until opportunity permits thorough cleansing. The spot-plate is the article that is most apt to show persistent stains, and one on which stains are most objectionable. Gold and silver stains can be removed by a little cyanide solution; platinum stains by aqua regia. Plain hot water, with or without soap, is sufficient for most requirements. A washing compound called “Laboratory Calgonite,” sold by chemical supply houses, is recommended for use with hard water.

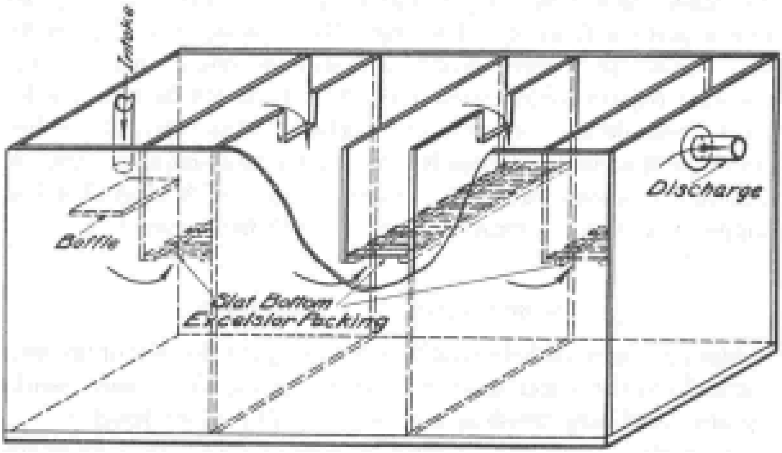
WASH-BARRELS AND FILTER-PRESSES

Many schemes are being used for salvaging the fine bits of precious metal from the water used in washing hands, tools, work, work-aprons, scrubbing brushes, and so on. The older jewelry shop uses wooden barrels, usually three or more in a train, through which the water passes slowly while the metallic particles are settled out by gravity. Wooden tanks, or concrete tanks with wooden or concrete partitions, are also used, and frequently agglutinants (such as alum or ferrous sulphate) are added; and usually the water passes finally through a layer of excelsior or sawdust which later is dried and burned.



One arrangement of wash-barrels.

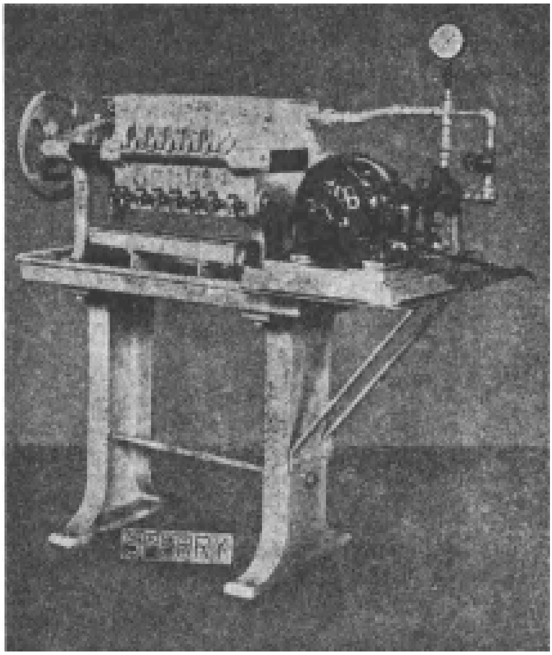
But within recent years the filter-press—a pumping device which forces the liquid through filters—has become increasingly popular. There are several types on the market, and descriptions will be found in the Chemical Engineering Catalogue and in periodicals that cater to chemical engineers. The set-up generally consists of one barrel in which the wash-water collects until it reaches a certain



One arrangement of settling tanks.

level, at which the pump automatically operates, forcing the liquid through a firm cloth or paper-lined filtering medium. The liquid escapes perfectly free from all sediment.

The filter-press has several advantages over the settling barrels. For one thing, it occupies much less room. Second, it is more sanitary—the water is filtered clear and discharged into the sewer within a few hours, instead of standing until odors may develop. The filter-press yields a compact, almost dry cake, much less unpleasant to handle than the slimy mud that was collected at intervals from the bottom of the settling barrels.



A small filter-press, with motor-driven pump, for handling 50 to 100 gallons of jewelers' wash waters per day. Larger and smaller units are available. The unit shown is complete except for filter cloths and the pipe from the supply barrel and the discharge line to the sewer.

Courtesy of D. R. Sperry & Co.

The primary advantage of the filter-press, however, is that it really removes all the metallic particles, a thing that the old settling tanks rarely did. It has been proven repeatedly that particles of platinum and gold will literally float through long series of settling tanks, being carried over by soap scum and grease films. One enterprising janitor in a New York jewelry building installed a trap in the basement and captured sometimes as much as seventy-five dollars' worth of metal a day, in spite of the fact that every jeweler in the building had a settling-tank system.

When a filter-press is used, it is rarely necessary to add alum or other agglutinants (except when metal is known to be *in solution* in the wash water). The first cost of a small filter-press is only a little more than that of a train of good settling barrels, and in most localities the cost of power to run the pump is so low as to be amply covered by the additional metal saving. Labor cost is low, and as we said above, there is a saving in floor space.

THE COTTRELL PRECIPITATOR

It has long been known that when gold or silver is melted in the ordinary furnace, fine particles are carried up the flue and may be lost. Various schemes for salvaging this dust have been employed, including the passage of the dust-laden air through long chambers in which the particles were given an opportunity to settle. Another device is a series of cloth bags. When large quantities of gas are evolved, this becomes quite a problem.

The Cottrell precipitation process, widely used to capture smoke, Portland cement dust, acid mists, etc., is also employed by most of the Mints and larger refineries. The equipment is expensive and bulky, and so far the method has not been adapted to the needs of the small establishment. In Sir T. K. Rose's book THE METALLURGY OF GOLD, page 459, the process is described as follows:

"The fumes, preferably at a temperature of 90° C, are conducted into a chamber in which are suspended a number of tubes, down the centers of which are a corresponding number of wires with cross-shaped sections or roughened surfaces, and weighted at the ends to keep them taut. Plates may replace the tubes, in which case two wires are placed opposite to each 4 or 6 inch plate. A high-voltage unidirectional current passes across the gap between the wires (positive electrodes) and the tubes or plates (negative electrodes). The particles of gold and other materials in the intervening space are thereby given a positive charge of electricity. They then flow to the negative electrode where their charge is neutralized and they may accumulate until shaken or washed off periodically.

"The voltage used is usually between 50,000 and 100,000, and the intensity is augmented by the peculiarly roughened shapes of the anodes. It is stated that 97 to 98 percent of the gold and 98 to 99 percent of the silver passing away as fume is thus recoverable."

For a description of the equipment and procedure used by one large plant to recover the precious metals from furnace fumes, see RECOVERY OF PRECIOUS METALS FROM ELECTROLYTIC COPPER REFINING at the Canadian Copper Refineries Plant, Montreal East, Quebec, by C. W. Clark and A. A. Heimrod. This paper, published in the 1932 Transactions of the Electrochemical Society (New York), tells how the fumes are first led through large chambers to permit cooling and the settling of the larger particles, then through towers in which they encounter a shower of water, finally through the Cottrell electric precipitator. Interesting statistics on the efficiency of the system, which is high, and the power consumption, are included. Descriptions of some other installations will be found in Chapter XXII of this book.

CHAPTER XXI

PROCESSES USED BY THE PROFESSIONAL REFINERS

Materials handled by the professional refiners. Virgin metals. By-product metals. Secondary metals. The Miller chlorine process. The various electrolytic methods. Possible variations. Advantages and disadvantages of the electrolytic methods. Can professional methods be adapted to small-scale operation ?

* * * *

In this chapter we shall describe the materials handled by the professional refiners, and the processes used by them, some of which have not been described or even mentioned in earlier parts of this book. In Chapter XXII a few typical large establishments will be described in detail, and literature in which the serious student can find further information will be mentioned.

Occasionally a jeweler or dental mechanic who plans to refine the wastes accumulated in his own shop will read up on the processes used by the big refiners, with the idea of using them on his own materials. This idea is only rarely feasible, for reasons that will soon become clear, but the reader's interest in the big plant is certainly legitimate. Hence these two chapters.

The materials refined by the big plants are of many kinds, and the procedures will differ with the kind and quantity of metals and impurities that are present, which are rarely alike in any two plants. For our purposes it is convenient to divide these materials roughly into three groups—virgin metals, by-product metals, and secondary metals, and to discuss them under those headings.

The various national Mints, though established originally to manufacture coinage and maintain a market for the gold mines of the nation, also have occasion to refine many sorts of materials, both virgin and secondary, and operate well-conducted plants, using processes similar to those of the commercial refineries.

VIRGIN METALS

Gold, silver, and the platinum group metals are found native in many forms, and contaminated with a wide variety of impurities, both metallic and non-metallic. Nuggets and dust are found in river beds, loosely mixed with sand or gravel from which they are separated by panning, by gravity separation, or by other methods. As men work out these alluvial deposits, they turn to the various hard metal-bearing materials met with in veins, crushing the rock and concentrating the metal particles by one technique or another. The whole story of the extraction of precious metals from their ores is long[1] and fascinating, but has no place in this book. Fortunately the story has been well told in the literature, and the student can find it in almost any reference library. The Encyclopedia Britannica in its articles on Gold, Silver, and Platinum, offers many suggestions, and others will be found in the bibliography at the end of this book.

It is the practice in most mines, after separating the precious metal from the sand or rock, to melt it into bars and ship it to a refinery, which sometimes is close by, but may be thousands of miles away. It is not until then that our interest in it begins.

The gold bars, as well as the nuggets and dust from natural deposits, are always impure, rarely containing as much as 90% gold. Such gold is usually brittle, and in modern practice, whether brittle or not, is always refined before being used. The ancients refined gold by what they called "cementation"—plates of gold were stacked in an earthenware pot, and surrounded and separated by powdered porous stone or brickdust, mixed with common salt and sulphate of iron. The pot was covered and heated strongly, just short of the melting point of the gold. Silver and most other impurities were converted into chlorides, which oozed out and were absorbed by the brickdust.

During the 16th century, nitric acid was used in refining gold. The gold was melted with three times its weight of silver (inquartation), granulated in water, and boiled in nitric acid, practically as described in Chapter VI. The silver was recovered from solution

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[1] T. K. Rose's authoritative book THE METALLURGY OF GOLD devotes 319 of its 541 pages to the various general methods of extracting gold from its ores including panning, hydraulic separation, crushing, amalgamation, grinding, gravity concentration, flotation, dry crushing, roasting, and the several cyaniding processes.

and used again and again. In the 19th century, sulphuric acid, being cheaper, largely replaced the nitric acid. All the processes described in earlier chapters of this book are in use by the professional refiners, at one stage or another of their routine, sometimes on a large scale, sometimes on a small scale, depending upon circumstances. In addition to the procedures already described, there are two very important methods, used in large plants, that have not as yet been discussed. These are the Miller chlorine process for gold, and the several electrolytic processes for gold and silver. These will be described briefly in this chapter, and in Chapter XXII some typical plants that use them will be described in full detail.

BY-PRODUCT METALS

Even the highest grade native copper is never pure. Base metals are always present, and often we find silver, gold, and platinum group metals as well. Much copper is used in the electrical industries because of its high conductivity. Conductivity is reduced by impurities, even when present only as traces, and so the demand is for copper of very high purity. The electrolytic refining of copper, of which more will be said shortly, produces copper of high purity and high conductivity, and at the same time permits the accumulation of the silver, gold, and platinum-group metals as by-products. The story of electrolytic copper refining[2] is fully as long and fascinating as that of the extraction of gold from its ores, but only a small part of it has a place in this volume, namely the recovery of the precious metal ingredients. The principles of the process will be discussed briefly in this chapter, and in Chapter XXII a plant that carries it on will be described in detail.

Native silver, native nickel, and native lead also are apt to contain precious metals as impurities, which can be separated out and finally refined, either by familiar acid methods or by one or another of the new methods to be described in this chapter. Considerable quantities of platinum-group metals are obtained as by-products in the refining of Canadian nickel.

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[2] See THE ELECTRO-PLATING and ELECTRO-REFINING OF METALS, by Watt and Philip. 680 pages. D. Van Nostrand & Co.

SECONDARY METALS

The professional refiner with whom the jeweler or dentist is most apt to be acquainted is the one who buys the old jewelry, dentures, and sweeps that have been the subject of this book. These materials are refined in many cases by precisely the methods that have been described here. In other cases the methods that will be described shortly—the Miller chlorine method and the various electrolytic methods—are used.

THE MILLER CHLORINE PROCESS FOR GOLD

This method was first used in Australia, where acid was expensive, and is now employed in a number of large refineries. Small operators such as jewelers have not as yet adopted it, though in the opinion of this writer it would be suitable in many establishments, both large and small. The gold, which should first be brought to a fineness of about 700, is melted, and a stream of chlorine gas is bubbled through it, converting silver and the base metals into chlorides which come to the surface and can be bailed off. Platinum-group metals cannot be removed by this process, so its usefulness is confined to materials that are known to be free from this group.

The following description of the principles of the method is based on T. K. Rose's THE METALLURGY OF GOLD, pages 466 et seq., of the seventh edition.

The method was first proposed by Lewis Thompson, and in 1867 F. B. Miller installed it in the Sydney Mint. Chlorine is passed into molten gold covered with borax, and combines with all metals present except those of the platinum group. Some chlorides volatilize and pass up the flue. When the gold approaches a fineness of 900, gold chloride begins to appear in the fumes that pass through the slag. The end-point is reached when a peculiar stain, caused by gold chloride, appears on a clay pipe-stem held in the fumes. The remainder of the slag is then bailed off and the gold cast into ingots. It is usually about 996 fine, the residue being mainly silver, with 0.5 or 0.6 parts per thousand of base metal, mostly copper.

A clay pot is used, as a graphite pot would reduce the silver chloride back to silver.

The slag that is bailed off will contain about 2 percent of the gold, mainly as small crystals; the slag is therefore melted again with some soda ash, to reduce some of the silver chloride to silver, which on settling carries the gold crystals down with it. This alloy then passes through the process again. The remainder of the silver chloride is freed of base-metal chlorides and reduced with iron.

A modification of the process consists of the addition of air to the chlorine gas passed into the molten gold, so that part of the metal is oxidized rather than chloridized. This modification was introduced at the Perth (Australia) Mint in 1917.

The chlorine gas is usually bought compressed in iron cylinders, but in isolated regions where tanked chlorine is not available it must be generated on the spot from manganese chloride and hydrochloric acid—an unhandy process which is avoided whenever possible.

The chlorine method is especially suitable for gold over 700 fine with the remainder mostly silver. Gold of lower quality can be treated, but the time of treatment is longer and the cost greater. Bullion of suitable composition is obtained when possible by mixing. If the silver is below 50 parts per 1000 there is some difficulty in removing base metals.

Base metals differ considerably in their behavior. The chlorine attacks the different metals and non-metals in an order believed to be something like the following: zinc, iron, antimony, tin, arsenic, copper, lead, bismuth, silver, tellurium, selenium, gold, with the platinum metals somewhere near gold.

It is certain that dense fumes of the volatile chlorides of zinc, iron and antimony are given off in the early stages. Lead is said to be erratic in its behavior, the last traces being difficult to remove and occasionally remaining in the finished product and making it so brittle that it must be repurified, by one method or another. Tellurium is the most difficult of the elements to eliminate. This is common in some gold ores, but almost never present in secondary gold, so would cause no difficulty to the jeweler-refiner. Platinum metals, if present, remain with the gold.

The recovery of the silver from the silver chloride slag is simple in principle, but has some practical difficulties; these are discussed in Chapter XXII in the detailed description of the Homestake refinery.

The one great problem is the fumes. Chlorine itself is one of the most corrosive and unpleasant of gases, being used in chemical warfare for its deadly effects. The volatile chlorides are of the same order of unpleasantness, copper chloride being particularly distressing. Different kinds of condensing chambers are used—water sprays, baffles, screens, and so on. The Cottrell process appears to be far more effective than other schemes.

One great advantage of the chlorine process is its rapidity, as it brings 98 percent of the gold to a marketable form in a few hours. The plant costs little, and can be expanded readily to meet growing requirements, and the operating costs are low.

Its main disadvantage, as we said, is the fumes. Ordinary systems are usually not able to cope with them. However, once the fume problem is conquered, the method is easy, flexible, and economical.

A description of the equipment and procedure used in this process by the gold refinery of the great Homestake Mine will be found in Chapter XXII of this book.

THE VARIOUS ELECTROLYTIC METHODS

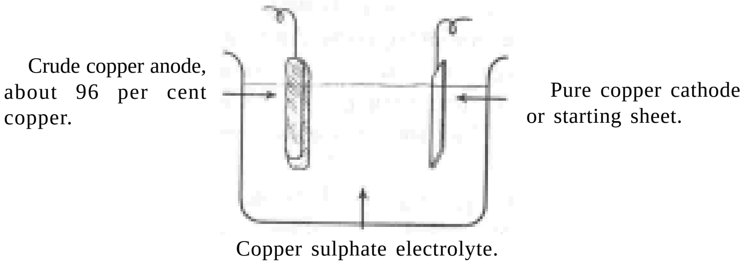
Every jeweler who has done gilding will understand the basic principle of electrolytic refining. In all cases an anode of impure metal is hung in a solution (“electrolyte”) and is decomposed by the electric current. As this goes on, pure metal deposits out on a cathode. The impurities either drop down as a sludge or go into solution in the electrolyte. There is the whole story in one paragraph, but the practical applications of this principle have filled many books and occupied many engineers and chemists for many years. The method is simple in theory, but its successful application is not easy.

There are several kinds of electrolytic refining. The reader should understand at least three of these—copper, silver, and gold, even though his main interest may be with gold only.

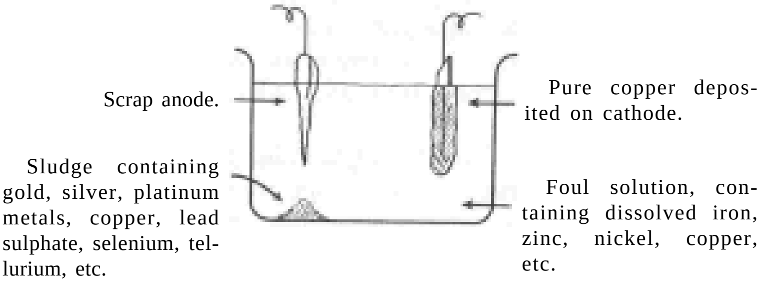
(I) ELECTROLYTIC COPPER REFINING

Crude copper, after various appropriate treatments, is melted and cast into huge anodes. Sometimes secondary metal such as scrap copper from old dynamos, or scrap from the manufacture of cheap gold filled or gold plated jewelry, is melted in with it. These anodes usually run about 96 percent copper, the remainder being precious metals with traces of many other elements—zinc, nickel, arsenic, tellurium, selenium, and often several others, depending upon the source.

The sketch illustrates the principle only; the actual cells contain many anodes and many cathodes, alternating. An electric current of low voltage but high amperage is used. After a time the condi tion suggested by the second sketch has come about, and the scrap anode is melted in with the next batch of anodes, the cathode is ready to be melted into some marketable form, and the electrolyte (now foul with dissolved zinc, iron, nickel, and other metals) is treated for the recovery of such as have value. Our interest centers upon the sludge or slime, in which are concentrated the precious metals, mixed with more or less copper, selenium, tellurium, arsenic, and other elements.



Copper cell at start of electrolytic refining.

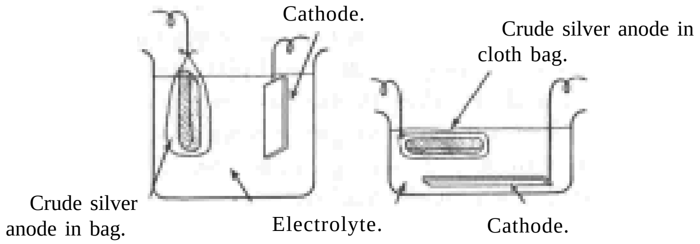


Copper cell at end of electrolytic refining.

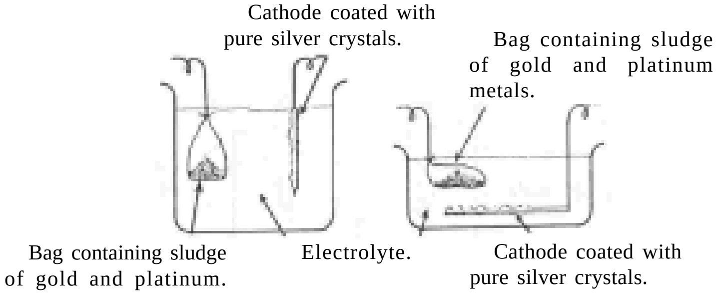
This sludge or mud is next washed, dried, roasted at about 700 degrees F., leached in dilute sulphuric acid to remove copper, and then melted in a furnace with fluxes to remove selenium, tellurium, and as much more of the base metals as possible. In the silver refinery of the Raritan Copper Works at Perth Amboy, New Jersey (see Chapter XXII), the metal that remains after these treatments runs about 980 parts silver, about 15 parts gold, and the remaining 5 parts are platinum-group metals and a few odds and ends. This silver-gold alloy—they call it doré silver—is then cast into anodes, somewhat similar to but smaller than the copper anodes, and is ready for the electrolytic silver refinery.

(2) ELECTROLYTIC SILVER REFINING

The sketch shows the principle only; the actual cells may be arranged quite differently. The impure silver may consist of washed and purified slimes from a copper refinery, or may be secondary silver obtained in some way from old jewelry, old coinage, old photographic wastes, or what not. For economical operation, the composition of the anode must be carefully adjusted, the silver content being kept as high as possible.



Silver cells at start of electrolytic refining. The Moebius or vertical arrangement is shown on the left, and the horizontal Thum or Balbach-Thum arrangement is shown on the right.



Silver cells at end of electrolytic refining. The Moebius arrangement is to the left, the Thum or Balbach-Thum arrangement is to the right.

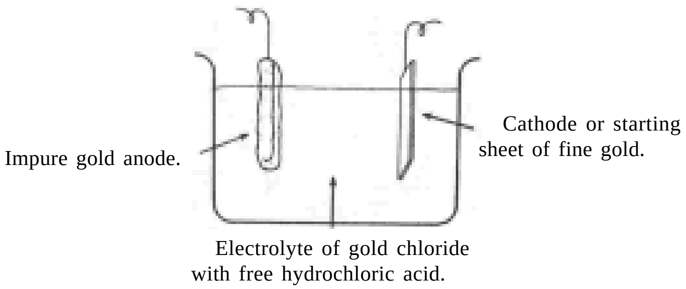
At the end of the process, pure silver has been deposited out on the cathode, some impurities have gone into solution in the electrolyte, while gold and the platinum metals, if present, have dropped away as a sludge.

Two cell arrangements are in common use. In the Moebius method the anodes and cathodes hang vertically, each anode being encased in a cloth sack, and each cell containing several anodes and cathodes, alternating. In the Thum process, also called Balbach-Thum, the single anode is supported in a horizontal position by a wood frame, cloth lined, the graphite cathode lying on the floor of the flat shallow cell. Electrolyte of the same composition is used in both arrangements.

The pure silver that collects at the cathode is washed well and melted down for market. It usually runs about 999 fine. The cloth sacks have captured the sludge of gold and platinum-group metals, which is washed well and then treated by methods appropriate to its composition. Thus, if platinum-group metals should be absent, this gold may require only a boiling in sulphuric acid to make it ready to be melted down for the market.

(3) ELECTROLYTIC GOLD REFINING

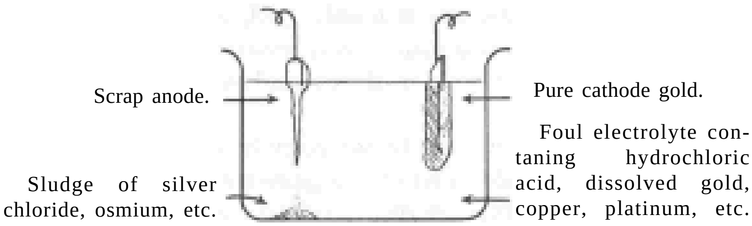
Here again the sketch shows only the principles, the actual cells usually containing several anodes and several cathodes, alternating. The anodes may be made up of the washed sludge from an electrolytic silver cell such as that just described, or of virgin or secondary gold from other sources. The anodes in this process—called the Wohlwill process—frequently run as high as 980 parts gold, the



Gold cell at start of electrolytic refining by the Wohlwill process.

remainder being silver, platinum-group metals, and copper. Every effort is made to keep the gold content as high as possible.

At the end of the process the cathode ("starting sheet") has become heavy with pure deposited gold, the silver has formed a sludge of silver chloride, while the copper and most of the platinum-group metals have gone into solution in the electrolyte. The electrolyte, which by this time is much the same thing as the aqua regia solutions containing gold and platinum that were described in Chapters XI to XVII of this book, is refined by acid methods with which the reader is already familiar, the exact procedure depending upon which metals are present and in what proportion.



Gold cell at end of Wohlwill electrolytic refining.

POSSIBLE VARIATIONS

In the precious metal refinery of the Raritan Copper Works at Perth Amboy, New Jersey, all three kinds of electrolytic cells are in operation—copper, silver, and gold. Another plant, handling considerable low-grade jewelry scrap, has copper cells and gold cells, but no silver cells. It melts up the low grade gold scrap with sufficient added copper to make it a "copper proposition," and refines it as described above. The sludge contains only a little silver, but much gold and some platinum. After roasting and a treatment with sulphuric acid to remove the copper and silver, this sludge is cast into anodes and refined as a "gold proposition" by the Wohlwill method.

In a third plant—the plant at Acton, England—the raw materials contain much platinum and palladium, with only a little gold and silver. Here, as will be described in Chapter XXII, the procedure is essentially an acid process similar to that described in Chapters

XI to XVII, the gold being precipitated by copperas, and the platinum by ammonium chloride. The gold is subsequently repurified in small Wohlwill cells.

Another plant, handling high grade stuff only, has no copper cells, only silver cells and gold cells. It begins by making up silver anodes, adding enough pure silver to run the fineness up to about 900. The sludge from this electrolysis is mostly gold, and is treated by the Wohlwill process. In this plant it is necessary to have considerable fine silver on hand, and it is used over and over in making up the first anodes.

This does not exhaust the list of possible variations. In Chapter XXII other possibilities will be suggested, and it should be clear to the reader that hardly any two establishments can be expected to follow precisely the same routine.

ADVANTAGES AND DISADVANTAGES OF THE ELECTROLYTIC METHODS

The above summary gives principles only, and does not mention the many precautions that must be observed in the actual practice of electrolytic refining. When properly carried out, the methods yield metal of high purity at a very low cost per ounce, and with relatively few fumes. The installation cost is high, and the work must be done under the supervision of highly trained personnel. However, since it is almost as easy to supervise a large plant as a small one, the labor cost per ounce is usually low. The main disadvantage of these methods is their slowness, and the fact that much precious metal is permanently tied up in electrolyte, scrap anodes, and starting sheets. (The Miller chlorine process, in contrast, brings 98 percent of the gold to marketable form in a few hours.) As compared with the acid methods given in Chapters I to XVII of this book, the striking thing about the electrolytic methods is that the “impure” silver and “impure” gold may run as high as 980 fine *when the process begins.* It is true that anodes of lower quality are being worked, but as the quality goes down the costs of operation go up.

If the reader is experienced in gilding or silver-plating he will understand this necessity for a high-quality anode. He will recall that even small impurities in his gilding bath can affect the color of the deposited gold. The more impure the anode, the more quickly the electrolyte becomes foul and the sooner the impurities will contaminate the cathode. (This contamination may be either an actual co-deposition or perhaps merely the mechanical inclusion of small bits of metal on the rough cathode surface.)

Some impurities if present in sufficient concentration can actually stop the process. Thus in a silver cell, an anode containing much gold will soon coat over with an adherent layer of gold sludge that will prevent further decomposition of the silver beneath. And if the gold anode in a Wohlwill cell contains too much silver, a film of silver chloride on its surface will in the same manner eventually halt the electrolysis.

These difficulties are lessened by various expedients. The adherent gold sludge can be scraped off mechanically, for instance. And a very ingenious method is sometimes used in the Wohlwill cell: a weak *alternating* current of electricity is sent through the system, superposed upon the direct current that accomplishes the electrolysis; this produces an electrical pulsation that dislodges the silver chloride layer and permits the work to continue.

The electrolytic refining of gold and silver is spoken of as involving relatively few fumes. This is true, but it most certainly is not entirely free of fumes. Most routines call for various additional processes that involve fumes, and there is considerable fuming in the Wohlwill process itself, enough to require an exhaust fan over the cells. The foul electrolyte, which is a hydrochloric acid solution containing dissolved gold, platinum metals, and base metals, must be refined by acid methods, and the platinum and palladium sponge must be reduced (with the formation of fumes) by methods with which the reader is already familiar.

The necessity for almost pure metal to start with is, of course, one of the reasons why electrolytic methods are not generally suited to the needs of the jewelry shop and dental laboratory. Thus, suppose a jeweler has on hand some 14-k or 12-k scrap, mixed with platinum; to refine it successfully by an electrolytic process he must first raise its fineness considerably, either by melting the scrap in with a generous quantity of fine gold, or by a preliminary treatment by familiar acid methods, or by adding enough silver to make it a silver proposition. All of these expedients involve so much expense that they tend to undo the advantages attaching to the electrolytic procedure.

In spite of its simple aspect, an electrolytic cell is not a fool-proof device. It calls for close and intelligent supervision. For example, if the bath becomes too highly contaminated, the deposited cathode metal will be impure and the whole job will be to do over again. Sometimes crystals form on the cathode and grow until they touch the anode and cause a short circuit. If the bath is stirred too vigorously the sludge will churn up and be caught and included in the cathode; if stirred too little the bath will become locally exhausted and the operating costs will run up. And so on and so on. As one experienced worker phrased it: “When you put in an electrolytic system your troubles are not over; they have just begun.”

CAN PROFESSIONAL METHODS BE USED IN THE SMALL SHOP?

The purpose of this book is to tell how *some* professional methods —those described in the first sixteen chapters—can be learned and utilized by any intelligent non-chemist who is willing to make, *in order*, the acquaintance tests described herein, and to follow *step by step* the procedures outlined. Twenty-five years of experience have proven that this can be done.

In this writer’s opinion, however, the electrolytic methods cannot be operated economically by the non-chemist working alone. It is believed, further, that present electrolytic methods are rarely suited to small-scale operation, even under the supervision of a trained electro-chemist. It is true that small systems have been set up—cells holding about a quart of gold chloride, for instance. In such a cell a trained worker can produce cathode gold of as high quality as he might desire, with mental satisfaction, no doubt, but probably at unduly high cost, and the small cell will require almost as much attention as an acid system handling many times the amount of metal per day. And it is a matter of record that electrolytic systems of considerable size have been installed and later abandoned, usually for economic reasons.

Another “professional” method is the Miller chlorine method. In this writer’s opinion, this method might well be considered by some of the smaller establishments. It has its hazards and its limitations, true, but one can begin work on a small scale at slight expense, learn the technique, and then expand if desired. The interested reader will find further information on the method in Chapter XXII.

CHAPTER XXII

SOME LARGE PROFESSIONAL REFINERIES

The Irvington Smelting and Refining Works. The Miller Process at the Homestake Mine. The Raritan Copper Works. The United States Assay Office. The plant at Acton, England. Some other large plants—Copper Cliff; Montreal East; Old Hickory; the Royal Mint at Ottawa, Ontario.

* * * *

In this chapter we shall describe in detail a few typical large refineries. The descriptions that follow are adapted or quoted from papers that were, in most cases, written by men who are themselves at work in these establishments. We are greatly indebted to the publications in which the original papers appeared, for permission to quote.

THE IRVINGTON SMELTING AND REFINING WORKS

Materials with which the reader is familiar, including floor sweeps and jewelers' low grade wastes, are refined in this plant at Irvington, New Jersey. The processes include treatments by blast furnaces, converters, cupels, electrolysis, roasting, and leaching, as well as by many of the acid processes mentioned in this volume. The following paragraphs are adapted from an article by Adolph Bregman entitled IRVINGTON SMELTING AND REFINING WORKS, which appeared in The Metal Industry (New York), vol. 25, pages 183-187, May, 1927.

The Irvington Works recover gold, silver and the platinum metals. The copper with which these metals are normally associated is turned out as bluestone (copper sulphate crystals).

Raw Materials

The raw materials treated are either primary, such as copper concentrates resulting from mining and milling operations where precious metals are associated with the copper, or secondary, such as jewelers' sweeps, copper bullions containing silver or gold, and a great variety of waste materials that carry values.

Sampling

The sampling of fine materials is done by the coning and quartering method. Bullions and other metallics are sampled by drilling or by melting and granulating in water.

In the sampling room is installed an exhaust system leading to a small Cottrell precipitator, which recovers the dust from the air exhausted. The main purpose is to keep the room under suction, so that no dust-laden air will find its way to the outside atmosphere or to other parts of the plant.

Smelting Operations

Sweeps and other fine materials are charged into a pug mill in which they are mixed with water before moving to the blast furnace. Slaked lime is added to this mixture as a binder, when the materials are such as would tend to cause excessive flue-dust during smelting. The water used in the pug-mill is waste solutions from other parts of the plant, and contains some platinum by-metals which otherwise might be lost, or recovered only with difficulty.

Sweeps

The highest grade of sweeps, concentrates and similar materials, and also rich copper bullions, are smelted directly in the cupels or "test" furnaces. The lower grade bullions are charged directly into the converter. The test furnaces handle also various rich products from other operations in the plant, as noted later on.

There are three blast furnaces, two having a capacity of 30 tons each per 24-hour day, and one of 50 tons. The latter is arranged for use in conjunction with a small basic-lined converter for producing copper shot from the matte delivered by the furnace.

Sweeps of medium grade and other materials adapted to blast furnace treatment are usually smelted with lead as a carrier, in the blast furnaces, the lead being supplied by including litharge (lead oxide) in the charge. A typical blast furnace charge of this nature includes:—

Muddled (mixed with water) materials, such as sweeps, concentrates, etc.

Leady matte from previous charges.

Fluxes (limestone, gypsum, pyrite cinder, or slag high in iron).

Litharge (if lead is to be used as carrier).

Return slag, as ballast.

From the lead bullion resulting from such a charge, the precious metals can be recovered promptly, and the litharge returned to the blast furnace for re-use.

When running leady charges the lead bullion is tapped from the lower of two tapping spouts in the crucible of the blast furnace, receiving the lead and matte together in conical iron pots. The matte forms an upper layer in the pot, solidifies quickly, and is removed with a chain link which has been partly inserted while the matte was yet molten. The lead is then ladled out into pigs.

Lead is not used in the blast furnace charge when the materials for treatment would produce matte in their own right, merely by smelting down. In such cases the furnace is run, not as a lead furnace, but as a straight copper matting furnace; the precious metal values are collected in the resulting copper matte, and eventually are found in the copper shot produced therefrom in the converter. When such materials are being smelted, it is found economical to include in the charge low grade sweeps or other materials which of themselves would not produce matte, and which otherwise would have to be smelted separately with lead. In this way the expense of recovering these values from lead bullion is avoided, and their cost of reduction is brought more nearly in range with the low return that the smelter receives for their treatment.

When copper matte alone is produced, it is tapped from the 50-ton furnace into an oil-heated settler or fore-hearth, from which it is tapped at intervals and taken in a cast steel ladle to the converter, which has a capacity of 7 tons of copper per 24-hour day. The leady matte likewise reaches the converter eventually, after it has been used over and over repeatedly until the quantity on hand has become too large to hold.

In the converter the sulphur and any iron and lead contained in the matte are substantially removed, yielding a final product high in copper and containing the gold, silver, etc., that had been in the matte. The copper is then poured off through a launder into a pit of water, in which it is granulated into shot form.

Of the converter slag, which is high in iron, the cleaner portions are reserved for blast furnace flux, while the dirty or more highly metallic portions are run down in one of the blast furnaces into the form of 200-lb. blocks which like the low grade bullions, are charged into the converter along with molten matte.

The smelting plant includes also two oil-fired tilting furnaces, which can be used to cast anodes or to remelt metal for producing shot.

Air is supplied to the blast furnaces and the cupel furnaces by a turbo blower, and two positive-pressure blowers are held in reserve. The warm water from the blast furnace jackets is held to maximum temperature and minimum volume by thermo-static control, at the furnace, and is afterwards pumped to boilers and other parts of the plant for use where required, thus utilizing both the water and the heat. Thermostatic control and recorders of various kinds are in liberal use throughout the entire works.

Bluestone Plant

The copper shot made by the converter is charged into lead-lined tanks, in which it is treated with steam, air, and sulphuric acid solution, whereby the copper is taken up as sulphate in solution, leaving behind the precious metal slime. The solution when heavily charged with copper sulphate is passed through filter-presses to remove any sediment, and then is run into crystallizers made of concrete with acid-proof brick for lining, or wood with lead lining. In them are hung lead straps, and when the crystals have deposited upon these straps and upon the sides of the tank, the mother liquor is siphoned off and the crystals are removed and placed in containers.

The bluestone is then washed and dried in a centrifuge, after which it passes through a trommel screen for sizing into large and small crystals before barrelling. A special granular bluestone can be made by running either of the above through a pulverizer.

Cupel Furnaces

Lead pigs or lead bullion from the blast furnaces are charged into oil-fired cupel or “test” furnaces where they are subjected to melting and air oxidation. Litharge is formed as a liquid floating upon the molten lead, and is allowed to overflow into pots or molds. This litharge, being lean in precious metals, is returned to the blast furnace as before described. The silver bullion remains behind in the hearth of the test furnace and when enough has accumulated the feeding of lead bullion is discontinued, the lead remaining in the bath is driven off and the silver, then comparatively free of lead but carrying gold and the platinum metals, is ladled out into molds.

If the silver bullion is low in gold and platinum metals, anode molds are used and the anodes are sent to the electrolytic silver department. If, however, there is a large quantity of contained gold and platinum metals, the bullion is cast into thin slabs for the parting process, in order to expedite the recovery of the gold and also because the presence of excessive quantities of platinum metals renders the material poorly fitted for the usual process of silver electrolysis.

Parting Plant

The parting or separation plant consists mainly of several cast iron kettles heated by oil burners. Here the silver bullion is treated with boiling sulphuric acid, the fumes from which are exhausted through hoods above the kettles and pass to an acid Cottrell installation to prevent pollution of the atmosphere. The resulting silver sulphate solution is decanted off from the residue, which consists of gold and the platinum metals. This residue then goes to the Wohlwill electrolytic refining department. The silver is removed from the sulphate solution by cementing out on copper sheets; the cement silver then is melted, cast into anode form and electrolyzed. This further refining by electrolysis is necessary because of the fact that platinum by-metals are present and show some tendency to go over with the silver sulphate solution, partly in solution and partly in suspension. The cement silver, therefore, contains sufficient traces of these metals to require the additional refining operation.

The Electrolytic Silver Refinery

The electrolytic silver refinery has been improved and remodeled within the past few years and its capacity increased to about 700,000 ounces of silver per month, without enlarging the installation. Silver nitrate is used for electrolyte, and the silver anodes are wrapped in muslin sacks to hold the slimes. Mechanical rakes, constructed and operated in a simple and effective manner, in accordance with a patent owned by the Company, are used to brush or break off the longer silver crystals as they form upon the cathodes. These fall to the bottom of the cell, and at regular intervals each cell is emptied and cleaned. The silver crystals taken from the cell are washed, dried in a gas-fired rotating furnace, and after melting in crucibles are poured into bars ready for the market.

The slimes left in the muslin sacks contain gold and other precious metals and are sent to the Wohlwill department for further refining, in the same manner as the gold and platinum metals obtained from the parting.

Wohlwill Gold Refining Department

The raw material received consists of “sponge gold” residues from the parting process and slimes from the silver refining process. These are melted, cast into anodes, and electrolyzed with direct current at about 15 volts, in an electrolyte of gold chloride solution with some free hydrochloric acid. The tanks are of white porcelain and are set into a steam bath under a hood. The resulting cathodes are fine gold and are melted and cast into bars for the market, but the slimes which consist largely of silver, gold, and some platinum by-metals, are reserved for further treatment. Platinum and palladium enter the electrolyte, from which they are subsequently recovered.

General Considerations

The main reason for the existence of a plant such as this is not the recovery of copper or the manufacture of bluestone, but rather the recovery of precious metals,—gold, silver, platinum, and the platinum by-metals. Copper as such can be recovered more economically by the large copper refineries, while bluestone is essentially a by-product which ordinarily would prove unprofitable unless, as here, its production is in conjunction with and secondary to some other process.

THE MILLER PROCESS AT THE HOMESTAKE MINE

The refinery of the Homestake Mine at Lead, South Dakota, handles only the gold from its own mine. No platinum group metals are present. In an illustrated paper entitled BULLION PARTING AT THE HOMESTAKE MINE, in Mining and Metallurgy (New York), pages 500 to 504, December, 1935, Nathaniel Herz describes the equipment and procedure of the Miller chlorine process as employed there, and also explains why the chlorine process was chosen rather than electrolytic methods or acid parting. Parts of this paper are quoted below.

The bullion to be treated is of two kinds. That recovered from the ore by amalgamation contains 800 to 820 parts gold with 175 to 190 parts silver, and makes up about 60 percent of the production. The other 40 percent has been recovered from the ore by cyanidation, and runs 730 to 755 parts gold with 205 to 230 parts silver. We quote:

Acid parting and the Moebius electrolytic process both require a bullion with a silver to gold ratio of 2 or 2.5 to 1. This would necessitate keeping a large stock of silver for alloying, and the parting of something like 30,000 to 35,000 oz. of alloyed bullion weekly. The acid or power needed for these processes and the large installation for such quantities eliminated both of them from consideration. Similarly, the Wohlwill process was eliminated because it requires a bullion over 900 fine in gold; that would require a stock of gold for alloying and the parting of between 30,000 and 40,000 oz. of alloyed bullion weekly. This left the Miller process as the one adapted to the conditions, as it is suitable for bullion of the class under consideration, can produce refined gold suitable for shipment in a few hours, and may be installed in a small space. Therefore, plans were made for equipment for chlorine parting sufficient to refine the weekly cyanide plant output in one day and the amalgamation output in two.

Melting Furnaces

The melting furnaces are of local design, stationary, built directly against the stack, with good covers and flue connections. This is advisable here, because there is always a remote possibility of mercury vapor from an imperfectly retorted lot of amalgam; furnaces without a positive flue connection might allow mercury vapor to escape into the room unless well hooded and provided with positive draft. The furnaces have a cylindrical iron shell, and a sloping cast-iron cover plate over each pair. This cover plate supports the doors, and has a horizontal ledge in front to hold moulds when pouring bullion bars, or a saddle-shaped iron block to steady the crucible when pouring bullion into the parting crucibles. These furnaces are 30 in. in diameter outside, and 18 inside. The inside depth varies from about 21 in. in front to 28 in back, owing to the sloping cover.

Crucibles

The crucibles in use are generally No. 100 graphite melting pots; sometimes No. 50 pots are used for small lots. The space between the furnace lining and the crucible is much greater than is customary in tilting furnaces, but is needed for the tongs used in pouring. The furnaces are lined with a monolithic rammed refractory, but are of such a size that a standard cupola block may be substituted if desired.

Parting Furnaces

The parting furnaces are also of local design, and are made to accommodate No. 18 French clay crucibles, which are about 11½ in. high and 5¾ in. outside diameter, within No. 18 graphite guard pots. The furnaces are 18 in. outside diameter and 24 in. high, with the inside diameter and depth 11 and 21 in. respectively. They are lined with a rammed refractory, making repairs to the bottom easy. These furnaces, of which there are eight, are arranged along a horizontal flue installed along one of the 40-ft. sides of the room, and are raised above the floor so as to bring the tops to a convenient working height, about 30 in. They are spaced 3 ft. center to center, with a portable iron working table about 16 in. square between each pair of furnaces. The flue connections are about 5 by 6 in. and are well below the furnace tops, being about at the level of the tops of the crucibles. The flue is supported on a steel stand; the gas and air lines are carried below it with feeders coming between pairs of furnaces, each furnace having individual control. There is a short vertical stack, which connects by means of a short suspended horizontal flue to a tile tower leading into the large brick stack at a point about 20 ft. above the floor. This tower has a water spray in it to wash out excess chlorine before delivering to the outside atmosphere and to recover some volatilized silver chloride. All flues are of firebrick except the tile tower and its base, which are of acidproof stoneware.

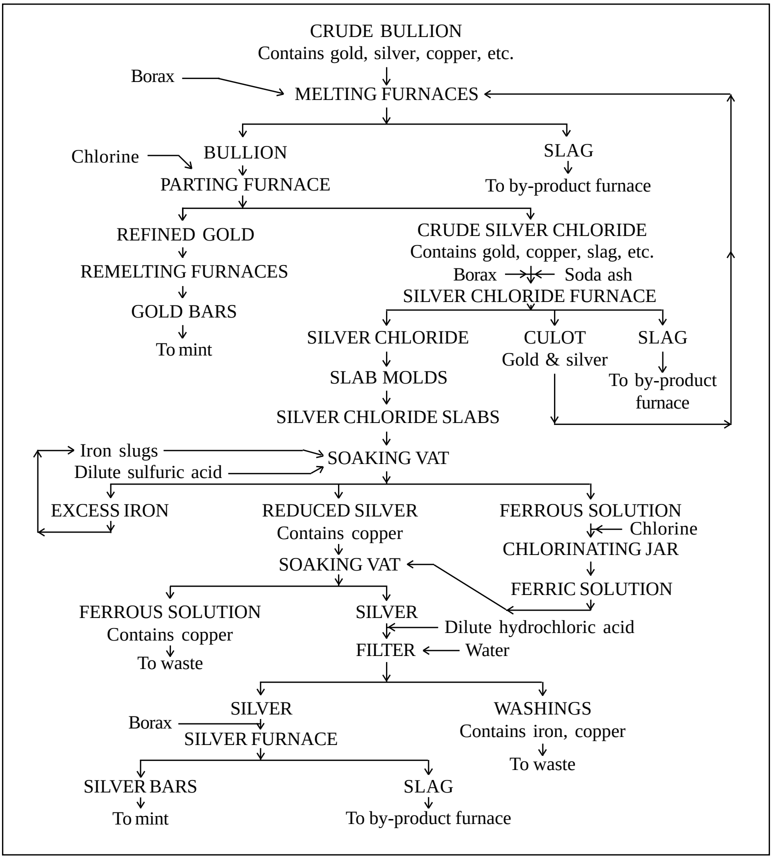
Chlorine Supply

Chlorine is obtained in 100-lb. cylinders, which are kept in a small brick house adjoining the refinery. Connections are made by standard chlorine fittings to flexible copper tubing leading to the pipe supplying the furnaces. This pipe is of seamless steel, carried above the front of the flue, with duplicate control valves for each furnace. The pressure on this line is sometimes a little high when starting a run, but it soon drops owing to the cooling of the liquid chlorine by evaporation. To keep the pressure up to the desired point, it is usually necessary to connect two or three cylinders to the line. In real cold weather a small steam radiator in the chlorine house is required to keep the temperature up to a point that prevents freezing of the chlorine in the cylinders.

The hydrostatic pressure of molten gold is nearly 10 lb. per foot of depth, and as the working depth is something like 6 in., good control is obtained with ease when the line pressure is from 20 to 40 lb. The valves in use are ½-in. high-pressure bronze valves with disk and seat of nickel alloy, and packed with asbestos. From the control valve an asbestos-covered rubber chlorine hose connects to the clay tube admitting the chlorine to the bullion being treated. This hose is held in place by clamps so as to put no strain on the clay tube, which is about 25 in. long and ½ in. in diameter outside; the bore is about $^{3}/_{16}$ in. In operation it reaches to the bottom of the crucible. Furnaces are covered with two fire-clay tile, allowing a small opening for the chlorine tube to enter and for observation.

Procedure

Parting is conducted in this manner: The clay crucibles are prepared by filling with a hot borax solution, which is poured out after about five minutes. Then the crucibles are dried for several days on a warm flue. When put into service, they are placed in the graphite guard pots in cold furnaces, and preheated slowly to avoid cracking. While they are being preheated, the crude bullion is melted in one or more of the large furnaces with the addition of a small amount of borax to flux impurities; a little sand is added to the flux when melting cyanide bullion. This slag is partly skimmed off, using a spiral iron skimmer; it is unnecessary to complete the skimming at this stage. Then the parting crucibles in their guard pots are carried to the melting furnaces and the molten bullion poured into them. The charge is about 650 oz. per crucible, although charges of over 700 oz. have been handled occasionally. As soon as the crucibles are replaced in the parting furnaces, the clay tubes are lowered to a point just above the bullion to preheat them for a few minutes. A few ounces of borax glass is added to each crucible; if lead is present in the bullion a little fine sand is also added. A small stream of chlorine is now turned on and the tubes slowly lowered to the bottoms of the crucibles. The chlorine flow is increased gradually and is all absorbed by the bullion.



Flow sheet of Homestake parting plant

The various metals present, with the exception of gold, combine with chlorine at rates depending upon the heats of formation of the chlorides, with a certain amount of overlap depending upon relative concentrations present. Lead is volatilized rapidly; soon the white fumes of lead, if present, are replaced by darker fumes of cuprous chloride; copper is only partly volatilized, and the formation of liquid silver chloride starts soon after. The early silver chloride is more cupriferous than that formed toward the end of treatment, but if much copper is present it is found in all the chloride and some is found in the fine gold. The silver chloride formed occupies about 2½ times the volume of the silver from which it was produced, so it must be removed from the crucible at intervals. This is done by bailing it out with small triangular crucibles, pouring it into shallow moulds. The chloride is allowed to rise almost to the top of the crucible before bailing; after skimming, more borax glass is added and the chloride again allowed to build up. The rate of formation of silver chloride is about 1 oz. per minute during most of the treatment; with 20 percent silver, a charge is nearly parted in a little over two hours. Sometimes additions of small pieces of crude bullion are made at intervals during the parting as silver is removed.

The End Point

When the amount of silver present diminishes toward the end of parting, the chlorine is incompletely absorbed, so the rate at which it is supplied is diminished to reduce the splashing tendency. The crucible is covered with a slotted cover, convex downward to hold back this splashing. When practically no more chloride seems to be forming the charge is skimmed as completely as possible and the gas allowed to continue through the bullion at a low rate. The end of the parting can be judged by experienced operators by observation, but it is difficult to describe it. A test is sometimes used, consisting of turning on more chlorine and holding a cold clay tube in the crucible above the gold. A certain brown stain on the tube is an indication of the end point. This must be used with some judgment, as under some conditions there is a rather different tint of brown produced somewhat earlier by volatilization of copper. The appearance at the end is rather distinctive. When silver is present in any quantity, the surface seems to have streaks that appear at a higher temperature than the rest; this may be actually so, due to the heat of formation of silver chloride. When the parting is finished, the surface of the gold has a different luster than previously; this may be described as a high luster, almost adamantine, with some semblance of transparency. This may not be true transparency, but the gold beneath the surface has a greenish cast by artificial light which gives it this appearance. When this stage is reached, the chlorine tube is withdrawn, the valve closed, and the gold poured at once into bars. With ordinary care, the gold bars as shipped are about 994 in fineness.

When there is as much silver to be removed, as in the Homestake bullion, the preliminary treatment of the crucibles with borax solution is of considerable advantage. The use of a little borax slag, as advised in some references to chlorine parting in other places, would be sufficient if little silver is present; the longer time and greater depth of silver chloride lead to more absorption by the crucible if it is not treated to make it less pervious. When tried without the borax treatment, it was found that chloride passes entirely through the clay wall and is reduced to metal by the flame; sometimes enough of this reduced metal was found in the guard pot to contaminate the gold unless great care was taken in pouring.

This completes the gold treatment, which is rapid and comparatively simple; about 98 percent or more of the gold is available for shipment in a few hours.

Treatment of the Silver Chloride

Recovery of the gold in the silver chloride is the next step in the process. Some is present in visible shots that adhered to the skimming crucible; some may be present in such finely-divided form as to be invisible. It is recovered by remelting the silver chloride under a borax cover and reducing a portion of the silver by the gradual addition of a little soda ash. This is done in graphite crucibles; it was tried in the larger furnaces in lots of 100 lb., but there was some loss by volatilization of silver, and no method for its recovery. Now the operation is conducted in No. 18 crucibles in the parting furnaces so that the water spray can recover the volatilized silver. Experiments are under way with heavier slag covers; perhaps the loss may be eliminated in this way.

The charge used at present is about 20 lb. of chloride, 1½ to 2 lb. of borax glass, and 1 lb. of soda ash added in small increments after the charge is fused. The reaction forms sodium chloride and liberates carbon dioxide and oxygen, as silver oxide is unstable above 300° C. The reduced silver, in dropping through the melted chloride, carries all the gold down with it. The temperature must be high enough to melt the alloy into an ingot in the bottom of the crucible; then the heat is turned off and the charge allowed to cool to a dull red heat. The nearly solid slag is removed, and the purified silver chloride dipped out and poured into shallow iron moulds making four cakes each 6 by 8 by about ¼ in. The last of the chloride is poured into these moulds and the button of gold-silver alloy removed and added to a subsequent lot of crude bullion for parting. Twenty pounds of silver chloride gives about 3 lb. of alloy containing about 20 percent gold. Thus, something like ten to fifteen per cent of the silver is reduced and returned for a second chloridizing. The slabs of silver chloride now contain no impurity of consequence except copper.

As now operated, the chloride cakes are packed in “soaking vats” of acid-proof stoneware. These receptacles are rectangular trays of 12 gal. capacity, 6 in. deep inside, and about 20 by 24 in. They hold about 75 lb. of chloride cakes, alternated with layers of iron punchings spaced about 1½ in. center to center. Dilute sulfuric acid is added to start the reaction, which is allowed to continue for two or three days. The liquid is then removed, as it is saturated with iron salts, stopping all action. A fresh lot of very dilute acid is added, and in a day or two the action is complete. The silver and copper are all reduced to metal, but not alloyed. The metal is removed, picking out the remaining iron slugs for further use. The reduced metal is now washed with water, partly air-dried, and melted into bars averaging over 990 fine.

When bars of higher fineness were made the copper was removed by leaching with ferric chloride. The reduced metal, after removing the iron slugs, was placed in a soaking vat and treated with a ferric chloride solution made by passing chlorine into some of the ferrous solution produced by the reduction of the silver chloride with iron. The chlorine is absorbed by this solution readily by feeding it through an alundum diffuser. The reduced copper in the silver is finely divided, and most of it is found on or near the outside of the cakes, as it tends to travel to the iron; this condition makes its solution both rapid and complete. That is fortunate, as the process is very sensitive owing to action on the silver, tending to form chloride again. Silver is insoluble in this solution, but both ferric and cupric chlorides react with finely divided silver, producing a surface layer of chloride. Therefore, the amount of ferric solution used must not be too great, and the contact not too long. A day is enough to dissolve the copper.

Due to the reaction with silver, most of the copper is in this solution as cuprous chloride and not the cupric salt as in leaching copper ores. This necessitates a wash with acid before water, or the dilution would cause the precipitation of cuprous chloride. The washing is done by placing the silver in shallow canvas bags in the upper part of acidproof stoneware suction filters, which are used as gravity filters because the charges leach freely. After washing several times with acid of increasing dilution, the last of the acid is washed out with water and the silver removed and partly air-dried. It is melted with a borax slag; if there seems to be an appreciable amount of chloride present, it may be reduced by adding some soda ash to the borax. If much chloride appears after melting, the bars are not poured, but the metal is allowed to solidify in the crucible. The slag and chloride are removed and the silver remelted and poured. Silver has been produced by this method that is 999 to 999½ fine, the impurity being largely iron.

Protection for Workmen

Some observations on the operations may not be amiss at this point. Shallower furnaces could be used for the parting operation, but the effect would be to increase the fumes in the furnace room. With the depth used and a good flue draft, the fumes are slight and the operators suffer no discomfort from them. There is an exhaust fan in the wall above the furnaces, producing a distinct draft away from the men. The operators wear asbestos aprons, sleeves, and mittens, as well as dark furnace spectacles. When pouring, they also wear asbestos leggings to guard against burns in case of spills.

The tile tower with water spray removes most of the free chlorine that escapes into the flue; also some silver chloride is recovered by filtering the water.

* * * *

THE RARITAN COPPER WORKS

This large plant, at Perth Amboy, New Jersey, is engaged primarily in the large-scale refining of copper. In Chapter XXI we showed how impurities in the crude copper accumulate as slimes or sludge during the corrosion of the copper anodes. These slimes contain not only the precious metals, but also many other materials, and a complete by-products refinery such as this one will market six or eight metals—gold, silver, platinum, palladium, selenium, tellurium, and in some cases arsenic, antimony and nickel, as trade conditions dictate.

In a paper entitled RECOVERY OF PRECIOUS AND SECONDARY METALS FROM ELECTROLYTIC COPPER REFINING, appearing in the Transactions of the American Institute of Mining and Metallurgical Engineers, vol. 106, pages 427 to 440 (1934), M. A. Mosher describes the equipment and procedures employed. The following paragraphs are adapted from his paper.

The raw sludge that collects during the electrolytic corrosion of the copper anodes is washed, roasted, leached in sulphuric acid, washed again, and furnace-refined with fluxes to remove as much as possible of the base metals including arsenic, antimony, selenium, tellurium, and others. (These processes are described in detail in Mr. Mosher's paper, but are only summarized here because they are not of immediate interest to the worker in precious metals.)

The metal that remains after these treatments—it is called doré, or doré silver—averages 980 parts silver, 15 parts gold, and the rest plati num group metals and others. This silver-gold alloy is then ladled out into water-cooled double-face, reversible molds to produce anodes for the subsequent electrolytic refining. Two types of anode are cast, one 19¼ by 21½ by ½ inch for the Thum electrolytic process, and the other 6¼ by 9 by ½ in., with a small lug at one end, for the Moebius process.

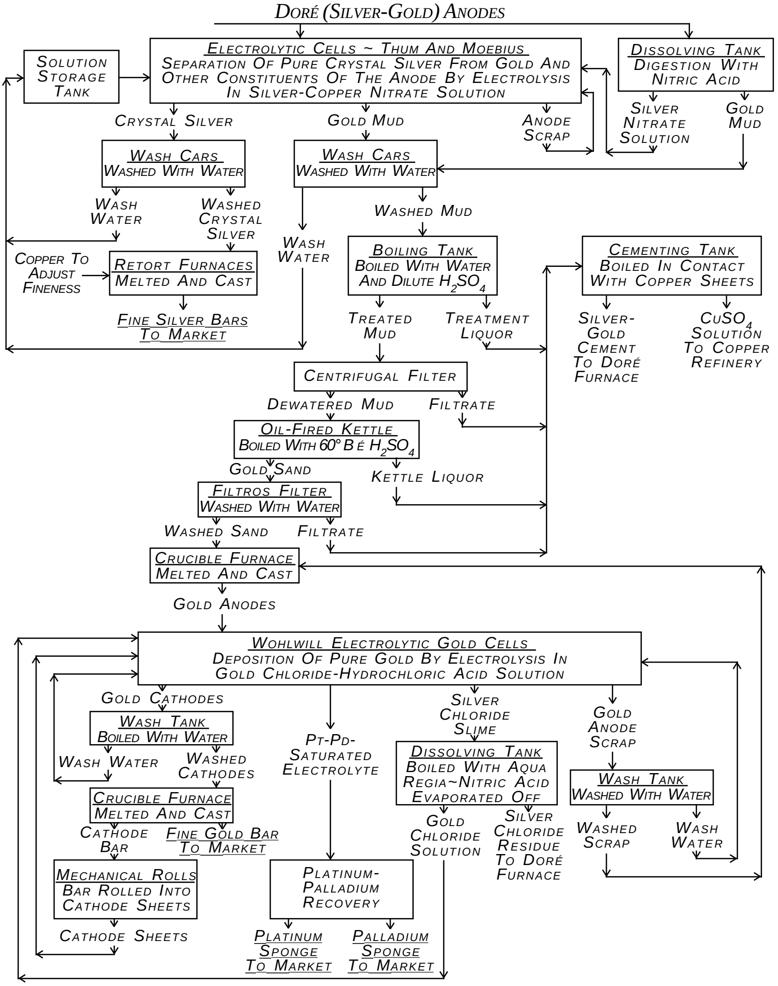
Electrolytic Parting and Refining of Silver and Gold

The standard processes employed for the electrolysis of silver-gold anodes do not lend themselves to the elimination of any appreciable amount of base-metal impurities, since the latter may be rendered soluble as the anode corrodes and then be plated or cemented out at the cathode with the silver. The anode metal is brought to the highest possible purity therefore in the doré furnace, 995+ parts of silver plus gold, and the electrolytic treatment becomes simply a parting process to separate the silver from the gold and any other precious metals the anode may contain. Two types of electrolytic equipment are commonly employed, the Thum or horizontal process, and the Moebius or vertical process, each having its advantages and disadvantages, which will be discussed later.

In the Thum process the anode is placed within a wooden frame lined with muslin and covered with a close-fitting canvas sack. This frame in turn is placed in a heavier frame which, resting on the sides of the electrolytic cell, is partly immersed in the electrolyte and equipped with slats across the bottom to support the weight of the anode. This anode frame assembly covers about one-half the solution area of the cell, leaving the other half open. The cells themselves, measuring 48 by 24 by 7 in., are asphalt-lined concrete tanks. The bottoms of these tanks, which must serve as cathode surfaces, are lined with slabs of graphite and carbon ½ in. thick. The current enters the cell through a silver contact piece which rests on the submerged anode in the tray, and is conducted from the cell through another silver contact which rests on the graphite slabs underneath the solution at the open end of the cell. The silver corroded from the anode passes through the muslin and canvas diaphragms, deposits on the carbon-slab bottom underneath the tray, and is scraped forward periodically by hand to the open end of the tank to make way for continued deposition. The accumulated deposit is removed from the open end of the tank to a filter-bottom wash car once each shift. As the anode corrodes away, another is placed on top of it so that each anode in turn is completely electrolyzed, leaving no scrap to be remelted.

The anode current density is 50 amp. per sq. ft. with a maximum current per cell of 150 amp. at 3 to 3½ volts, the cells being arranged in series in sections of 21 tanks. The electrolyte is a neutral silver-copper nitrate solution analyzing 60 grams per liter silver and 40 grams per liter copper.

In the Moebius or vertical electrolytic parting process the same solution and current density are employed, but the anodes and cathodes are



Flow sheet of electrolytic refining of precious metals at the Raritan Copper Works.

suspended vertically in a cell measuring 24 by 29 by 22 in. The anodes, 9 by 6¼ by ½ in. with a lug for hanging, are suspended in rows of three in canvas bags, the anode bar across the tank carrying the sack and its frame as well as the hangers supporting the anodes themselves.

Cathode sheets of chromium iron 12 by 20 by 1/16 in. are suspended from the busbars at the sides of the tank. The cathode surfaces are continually scraped free of the crystal silver deposit by wooden blades attached to an oscillating rack which rests on the framework over the tanks and is mechanically operated. The crystal silver scraped from the cathode sheets falls through the solution into a wooden tray, which is suspended from the electrode assembly frame over the tanks. As the anodes corrode away new ones are hung in their places and the scrap lugs, which otherwise would have to be remelted, are placed in the Thum anode trays for complete corrosion.

Each tank contains five anode groups and six cathode sheets, connected in parallel. The cells are connected in series in sections of six with a maximum current density of 450 amp. at 2½ to 3 volts.

After a full producing day the entire operating equipment of a section is mechanically raised as a unit to a position 1 ft. above the cells. The trays, which have hinged bottoms, are then emptied of the accumulated crystal silver deposit into filter-bottom wash cars.

The advantages of the Thum process are: (1) Mechanical and current conductor simplicity, which make for low cost of installation and maintenance; (2) complete corrosion of the anodes, which may be of any size, shape, or weight within the capacity of the anode tray; (3) no necessity for shutdown while the crystal silver production is being removed.

The disadvantages are: (1) Corrosion from but one face of the anode, resulting in low production per unit of floor space and volume of electrolyte; (2) dependence on and cost of hand labor for scraping the deposit from the cathode; (3) lack of regular stirring or circulation of electrolyte in the cell.

For the Moebius process the advantages are: (1) Low labor cost due to mechanical scraping of the deposit from the cathode, with the added benefits of regular stirring of the electrolyte, a more uniform deposit, and a current efficiency of 98 percent, which is 5 to 10 percent higher than that obtained in the Thum process; (2) close spacing of electrodes, together with corrosion of both faces of the anodes, resulting in high production per unit of floor space and volume of electrolyte; (3) no necessity for muslin diaphragms, because the anode does not rest on the accumulated gold mud.

Its disadvantages are: (1) Mechanical and current conductor complexity, resulting in a high installation and maintenance cost; (2) complete shutdown necessary for the removal of the crystal silver production.

In both the Thum and Moebius processes the gold accumulates around the anodes in the sacks as a black slime or mud contaminated with particles of silver and basic copper salts. This mud is removed from the Thum trays after every three days of operation by taking out the muslin tray lining and washing it into filter-bottom wash cars. In the Moebius system the anode sacks are removed from the assembly and washed out after the same period. The solution is filtered off the mud in the wash cars and the mud transferred to a wooden boiling tank 3 ft. in diameter by 3 ft. deep, where it is boiled up with water to which is then added a small quantity of sulfuric acid to break up the basic copper salts. After settling has taken place the wash liquor is siphoned off and the mud is transferred to a Tolhurst centrifugal filter to be finally washed with water and dried. The dewatered mud is charged into an oil-fired cast-iron kettle 4 ft. in diameter, where it is boiled for about 3 hr. in 60° Bé. sulfuric acid. This boiling removes the copper and most of the silver from the mud and leaves a residue of brown sand which assays about 970 parts gold. This sand is thoroughly washed on a Filtros-block filter ready for melting down for the production of gold anodes.

Silver-copper nitrate wash waters from the washing of crystal silver and the preliminary washing of the gold mud are filtered and elevated by means of a small hard-rubber pump to a chemical stoneware storage tank from which hard-rubber distribution lines run convenient sections of the parting plant. This wash water is used to make up electrolyte evaporation and withdrawals resulting from the removal of crystal silver and gold mud. Sufficient electrolyte is entrained in the latter and destroyed in its subsequent treatment to obviate the necessity of special withdrawals to maintain the purity of the electrolyte. Silver nitrate solution for replenishing the electrolyte is made by digesting doré anodes in nitric acid.

Gold mud wash water containing sulfuric acid and the strongly acid boiling kettle liquors, as well as the water resulting from the washing of the gold sand, are collected in a sump tank and pumped to a special cementing tank in the slime plant, where the precious metals are precipitated by boiling the solution in contact with copper sheets. The gold-silver cement thus produced is periodically refined and cast into anodes in the doré furnace.

Melting and Casting of Silver

The crystal silver, after being thoroughly washed with water in the wash cars, is charged into clay-graphite retorts and melted. These bottle-shaped retorts, 38 in. high, are mounted in oil-fired tilting furnaces of the Faber-du-Faur type and hold a charge of about 30,000 troy ounces. The consumption of light fuel oil with a small Quigley-type burner is 8 to 10 gal. per hour. The charging and melting of a full charge requires 5 to 6 hr., after which the molds are brought up on a carriage and the standard-size bars are poured by tilting the furnace, about 45 min. being required for the casting of the usual 25,000-oz. lot in 1000-oz. bars. The fineness of the silver is adjusted to 999, the standard for the fine silver market, by adding to the melt, just before pouring, a few ounces of pure copper.

Electrolytic Refining of Gold (Wohlwill Process)

The gold sand is melted in No. 25 graphite crucibles in a cylindrical oil-fired crucible furnace, the Quigley-type burner consuming about 8 gal. of light fuel oil per hour. The metal is cast into vertical closed molds to produce gold anodes averaging 980 fineness and 140 troy ounces in weight, the dimensions being 9 by 5 by $^3/_8$ in. The electrolysis of these anodes is accomplished by the Wohlwill process, in which from six to eight of them are suspended in pairs from silver anode bars in the electrolyte in a small stoneware electrolytic cell measuring 20 by 12 by 12 in. Cathode starting sheets of fine gold rolled to a thickness of 0.003 in. and having an immersed area 12 by 2 in., are suspended in rows of four from silver cathode rods spaced between the anode bars. A current of 450 amp. is put through the cell, giving a voltage of 1½ volts and an anode current density of 125 amp. per square foot with six anodes. The electrolyte is a gold chloride solution containing from 80 to 100 grams per liter of gold and 10 percent free hydrochloric acid. Heat to maintain the minimum operating temperature of 140° F. is obtained by means of a steam coil placed around the stoneware cell and enclosed by a lead-lined wooden box, sand being packed between the lead and the stoneware cell to give even distribution of the heat from the coil. Circulation of the electrolyte during operation is maintained by means of a Pohlé air-lift. The anodes are corroded to 5 percent scrap in from 16 to 18 hr., the pure gold plating out on the cathode sheets in a rough, somewhat nodularized, crystalline deposit which adheres firmly.

The cathodes are removed from the cell, thoroughly washed, dried and melted down in a clean crucible from which the gold is cast into an open mold to produce a bar weighing from 700 to 800 oz. and assaying 999.7+ parts per thousand. The anode scrap is washed, dried and remelted with the next batch of gold sand.

Silver, the chief impurity in the gold anodes, forms silver chloride during the electrolysis and falls to the bottom of the cell as a slime together with varying amounts of gold. This slime is removed periodically, leached with aqua regia for the removal of gold and the production thereby of gold chloride solution to be used in replenishing the electrolyte, the gold content of which is gradually depleted during electrolysis. The silver chloride remaining after this leach is returned to the doré furnace.

Strong wash waters are used to take up electrolyte evaporation, while dilute waters are sent to the cementing tank. Auxiliary equipment used in this process consists of two electric drying ovens and power-driven 6-in. rolls for the rolling down of a small bar of fine gold into cathode starting sheets when needed.

Fine silver bars are first weighed on a springless scale and finally weighed with careful checking over a bullion balance of 3000-oz. capacity and 0.005-oz. sensitivity. Fine gold is weighed in the same careful manner.

Platinum and Palladium Recovery

Any platinum and palladium present in the original raw slime is finally concentrated in the gold anodes and during their electrolysis goes into solution in the electrolyte, the platinum and palladium content of which can be permitted to go as high as 60 grams per liter. The electrolyte is then removed, oxidized with nitric acid, and the combined salts of platinum and palladium precipitated by the addition of ammonium chloride. Separation and eventual refining of the platinum and palladium are carried out by the usual chemical methods, both metals being produced in the sponge form and of 99.5+ percent purity.

Summary of Major Equipment and Plant Capacities

The slime plant, with 10 slime-leaching tanks, can handle 120 dry tons of raw slime per month and turn out from 60 to 90 dry tons of treated slime per month, depending on the percentage of silver it contains.

The furnace plant, with two of the three furnaces for the refining of slime to doré in continuous operation, can refine 150 dry tons of treated slime per month, there being ample capacity to handle, in addition to the output of the Raritan slime plant, any treated slime or crude doré bullion received from other plants of the Anaconda Copper Mining Co. The capacity production of two furnaces working on slime varies, according to the silver content of the slime, from 1,250,000 to 2,000,000 oz. of doré anodes per month.

The capacity of the parting plant, with the three 6-cell Moebius sections and six 21-cell Thum sections in operation, is 2,250,000 oz. of crystal silver per month. The melting of this amount and the casting into fine silver bars can be taken care of with one of the two retort melting furnaces in continuous operation.

Facilities for refining gold mud are ample to handle an amount containing 35,000 oz. of gold per month. The Wohlwill electrolytic plant with one of its two cells in operation will produce 25,000 oz. per month, so that its capacity is greater than that required to refine the gold resulting from full operation of the parting plant on doré running as high as 15 parts per thousand gold. Platinum and palladium refining facilities are adequate for the production of 200 oz. per month of the two metals. The selenium plant is capable of a production of 3000 lb. of powdered selenium per month and the tellurium plant can turn out 1500 lb. of metallic tellurium per month.

* * * *

THE UNITED STATES ASSAY OFFICE

The Assay Office in downtown New York has always attracted public interest. For many years it was situated on Wall Street, next to the historic Sub-Treasury Building, and across the street from the Stock Exchange and the office of J. P. Morgan & Co. The spectacle of a first class refinery, with its furnaces, flues, acid fumes, and so on, operated in conjunction with the storage of millions of dollars in bullion, surrounded by skyscrapers, was bound to capture the imagination. In 1933 the new and much larger Assay Office and refinery was opened at Old Slip and the East River, but the Wall Street building, still scarred with the marks of the unsolved Wall Street explosion, is retained for office and storage purposes.

With few exceptions, the procedures used are familiar ones. Electrolytic methods are used for refining both the gold and the silver. The materials that are received by the Assay Office are of many kinds, some being already of high quality. The regulations under which the Assay Offices purchase gold and silver are subject to change, and the reader is advised to obtain copies of the current rules from time to time. (See Chapter C of the Appendix.) Each deposit is melted down as received, a “dip” sample of the molten metal is granulated in water, and the resulting shot metal is used for an assay. Material running less than 900 fine in gold is handled in the silver refinery; if more than 900 fine it is a gold proposition.

Metal for the silver refinery is cast into anodes and refined much as in the Raritan plant, a modified Moebius or vertical cell arrangement being used. In making up the anodes, care must be taken to get the right proportions of silver, gold and other metals. This is done by sorting and combining the various lots, and by adding extra silver when necessary. Gold may run from 200 to 400 parts, preferably about 370; base metals should not go over 150 parts; and silver constitutes the remainder. Small amounts of the platinum metals are frequently present.

The electrolyte contains about 3 percent silver nitrate and 2 percent free nitric acid, and is kept in gentle circulation by an air pump. Muslin bags surround the anodes and catch the powder of gold and platinum that remains as the silver is dissolved away.

The cathode silver obtained in this process, when washed and melted, runs about 999.5. The electrolyte, as it becomes foul, is syphoned off and the dissolved silver is cemented out on copper plates. This cement silver is melted in with new incoming material, as necessary, in order to build it up to the desired silver content of 500 to 600 parts, to make new anodes of proper analysis.

The gold that is left in the anode bags is next washed and melted down with other high quality gold to form the anodes for the Wohlwill process, which is carried on in much the same manner as in the Raritan plant. The electrolyte contains 30 to 60 grams of gold chloride per liter, with about 10 percent free hydrochloric acid.

The silver content of the gold anodes must not exceed 5 percent, or the silver chloride coating that forms will soon interfere with the electrolysis. This coating, which formerly was scraped off by hand, is now loosened by the scheme, mentioned in Chapter XXI, in which an alternating current is superposed on the direct current. The gold that deposits out on the cathode, when washed and melted down, normally runs 999.8 fine, and frequently 999.9.

Whatever platinum metals were present are now accumulated in the electrolyte used in the Wohlwill cells. Ammonium chloride is added, and platinum precipitates as the familiar orange powder. The next procedure is one that has not previously been described in this volume: an electric current is now passed through the solution to plate out the remaining gold (in somewhat impure form) on a small cathode, and at the same time to oxidize the dissolved palladium, changing it over into such form as to precipitate the red palladium-ammonium-chloride salt that we encountered in Chapters XIII and XIV. The electric current here accomplishes the same effect that we produced with sodium chlorate.

Since the Assay Office is not authorized by Congress to buy platinum metals, but merely accepts them when offered, the recovery of these metals represents almost clear profit.

The floor sweeps and other low grade wastes are burned, crushed, sieved, sampled, and sold, as described in Chapter XVIII of this book.

The rinse solutions from the various operations contain much copper and some precious metal, both in solution and as finely divided particles. These liquids are collected in settling tanks and all the heavy metals are cemented out with scrap iron. Most of this cement metal is sold to a copper refiner after assay.

Both oil and gas furnaces are used at the Assay Office, and a Cottrell precipitator captures the fumes and dust.

* * * *

In the Report of the Director of the Mint for 1912, Treasury Document No. 2671, published in 1913, there is a full description of the procedures and equipment in use at that time. In the magazine *The Brass World* for September, 1913, an illustrated article based on the Director's Report will be found. Elry J. Wagor, in charge of the refinery at the Denver Mint, in his chapter on gold in Vol. 2 of Liddell's NON-FERROUS METALLURGY, gives added details and brings the story up to 1926. During the years since then there have been improvements in detail, and much equipment has been added, but there have been no radical changes in the general outline of procedure.

* * * *

THE PLANT AT ACTON, ENGLAND

In Chapter XXI we remarked that gold and platinum metals are obtained as by-products in the refining of nickel. The nickel and copper deposits of the Sudbury, Ontario, region contain considerable platinum group metals. These ores are refined by electrolysis, and also by the Mond nickel carbonyl process, in both of which methods the precious metals accumulate as crude concentrates.

The following paragraphs are adapted or quoted from a paper entitled REFINING METALS OF THE PLATINUM GROUP, a description of the process at the Acton (England) refinery of the Mond Nickel Company, Ltd. This paper, by C. Johnson and R. H. Atkinson, was read before the British Institution of Chemical Engineers on May 19, 1937, and an abstract of it appeared in the Industrial Chemist (London), pages 223 to 233, issue of June, 1937.

The Acton refinery receives residues from the Clydach nickel refinery, which operates the nickel carbonyl process, besides concentrates from the electrolytic nickel refinery and a smaller amount of concentrates from the electrolytic copper refinery which treats the company's blister copper. The residues from the Clydach refinery require further concentration before the platinum can be extracted economically with aqua regia. For this purpose they are smelted with litharge, fluxes, and charcoal in small tilting furnaces, with basic linings, to collect the precious metals and at the same time to slag off silica and base metals.

Chemical stoneware vessels are available in large sizes.

The principal reaction during smelting is the reduction of lead oxide to metallic lead which acts as a collector of the precious metals. Another important reaction is between lead sulphate, which forms approximately 50 percent of the Clydach residue, and soda ash according to the following equation:—

$$PbSO_4 + Na_2CO_3 = PbCO_3 + Na_2SO_4.$$

The lead carbonate immediately decomposes into lead oxide and carbon dioxide. The sodium sulphate separates in the moulds as a top slag, which is removed and leached.

Subsequent cupellation of the ingots in similar furnaces removes the excess of lead as litharge, which is used again in further smelting charges, and yields a precious metal alloy rich in silver, about four times richer than the Clydach residue.

If lead alloys are cupelled to a finish, that is, until litharge ceases to form, there is a probability of producing a cupelled metal which is not readily attacked in the course of the subsequent refining operations, hence the reason for partial cupellation.

This alloy is treated with boiling concentrated sulphuric acid, which removes most of the silver and about one-third of the palladium as sulphates. The residue contains the platinum, gold, and the rest of the palladium in a form particularly suitable for extraction with aqua regia, which is the next operation. From the solution of chlorides thus obtained, the gold is precipitated as brown gold by means of ferrous sulphate, and then the platinum as ammonium chloroplatinate by the addition of ammonium chloride, and lastly, the palladium is precipitated as palladosammine chloride. The only one of these operations which calls for special comment is the precipitation of palladosammine chloride. The palladium present as chloride is converted into soluble tetrammino-palladous chloride by the addition of excess ammonia solution according to the equation:—

$$PdCl_2 + 4NH_3 = [Pd(NH_3)_4]\,Cl_2.$$

When excess of hydrochloric acid is added, the sparingly soluble yellow compound known as palladosammine chloride is precipitated according to the equation:—

$$[Pd(NH_3)_4]Cl_2 + 2HCl = [Pd(NH_3)_2Cl_2] + 2NH_4Cl$$

The impure platinum salt is converted into metal by ignition, dissolved in aqua regia and reprecipitated as pure ammonium chloroplatinate, which, on ignition, yields pure platinum sponge. The impure palladosammine chloride is purified by dissolving in ammonia and reprecipitating with hydrochloric acid; the pure salt is converted into sponge by ignition.

The silver and the gold are purified electrolytically, by the Moebius and Wohlwill processes, respectively, special attention being given to the recovery of small amounts of platinum metals. All liquors resulting from the processes are treated with zinc, or iron, and acid to recover traces of the precious metals. In practice, it is found to be more economical to smelt the final insolubles and reduction residues than to attempt to recover rhodium, ruthenium and iridium from them by wet processes.

The lead ingots obtained by smelting are cupelled to remove excess lead and the resulting precious metal alloy is parted with nitric acid. The solution is treated in order to recover precious metals, especially palladium, platinum, and silver which dissolve during the operation.

Most of the rhodium, ruthenium and iridium present initially in the lead alloy are concentrated in the insoluble form from which they can be extracted and refined by chemical processes.

Rhodium is extracted by fusing the concentrate with sodium bisulphate. Subsequently the rhodium is refined by a modification of the process described by Wichers, Gilchrist and Swanger.

The insoluble from the bisulphate fusion is given appropriate treatments to remove platinum, gold and lead sulphate as a result of which a concentrate of ruthenium and iridium is obtained.

This concentrate is fused with caustic potash and potassium nitrate in spun iron bowls at a dull red heat to convert the ruthenium into soluble potassium ruthenate. The cakes are then dissolved in water; after settling, the clear solution is decanted into glass flasks and treated with chlorine. This treatment converts the ruthenate into volatile ruthenium tetroxide which distils over on raising the temperature. The tetroxide is absorbed in dilute hydrochloric acid containing methyl alcohol. Evaporation of the contents of the absorption vessels gives an oxychloride, $RuOCl_2$, which is reduced to metal by igniting in hydrogen.

There appears to be very little osmium in the precious metal concentrates received from the nickel refineries. It amounts to less than 1 percent of the ruthenium content, and on account of the similarity in properties of these two metals it will be found as an impurity in the ruthenium unless it is eliminated, which can be easily done by heating the ruthenium oxy-chloride to dull redness in a current of air. The resulting osmium tetroxide is absorbed in an alcoholic caustic soda solution and the osmium recovered *via* osmyl tetrammine chloride, $[OsO_2(NH_3)_4]Cl_2$, which can be ignited to metal in an atmosphere of hydrogen. The caustic fusion, besides converting the ruthenium into potassium ruthenate, which is soluble in water, also converts the iridium into an oxidized form which, although insoluble in water, is said to be soluble in hydrochloric acid. Actually aqua regia is used for dissolving the iridium.

The chloride solution thus obtained is evaporated, and a crude ammonium chloriridate obtained by adding ammonium chloride and oxidizing with small amounts of nitric acid. The crude salt is separated from the accompanying ammonium chloroplatinate by fractional crystallization; the use of a mild reducing agent facilitates the solution of the iridium salt. Recrystallization is continued until the desired purity is achieved; the salt is then decomposed by heating in a gas-fired muffle furnace. The partially oxidized metal is reduced by heating in hydrogen and is then further purified.

* * * *

Refining of the richer concentrates from the nickel and copper refineries which contain more than 50 percent platinum metals and very little silver, commences with the treatment by aqua regia.

In precious metals refining, the order of operations depends on the ratio in which the precious metals are present. The order described here is followed because it has been found to be the most suitable for these by-product concentrates, although it is realized that other sequences of operations might be more suitable for other types of material.

The average purities of the metals recovered from these concentrates are: platinum, 99.93 percent; palladium, 99.94 percent; iridium, 99.7 percent; rhodium, 99.7 percent; ruthenium, 99.7 percent; gold, 99.97 percent; and silver, 99.97 percent.

The high intrinsic value of the materials treated makes it imperative to reduce working losses to a minimum and to obtain the maximum yield as quickly and directly as possible. In practice, not more than 0.25 percent of the platinum metals contained in the concentrates is lost, while 1.25 percent is temporarily retained in furnace slags returned to the nickel refinery for retreatment. The remaining 98.5 percent is produced directly as refined metal. The losses occurring in the processes of extracting the nickel and copper are also very small, and it is estimated that 90 percent of the precious metals, probably excepting osmium, contained in the ore is ultimately recovered.

Chemical Plant for Refining Platinum

The chemical engineering problems in connection with the refining of platinum are of a specialized nature, with the result that experience in other fields is not always directly applicable. Moreover, the tradition of secrecy in the platinum industry up to the present has prevented refiners from pooling their experience except in a very general way. The state of affairs is in very marked contrast with what is known about the plant and processes for the refining of silver and gold.

These remarks are not intended to apply to smelting operations, which have received adequate treatment in text-books on metallurgy, but rather to the wet processes for refining crude platinum and platinum concentrates.

The very nobility of the platinum metals necessitates the use of powerful acids and other reagents for refining them, a circumstance ruling out many of the standard materials for the construction of chemical plant; for instance, even stainless steel can rarely be used. The scale of operations is small, even the refining of platinum is frequently described as large-scale laboratory work, and the refining of other metals of the group is on a smaller scale still. Mechanical operations are reduced to a minimum, and where machines have to be used the simpler they are the better. The highly corrosive nature of most of the reagents, together with the importance of reducing losses of valuable metals to a minimum, are the main reasons for avoiding mechanical handling. The total handling loss in all refining operations is probably under 0.1 percent.

Batch processes are also preferred to continuous processes because it is easier to check yields and make sure that precious metals are not going astray. For the same reason, namely accounting for precious metals, all units of plant must be easily accessible for cleaning out on the completion of batches.

The wet processes are operated in a building specially designed for this work after five years' experience in temporary premises. The principal feature is that the vessels are arranged on terraces. Successive steps of a process can be arranged in a line from the top of the building to the bottom, with gravity flow of the liquor from one vessel to the next. If a process requires more than five operations, the liquor from the fourth operation is elevated to one of the upper stages. In this way the number of times that the liquor has to be elevated is reduced to a minimum. Both acid eggs and centrifugal acid pumps have been used for elevating these liquors, and on past experience acid eggs are preferred, The general layout of the building also facilitates supervision and control.

The walls are built of white glazed bricks and the floors are constructed of chemical asphalt. Steam, water, vacuum, and compressed air are available on all the terraces. An overhead travelling crane enables any piece of plant to be replaced or moved to a different position.

In addition to a complete system for the removal and treatment of all fumes generated in the operations, general ventilation is obtained by Robertson ventilators in the roof supplemented by fan ventilation where required.

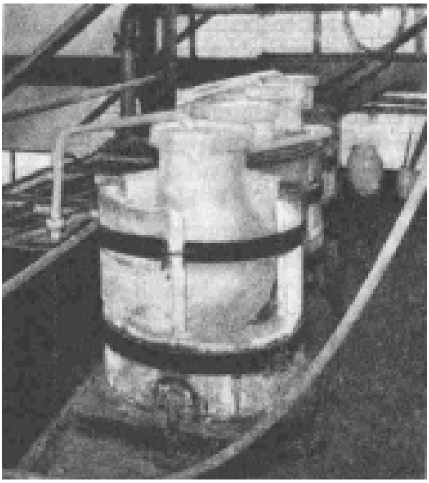
Wet Process Plant

Chemical stoneware is the most generally used material for the construction of plant for refining processes involving the use of acids, the two principal types of vessels being mixers or vats up to 100 gal. capacity, and vacuum filters up to 80 gal. capacity.

Aqua regia treatment of concentrates is normally conducted in steam-heated chemical stoneware vessels each of 140 liters capacity. A temperature of 90° C. is readily obtained, which is adequate for dissolving the finely-divided platinum, palladium and gold contained in the residues. Working under these conditions, there is the further advantage that there is no risk of bumping when heavy insoluble matter settles to the bottom of the vessel.

On the other hand, the conditions are quite different for dissolving mineral platinum, which is best done in gas-heated Vitreosil bottles of 70 liters capacity, using concentrated aqua regia at or near the boiling point. Evaporation of nitric acid solutions is done in similar Vitreosil bottles equipped with condensers.

Nitric acid treatment is carried out in gas-heated 20-liter basins made of Vitreosil, which are also used for sodium bisulphate fusions. Sulphuric acid treatment is done in pans made of fine-grained grey cast iron, each of 25 liters capacity, and heated by gas. Lead-lined wood and iron vessels are both used for liquors containing free sulphuric acid.



Vitreosil (fused quartz) retorts, for evaporating strong acids. Part of the asbestos jacket in the foreground has been removed to show the retort.

Courtesy of The Thermal Syndicate

Wooden tanks up to 300 gal. capacity, lined with soft rubber, are satisfactory for some of the operations, for instance, reactions where sufficient free hydrochloric acid is present to make lead-lined vessels unsuitable. Acid-resisting hose is used to convey acid liquors and to make connections for removing fumes from reaction vessels.

Steel vessels lined with hard rubber are preferred to chemical stoneware vessels for operations involving the use of hydrochloric acid in which the heat of reaction causes a rapid rise of temperature. Porcelain plant is used for small-scale purification work.

Auxiliary PIant and Services

An oil-fired boiler supplies low-pressure steam for process purposes and for general heating of the building.

The vacuum system consists of two 10 to 17-H.P. Nash Hytor centrifugal vacuum pumps maintaining a vacuum equivalent to 10 in. of mercury; a higher vacuum is considered inadvisable on account of the fact that stoneware filters are used. The vacuum mains consist of hard rubber pipes. Liquor catch pots and a vacuum scrubber protect the vacuum pumps from corrosion.

Two Broom and Wade air compressors, with automatic control to economise the power consumption, supply air for the acid eggs.

Drying of various intermediates and products, most of which are slightly acid, is done in gas-heated drying ovens, some of which are thermostatically controlled. Enamelled iron, Pyrex glass and ceramic dishes are used.

Residues, which sinter during calcining, or cake during drying, may have to be converted into powder for subsequent operations. For this purpose there are four 8-in. and one 14-in. disc pulverisers. Care is taken to collect and recover all dust produced during pulverising by means of a fan and bag system.

Removal and Scrubbing of Acid Fumes

The fumes given off during reactions include sulphur dioxide, sulphuric acid, chlorine, hydrochloric acid, oxides of nitrogen and nitrosyl chloride. Although stoneware fans can handle mixed acid gases such as these, it is more satisfactory to use an ejector in which the gases do not pass through the fan. In the latter system a fan delivers a jet of air at high velocity into a specially designed nozzle, which has the effect of creating sufficient suction to draw the fumes away from the reaction vessels. The acid fumes are neutralised in chemical stoneware scrubber towers by a sodium carbonate solution which is kept in circulation by centrifugal pumps.

The plant for the thermal decomposition of ammonium chloroplatinate and palladosammine chloride has been selected for special mention because it possesses some features of chemical engineering interest.

Ammonium chloroplatinate can be converted into metallic platinum by reducing the moist salt with zinc dust, but the resulting platinum is contaminated by any impurities in the zinc and requires further treatment, including ignition, before it is fit for sale. Consequently it is preferable to decompose the salt by heat when the following reaction occurs:

$$3(NH_4)_2PtCl_6 = 3Pt + 16HCl + 2NH_4Cl + 2N_2.$$

Although it is an easy matter to ignite a few grammes of either of these salts under laboratory conditions, the decomposition of 50 kg. a day presents an engineering problem. The best solution of the problem was not obtained at the first attempt, but a comparatively simple arrangement of plant has now been in use for several years, and fulfils the essential requirements of:—

(i) high purity of product;
(ii) trouble-free operation;
(iii) low cost of operation and maintenance;
(iv) efficient collection, removal, and neutralisation of the fume.

The dry salt is placed in Vitreosil trays which are slowly heated in muffle furnaces fired by gas. Particular care must be taken whilst heating the material from 310-370° C., after which the temperature is raised to 900° C. to complete the removal of volatile matter.

In accordance with the recommendation of Treadwell, the salt is wrapped in filter paper to reduce losses during decomposition. Treadwell also says there is a risk of the formation of volatile chlorcarbonyl compounds due to the action of carbon monoxide on the decomposing salt, but losses due to this cause can be avoided by careful operation.

The fumes evolved from the decomposing salt are drawn away through a Cronite tube, an alloy containing nickel, chromium and iron, into a sublimate box, where most of the sublimate settles, and thence into a flue leading to a central scrubbing plant where the hydrochloric acid is neutralised.

As the fumes are particularly unpleasant, it is important that the ammonium chloride sublimate should not be allowed to settle out prematurely and block the fume pipe. When decomposing palladosammine chloride it is advisable to place a small gas burner under the Cronite pipe as the fumes contain much more ammonium chloride than the fumes from the platinum salt:

$$3\,Pd(NH_3)_2Cl_2 = 3\,Pd + 4\,NH_4Cl + N_2 + 2\,HC1$$

and there is more likely to be trouble from blockage of pipes and flues.

* * * *

SOME OTHER LARGE PLANTS

For the sake of the serious student interested in large-scale refining, we shall summarize the procedures in three more large plants. No new methods will be introduced, but it will be observed that the choice and order of procedures will be determined by the ratio of metals that are present.

The Copper Cliff Plant. A paper entitled RECOVERY OF GOLD FROM BALBACH-THUM SLIMES AT COPPER CLIFF, ONTARIO, by Frederic Benard, appearing in Metals Technology of February, 1938, gives an excellent description of this refinery. The problem resembles in some ways that of the Raritan Copper Works. Crude copper is refined electrolytically; the sludges from the copper cells are then refined by the Thum (or Balbach-Thum) silver method, much like that used at Raritan. The sludges from these silver cells, however, contain much more platinum and palladium than those of Raritan, and the procedure changes here.

Because of this high percentage of platinum metals, acid methods are now employed. The slimes are dissolved in aqua regia, and the gold precipitated by ferrous salts, in a manner quite like that given in early chapters of this book. The dissolved platinum metals are concentrated (as in our Stock Pot) by a metallic precipitant, in this case scrap iron, and shipped to the plant at Acton, England, for further treatment. The gold, which came down as the familiar brown powder, runs about 995 fine, and is put through a re-purification in Wohlwill cells. The paper describes the equipment and the method of disposing of fumes, and gives a flow-sheet.

The Plant at Montreal East. This plant refines copper that contains some gold and silver, but practically no platinum metals. In many ways the procedure is the same as that used at Raritan, except that there are no gold cells—only copper cells and silver cells. The sludge obtained from the silver cells contains high quality gold —gold which after a treatment with boiling concentrated sulphuric acid is ready to be melted down for market.

A paper entitled RECOVERY OF PRECIOUS METALS FROM ELECTROLYTIC COPPER REFINING at the Canadian Copper Refiners Plant, Montreal East, Quebec, by C. W. Clark and A. A. Heimrod, describes the plant and its equipment in detail. It is published in the Transactions of the Electrochemical Society, pages 437 to 450, 1932.

The Recovery at Old Hickory Powder Plant. This particular plant was unique, and probably will remain so. It was built hurriedly in 1920 for one purpose—to recover the finely-divided platinum from the magnesia contact masses used in making sulphuric acid, and left in the hands of the War Department after the Armistice. It is mentioned here because the story proves how hastily-contrived equipment can, in an emergency, accomplish much. The procedure is now outmoded, the funds were limited, the time short, and the personnel insufficient. But 343,241 pounds of dirty contact mass were worked over and 8,812 troy ounces of platinum were recovered, all within about four months. An article entitled RECOVERY OF PLATINUM FROM USED CONTACT MASS AT THE OLD HICKORY POWDER PLANT, by A. L. Kibler, in the Journal of the American Chemical Society, vol. 14, pages 636-641, July, 1922, describes the equipment and procedure.

The Royal Mint at Ottawa, Ontario. In a handsomely illustrated paper entitled REFINING $2,000,000 OF GOLD PER WEEK, A. L. Entwistle, writing in Canadian Metals and Metallurgical Industries (Toronto), vol. 1, January and February, 1938, describes the treatment of crude gold bullion at the Royal Canadian Mint Refinery. When in 1914 it was found necessary to enlarge the plant, the Miller chlorine process was installed, and is still the main procedure in the new building erected in 1936. Only a few small electrolytic cells are occasionally used on bullion suspected of containing platinum metals. This bullion is chlorinated to about 97 percent gold, then treated by the Wohlwill process and the platinum metals recovered from the electrolyte. Entwistle's paper describes the routine of the reception of bullion, its testing and purchase, the equipment and procedure of the Miller process, and concludes with statistics on the plant's efficiency.

APPENDIX

CHAPTER A. MELTING THE PRECIOUS METALS

Part I. Platinum and its group. Fuel and equipment. Melting small lots of platinum scrap. Working and annealing. Melting platinum filings. Defective platinum. Platinum sponge and black. Large melts. Making up platinum alloys. The electric furnace. The oxygen torch. Spectacles. Crucibles and refractories: lime; zirconia; sand; contamination from the crucible; other refractory materials. The platinum group and occluded gases. Melting and working palladium. Melting the other platinum metals.

Part II. Melting gold and silver. Sources of information. Melting the fine gold powder. Melting lemel. Melting clean scrap. Deoxidizers. Fluxes. Casting precious metals. Making up new alloys. New light on old metals.

* * * *

PART I. PLATINUM AND ITS GROUP

The story of man's early efforts to melt platinum, culminating in the invention of the oxy-hydrogen blowpipe, forms one of the most dramatic chapters in the history of this metal. While much has been written on this subject, as well as upon the chemical and physical properties of the metal, the literature gives few details of the actual present-day technique of melting it, specially in small quantities. Platinum is being melted every day, not only in the refineries where it is sold, but also in the host of small jewelry shops and dental laboratories where it is worked. Since this book is written primarily for the small organization, this chapter will devote considerable space to this subject of small melts.[1]

FUEL AND EQUIPMENT

The melting point of platinum is so high—3191° F., or 1755° C.—that the furnace commonly used for melting gold is not adequate. A blowpipe burning city gas, in combination with oxygen from a

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[1] This section is adapted from THE MELTING OF PLATINUM, by C. M. Hoke, The Metal Industry, pp. 433-435, November, and pp. 468-470, December, 1936.

cylinder, is the device most generally used for melting platinum. When city gas of proper composition or pressure is lacking, hydrogen from a cylinder may take its place. Acetylene with oxygen provides heat enough for the purpose, indeed more than enough; but because of its tendency to form the brittle platinum carbide, as well as because it may melt the crucible, the oxy-acetylene flame is not often used in this work. The electric induction furnace is used in some cases, as will be described shortly.

This need for a high temperature has brought about some misunderstanding. Thus a textbook will say: “Platinum can be melted only with difficulty,” meaning that the melting point is high. This does not mean that the melter’s task is laborious, however. On the contrary, if he has proper equipment the task is accomplished quickly and without the slightest hardship.

Many kinds of crucibles have been used, as we shall see later. The most popular are those made of lime, or of a composition resembling the so-called sand crucibles used in melting gold. No flux is required.

The sketch shows a convenient arrangement of equipment. A one-inch gas supply pipe, with a $^3/_8$ inch service cock, will furnish enough gas for the average jewelry shop. The torch shown is suitable for melts up to 100 ounces, and smaller models are available for the smaller shop.

Melting a small quantity of platinum.
Courtesy of Hoke Incorporated.

Since platinum volatilizes appreciably under the oxygen flame (possibly through simple evaporation, possibly through the formation of oxides that are gaseous at high temperatures, then decompose on cooling) it is wise to use a torch that is big enough to accomplish the melting quickly and without undue “soaking.”

MELTING SMALL LOTS OF PLATINUM SCRAP

In a jewelry shop that makes platinum jewelry, clean scrap may be melted five or six times a day. We shall first describe the melting of a small quantity, 100 pennyweight or less. A melt of this size is usually made in a sand or clay crucible wide at the base and low on one side, as shown in the sketch. Usually this crucible is set inside another larger crucible, or perhaps in a cavity carved out of a silica insulating brick, to conserve heat and protect the table beneath.

The sheet-iron screen serves merely to prevent the scattering of small bits of precious metal. A canopy of the type used in annealing is not suited to this purpose as it throws the heat back into the operator’s face. Asbestos board protects the table.

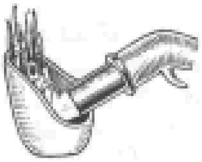
The rest of the equipment is shown in the sketch—tongs, hammer, anvil, dark spectacles, the torch with its hose, and the oxygen cylinder with its regulator and gauges. Since the melting of clean platinum produces no unpleasant fumes no flue is needed, and the entire outfit is portable.

The beginner is advised to learn how to melt scrap or clippings before attempting to melt filings.

The clippings are stacked up against the high side of the crucible. First the worker acquaints himself with the torch, turning on the gas and lighting it, then slowly admitting oxygen until a clear blue flame, with a noticeable roar, is obtained. If the crucible is new, he anneals it lightly by passing a flame over it to drive out moisture. The flame is then turned directly upon the metal, and if the flame is right, the edges of the metal will melt and run within a few seconds.

A slightly oxidizing flame is used; with too little oxygen the flame is yellow and sooty, not hot enough to melt platinum but capable of embrittling it through the formation of a carbide. If too much oxygen is used, the flame is apt to blow out, is too cool to melt platinum, and is also capable of embrittling it through causing adsorption of oxygen.

A few minutes’ practice is usually enough to enable even the beginner to get a satisfactory flame. The metal soon flows down and runs into a globule. The torch should be held at an angle—not straight up-and-down—playing upon the bottom of the crucible, and slanted so that the products of combustion are not reflected directly back upon the torch nozzle. Nor should the torch be held too close to the molten metal, otherwise the nozzle may melt.



Angle at which torch should be held.

Within a very few minutes 100 pennyweight of platinum will be molten; three or four minutes is about average time with the torch shown. If the metal does not melt promptly, it is because the flame is not right; perhaps the gas volume is inadequate; or the oxygen volume is too high or too low.

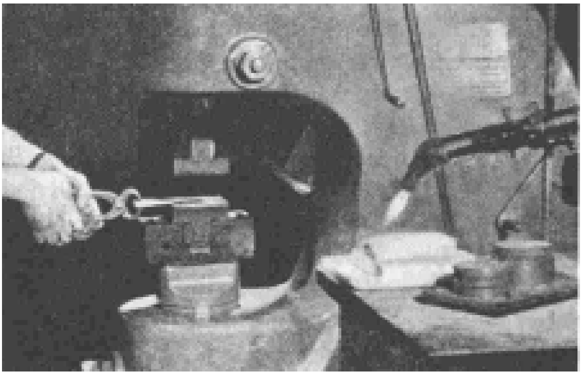
The next task is to mix the metal thoroughly by moving the flame around over it so as to revolve the molten metal; in that way any unmelted lumps will be liquefied. The metal should run around in the crucible like a little pool of mercury.

The worker next removes the flame and shifts his dark spectacles up onto his forehead. Then, with a wet tongs, he pushes the button (which by this time has solidified) out of the crucible, and places it bottom upward on a piece of clean refractory. The button will be rough, from its contact with the crucible, and will need smoothing. The worker promptly replaces his spectacles and turns the flame on this rough surface for a few seconds, long enough for it to run smooth, while any beads of sand from the crucible will slip to the edge. This process, usually called “sweating” or “flushing,” should always be carried out on a highly refractory surface such as a lump of lime, or the bottom of an inverted sand crucible.

WORKING AND ANNEALING

While the button is still white hot, it should be hammered hard on the anvil and shaped into a square block or bar. This hammering does more than shape the metal, however; it proves its quality, for if impure it will split under the hammer. Also, it makes the metal dense and hard, so that it keeps its polish when made up into an article of commerce. During this treatment the surface of the platinum may take up a thin film of iron, which should be removed by a hydrochloric acid dip.

The hammering sometimes leaves grooves in the metal which are too deep to be obliterated by the rolls; these may be easily removed by sweating. Sometimes the hot metal is placed under a drop-hammer in a die; this gives a dense and firm texture with little effort on the part of the workman.



Hammering a block of hot platinum.

Finally the block is cooled, then rolled, drawn or spun, during which treatment it hardens and will require occasional annealing. This is usually accomplished by passing a hot oxy-gas flame over it, or it may be heated in a gas muffle that is open to the air. Annealing with a smoky flame, or in a reducing atmosphere, is not advised as it might form carbides. Iridio-platinum requires a somewhat higher annealing temperature than soft platinum,

(For further details on the working and annealing of this group, the reader is referred to the books and papers mentioned in Chapter E, especially the following: PROPERTIES OF THE PLATINUM METALS, by Wise and Eash; FABRICATION OF THE PLATINUM METALS, by C. S. Sivil; and METALS OF THE PLATINUM GROUP, by Atkinson and Raper. Sivil's paper also gives a particularly interesting account of the early methods of melting, and Wise and Eash recommend optimum annealing temperatures of the various alloys.)

MELTING PLATINUM FILINGS

It takes longer to melt 100 pennyweight of filings than 100 pennyweight of clippings. For one thing, a gentler flame must be used or the small filings will be blown about. In addition, the many facets reflect the heat and make the process slower. Aside from these details, it is no more difficult to melt clean filings than clippings.

Dirty filings are another story. This brings up one more difference between platinum and gold: gold is readily freed from many impurities by a simple melting, but it is not easy to refine platinum in the same way. Under the flame, the platinum tends to combine with the impurities to form brittle compounds, such as the carbide. It is much easier to remove the impurities before melting the filings, and if this cleaning is properly done, the melting is easy.

As in the case of scrap, the filings are piled up against the high side of a sand crucible. Most workers prefer to handle 50 pennyweight or less at a time. When they have more than that on hand, they first make several small buttons, then melt them together into one large button.

A gentle flame is turned on at first, with enough oxygen to give the proper temperature, but without blowing or noise. This is directed at the bottom of the stack of filings, and slowly brought toward them. Soon the outer layer of filings will melt and run together. With that the flame is brought closer, and its pressure increased gradually, while the worker takes care to keep the bottom of the stack hot.

From here on the method is practically the same as for clippings. The metal runs down into the bottom of the crucible, the flame is moved around over it to make sure that all parts are molten. Finally the button is lifted out and sweated as before, and hammered while hot.

This is another instance where platinum differs from gold; gold is not hammered when hot, but platinum is better the hotter it is when hammered. When a crucible of molten gold cracks, the result is often disastrous; the gold seems to find the smallest crack and go through it immediately. But molten platinum acts quite differently; its surface tension is so high that the metal rounds up like a drop of mercury, and will remain on top of even a sizable aperture. This high surface tension is a characteristic of clean metal; when impurities are present the drop will flatten as it cools.

A melt of 100 pennyweight of clean filings should not take more than ten minutes. A skilled worker will accomplish it in much less time.

DEFECTIVE PLATINUM

Slovenly refining is the most frequent cause of defective metal. Incomplete refining may leave gold, silver chloride, copper, organic dirt and possibly other things in the filings. Gold shows itself by a bronze or purple stain on the crucible; silver chloride leaves a gray or black stain and gives a characteristic smell; copper colors the flame green during the melting operation. Organic dirt shows itself in a smoke that rises from the metal during and after melting, and the surface of the button may be dark or rough. Sometimes the button will flatten as it cools, instead of solidifying in a smooth globule.

A button that smokes or has a bad surface should be hammered with care, as it may be extremely brittle. Some workers try to "save" such a button by remelting it and letting the flame play on it for several seconds in the hope that the dirt will burn out. Such a procedure is rarely successful, and there is always a detectable loss of platinum. It is much easier and more economical to clean the filings thoroughly before melting them.

A second cause for defective platinum is improper melting. Sometimes platinum that has been properly refined will yield a button which when hammered will prove to be brittle, or pitted, or "double." All of these faults are caused by improper melting. They are easily corrected in one remelting, and should not occur after the operator has acquired a little experience.

Thus the beginner may find that his platinum bars will split under the rolls in a way that suggests alligator's jaws, or his platinum sheet will crack at the edges. When this happens, and the color of the crucible indicates that the platinum contained no metallic impurity, the chances are that an improper flame was used. Perhaps there was not enough oxygen in the flame; this may give a warty button of a dark color. Or perhaps there was too much oxygen, which was absorbed while the platinum was molten and did not have an opportunity to escape as it cooled; this gives a rough white button, which under close examination will be found to contain minute bubbles or pores.

Pits in the surface of an otherwise good button may appear when the metal is not properly sweated, being caused by beads of sand from the crucible.

"Double" platinum is caused thus: part of the metal melts and runs down into the bottom of the crucible, where it cools; later more metal melts and runs down over it, and the two layers do not flow together. Subsequently, when the button is rolled, a blister will show where the two layers failed to join. If a worker suspects doubles he will anneal the metal after rolling, as this makes the doubles more conspicuous. The way to avoid this is simply to keep the bottom of the crucible hot all the time, and to be sure that the metal is truly molten before it is allowed to cool.

The remedy for all these imperfections—brittleness, warts, pits, and doubles—is simply a remelting.

PLATINUM SPONGE AND BLACK

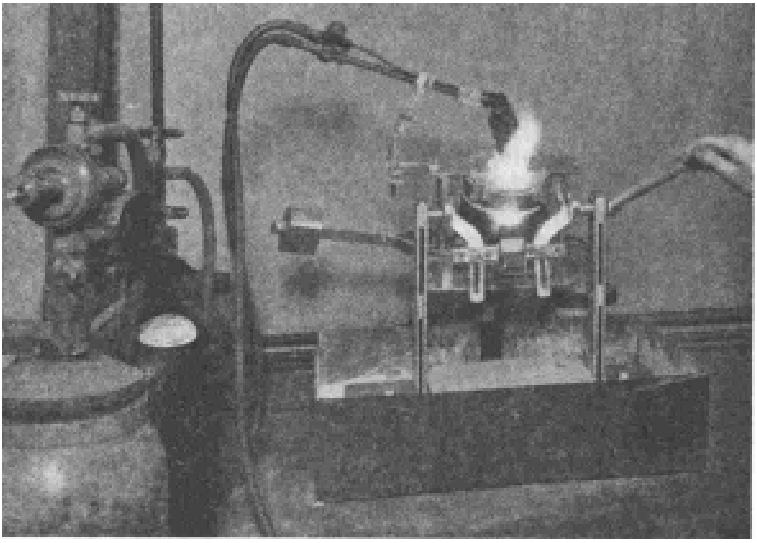
Platinum that has been through the acid refining is usually recovered as sponge, sometimes as black. The refiner does well, when burning the orange powder, to heat it until the sponge has contracted into a sort of clinker, so that it will not blow about under the flame. Some workers compress it firmly in a mold. Clean sponge is a pleasure to melt, and is handled the same as clean coarse filings. The black, however, being much more finely divided, must be handled with caution, a small and very gentle flame being applied at first, until the powder on the surface has run together.

LARGE MELTS

When large melts—40 ounces or more—are made, lime crucibles are preferred. These will be described later in detail. Lime holds the heat excellently, nor does its surface soften to permit the metal to sink into it. Sometimes two torches are used at once. Usually the metal is fed in a little at a time from ladles previously filled and set close at hand. With large melts it is impossible to stir the metal with the force of the flame; some other method of mixing must be devised. Sometimes a carbon rod is used; sometimes the crucible is set into a support with a long handle and semi-spherical base; as the metal melts the worker tips and tilts this support on its rounded base, effecting proper mixing.

When small amounts of metal are melted, the button cools so quickly that it is practically impossible to pour it into a mold.

Larger melts retain enough heat to permit pouring if desired, and usually they are cast into blocks, the forms being made of hard carbon sometimes lined with thin platinum foil.



Pouring molten platinum.

MAKING UP PLATINUM ALLOYS

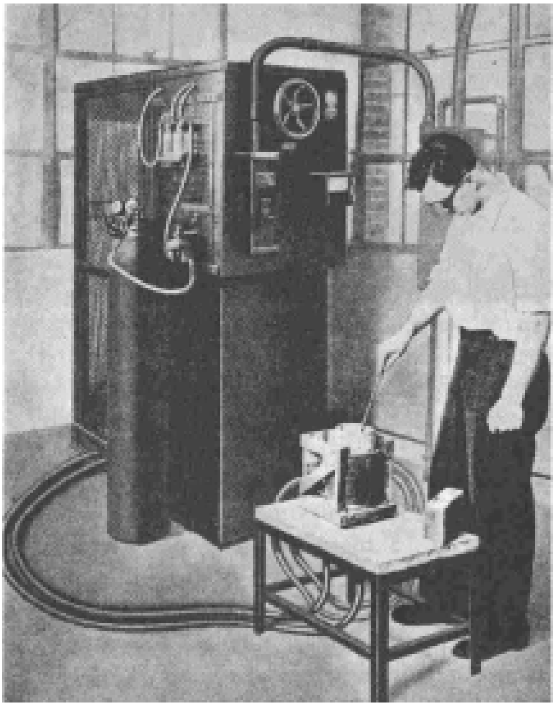
The lridio-platinum alloys are usually made by mixing platinum sponge and iridium sponge in proper proportion, and then melting. The combination has a higher melting point than that of pure platinum, but the technique presents nothing new.

Within the last few years many other platinum alloys have been studied, of which the most interesting are those used in dentistry. These are sometimes quite complex, containing gold as the major constituent, with silver, copper, platinum, palladium perhaps, and sometimes other metals, in varying proportion. When the proportion of platinum is low, these are prepared in the gold-melting furnace, the low-melting ingredients being melted together first, and platinum, usually in small pieces, being added toward the last. Or, gold and platinum may be melted together with the oxy-gas flame, the same as platinum alone, and this alloy is then melted in a gold-melting furnace with the other ingredients.

However, as the requirements of the dental profession have become more exacting, greater uniformity has been demanded in the manufacture of alloys. The electric furnace of the high-frequency induction type has proven very satisfactory for this work.

THE ELECTRIC FURNACE

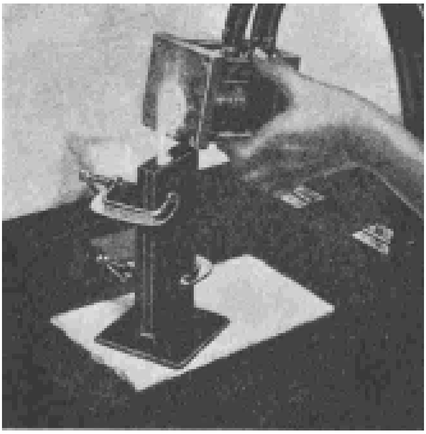
Ever since the Ajax-Northrup induction furnace was first developed, in about 1916, its application to the precious metal field was inevitable. Its cleanliness, convenience, freedom from fumes, and the startlingly high temperatures it produced, have led many workers to experiment with it. Its first application in this field was in the melting of silver, where it has been notably successful, and it is now being used also in melting the ordinary gold alloys, as



Ajax-Northrup High Frequency Induction Furnace. The converter is in the left background, the furnace proper in the foreground.

well as the special dental alloys. It has been extremely useful in basic research on the platinum alloys.

The outfit consists of two main parts, the converter which changes currents of commercial frequency into the high-frequency current, and the furnace proper. The latter is essentially a metal coil through which the high-frequency current oscillates. When a crucible containing metal is placed inside this coil, the electric eddy currents induced in the metal quickly raise its temperature to the melting point or beyond. Theoretically there is no limit to which this temperature can be raised; the practical limits are determined by the refractory that contains the melt, and the wishes of the operator.

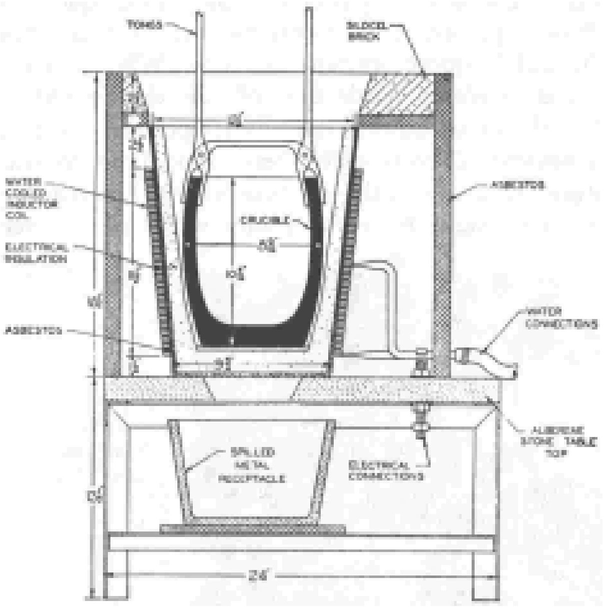


A very small Ajax-Northrup furnace. A type used in research work on the precious metals.

The furnace proper, or coil, may be small enough to be lifted bodily for pouring. Another convenience of the induction furnace is that it automatically stirs the melt—the eddy currents within it cause active turbulence in all parts of the metal. This is especially desirable in making up complex dental alloys with their many constituents. It is calculated that one plant alone has already melted up more than $10,000,000 worth of gold and platinum-gold alloys in a furnace of this type.

A final advantage of the induction furnace is that the atmosphere surrounding the melt can be controlled perfectly. Air can be admitted or excluded; hydrogen, nitrogen, or other gas can be substituted; or the whole operation can be carried on in a vacuum. These possibilities have been exploited by the research metallurgist as well as by the conscientious manufacturer.

Up to the present, however, the electric furnace has not supplanted the oxygen torch for the routine melting of the simple platinum and iridio-platinum alloys, either in large or small lots.



Ajax-Northrup furnace for precious metals, suitable for melts of a few pennyweight or as much as 1000 ounces of gold.

This is due mainly to the great difference in costs, the converter especially representing a sizable investment, while the oxygen outfit is within the means of even the humblest jewelry shop.

THE OXYGEN TORCH

Dr. Robert Hare of Philadelphia, the inventor of the oxy-hydrogen blowpipe, was the first to melt platinum in the modern manner; that was in about 1847. In 1859 the French chemists Deville and Debray designed an improved furnace for the purpose, consisting of a blowpipe and lime crucible. Innumerable improvements in details have been made since then, but the same principles are being used to-day.

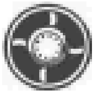
The simplest oxy-hydrogen or oxy-gas blowpipe consists of little more than two pipes and perhaps two stop-cocks. The early ones, which used both gases under fairly high pressure—up to 220 lb. per square inch—were apt to back-fire and burn inside the tubing, with resulting damage to the blowpipe and possible danger to the operator. With the advent of platinum as a fashionable jewelry metal, in the first and second decades of this century, many improvements of torch design appeared, attention being given to safety

Melting platinum with the oxygen-gas torch.

and efficiency. The rapid growth of the compressed oxygen industry was a big factor in the vogue of platinum. Indeed, without cheap and available oxygen, platinum would still be a laboratory curiosity.

By 1912 or so, it was a common sight in the larger jewelry shops to see the two large cylinders, one with low-pressure (200 lb.) oxygen, the other sometimes containing hydrogen, but much more often simple city gas compressed to the same 200 pound pressure. But early in that decade, Sam W. Hoke of New York City conceived the idea of a torch that would use city gas at ordinary house pressure—less than a pound—in conjunction with the inexpensive high-pressure oxygen. This was a much more convenient and economical arrangement. A patent was granted, and many of the early Hoke models are still in use.

The Hoke patent involved a mixing device close to the nozzle of the torch, by which the gas in the outer tube was slightly rotated, through rifling of the barrel, and the oxygen in the inner tube was broken up into many small streams, with the result that the two were mixed in the proper proportion, in spite of the difference in pressures behind them. The small cut shows the mouth of the torch; oxygen comes through the many small holes in the central cap; gas through the four large outer passageways.



Mouth of a modern oxygen-gas torch

Other successful models utilized the old injector or Venturi principle to attain the same end—proper mixing of oxygen and fuel gas. By means of minor adjustments the torches were adapted to natural gas or to hydrogen, as well as to city gas.

One big problem was the material for the nozzle. The heat of the flame is sufficient to melt most metals promptly, especially if the torch be held in such a way as to let the flame play back upon it. Other metals, such as some high temperature steels, do not melt promptly, but form copious scale which soon drops off into the molten platinum. The last, as any platinum worker knows, may be a real calamity. The ideal material for a nozzle is of course platinum itself, and some large plants are indeed using platinum nozzles. For the ordinary shop, however, other materials had to be found, of which the best so far are certain nickel alloys; these do not melt if the flame is held at the proper angle, and such scale as does form is closely adherent.

SPECTACLES

The light emitted by molten platinum is such that lenses almost as dark as those used by the oxy-acetylene welder are required. Most workers find cobalt blue the easiest on the eyes. The temples should be designed for quick doffing and donning; complicated straps or buckles are not convenient.

CRUCIBLES AND REFRACTORIES

Lime

Lime was the first choice for a crucible material; fresh high-burned lime. It was troublesome—it quickly absorbs moisture and becomes useless; since it is a natural product coming in irregular lumps, the purchaser often had to pick over many pieces before finding one of the right dimensions, free from cracks. A cup-like cavity was carved in a square block, and the block bound in sheet-iron and provided with a handle for tilting. A cover consisted of a second block, carved in an arch, with two holes, one for the torch nozzle, the other for the escape of the products of combustion. A crucible cannot be used often, nor can it be stored, and it seemed that the worker spent a great deal of his time carving lime. But even with these disadvantages, lime is still in general use, especially for large melts or where special purity is demanded. It holds heat amazingly well. If bits of lime stick to the metal, they can be readily soaked off in hydrochloric acid. A big factor in its popularity is its cleansing effect on the melt, as it absorbs minor impurities after the manner of a cupel.

To-day, in plants that habitually make large melts, instead of carving the natural blocks, they granulate dry lime and press it into blocks with a hydraulic press, using pressures up to 150 tons to the square inch. These blocks are then bound in sheet-iron, in the same manner as before. For a melt of 400 ounces—8000 pennyweight—a lime block 9 inches across and 5 inches high, outside dimensions, properly carved, is adequate. Just before use the crucible should be heated slowly to drive out moisture.

Zirconia

Zirconium oxide and zirconium silicate, highly refractory materials, have been shaped into crucibles for this work, especially by some of the larger refineries and Mints. They resist heat remarkably well, and a crucible can be used scores of times, day after day. They have not the cupelling effect of lime, but in most other respects are excellent crucibles. Probably the one factor that stands in the way of their general acceptance is their cost.

Sand

When platinum first came into use in jewelry, most melts were made in the familiar Hessian type sand or clay gold-melting crucible, with one side broken down. Even to-day crucibles of this class that get broken in transit are used for this purpose. Shortly, however, J. Goebel of New York provided platinum-melting models of a similar composition, with the high side and a flat bottom. The flat bottom is important, especially when filings are to be melted, because it permits the flame to reach and melt all the small particles. One big fault of the broken-down gold-melting crucible is its tapered bottom, in which particles will sink and escape the flame.

Contamination from the Crucible

Some workers have reported that the sand or clay crucible is apt to contaminate the melt with silicon or iron. However, for ordinary shop and routine work, this contamination, if it occurs, is too slight to affect the metal's usefulness. It should be recalled that an oxidizing flame should always be used; a reducing flame—one of a yellow color—can reduce sand to silicon or lime to metallic calcium, both of which elements are taken up by the molten platinum to its detriment. No doubt some crucibles have been blamed for contaminations which in fact were caused by an improper flame.

Other Refractory Materials

Graphite or carbon is not a suitable crucible material, because of its tendency to combine with platinum when hot. For the same reason, if a carbon stirring rod is used, it should not be left in contact with the molten metal for any length of time, and when graphite ingot molds are employed, they should receive little if any pre-heating.

Crucibles made of fused quartz have been suggested, also those made of aluminum oxide (Alundum). These substances, however, melt at so nearly the melting point of platinum that they are unsuitable. It is true that the sand-clay crucibles also soften under the flame, but so slowly that the melting job is usually finished before this softening has done any harm.

Beryllia and thoria, on which some experimental work has been done, are promising refractory materials, but at present their cost discourages general adoption.

THE PLATINUM METALS AND OCCLUDED GASES

The fact that the platinum group metals can absorb gases, especially when hot, has been mentioned repeatedly. It has caused annoyance to the artisan and confusion to the student. The literature contains countless references to it. The exact nature of the process has been the subject of much discussion. One student will speak of it as “occlusion”; another as “absorption”; another will use the term “adsorption” to suggest that it resembles absorption but is not quite the same.

All the metals of the group show the tendency to some extent. Thus when platinum is heated strongly, no visible oxide is formed, but volatilization occurs. This may be a simple boiling away, but perhaps it may involve the formation of oxides that are volatile while very hot, then decompose on cooling into metal and oxygen. As we have just pointed out, if too much oxygen is present in the flame while platinum is being melted, some of it can be entrapped as the metal solidifies, to occasion minute bubbles or blisters.

The reader will recall that osmium and ruthenium, when heated in air, form volatile oxides. These oxides can be captured and reduced back to metallic form without much difficulty; indeed if osmium oxide touches the mucous membrane of the eye, it breaks down and deposits a film of metallic osmium in the tissues. Molten palladium absorbs very large volumes of oxygen, and sometimes visible oxides form and disappear and form again. As we shall see shortly, this peculiarity must be borne in mind when palladium is being melted. To the serious student, this is one of the most fascinating aspects of this fascinating group.[2]

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[2] For a comprehensive review, see DAS VERHALTEN DER EDELMETALLE UND IHRER KUPFERHALTIGEN LEGIERUNGEN GEGENUBER SAUERSTOFF IN FLUSSIGEM ZUSTANDE UND BEIM GLUHEN IN FESTEM ZUSTANDE. By E. Raub and M. Engel. Mitt. Forsch. Inst. Probieramts Edelmctalle, pp. 1-12, June, 1939.

MELTING AND WORKING PALLADIUM

Except for a few details, the procedures used in the melting and fabrication of platinum are employed with palladium and its ordinary alloys. Most workers prefer hydrogen (with oxygen) instead of city gas, but both combinations are being used. Lime is the approved crucible material, some workers finding that they do not get good results with the sand crucible. For very small lots a hollow carved in a charcoal soldering-block is adequate No flux is required, either with this or any of the other platinum metals.

Because of palladium's ability to absorb much more oxygen while molten, a slightly different melting procedure is demanded. Begin work by turning a full hot flame on the scrap palladium, which will melt promptly, the melting point being lower than that of platinum. When all the metal is molten, instead of removing the flame abruptly, as is done when melting platinum, the worker will slowly reduce the oxygen supply, and at the same time slowly withdraw the flame, so that the button may solidify while being bathed in a reducing flame.

As the metal cools, the occluded gases are expelled, and sometimes the button swells suddenly and solidifies with a rough surface. If this happens, turn a small gentle flame on the top surface until it just runs smooth, then reduce the oxygen supply and withdraw the flame slowly, as before. This gives the absorbed oxygen an opportunity to escape. Do not melt the entire button—only its top surface. This sweating may have to be repeated.

Palladium and its ordinary alloys are rolled and annealed in much the same manner as platinum, being given their first reduction while hot, though they can be worked cold. If gas has been occluded, the edges of the bar will crack, and sheet will open up like alligator's jaws, and the metal must be remelted.

Films of colored oxides form when palladium is heated moderately, and disappear as the metal is heated further, only to reappear when it cools. One way to get rid of these films is to quench the red hot metal in water, thus cooling it before the film has time to form. Another way is to pickle the palladium while warm in dilute formic acid.

MELTING THE OTHER PLATINUM METALS

In any history of the platinum metals, the student will find mention of a mode of fabrication, used before the invention of the oxygen torch, in which platinum sponge was strongly compressed, then heated, first gently, then as strongly as possible in a wind furnace, and forged while hot, then rolled down or drawn into wire. This method is called Wollaston's process, and while not as convenient as the method of fusion with the torch, it offers certain advantages, such as freedom from contamination from the crucible or from the gases in the flame; and it is still occasionally used to-day, especially in melting and working the rarer metals of the group. (The same principle, sometimes called "powder metallurgy," is also used in the manufacture of tungsten wire, among other things.)

The oxygen flame and the electric induction furnace are also used, sometimes all three methods in combination. When we recall that these metals all have high melting points, all tend to absorb gases when hot, and that at least two of them have highly volatile oxides, it is easy to see why these metals present such fascinating vistas of speculation to the research student.

Rhodium. The classic research on the melting and working of rhodium was done by William H. Swanger of the National Bureau of Standards, and reported by him in 1929. (See Chapter E of the Appendix for details regarding this and other publications.) The melting point is higher than that of platinum, and the tendency to absorb gases is even more annoying than with palladium, but it is perfectly possible to melt rhodium with the oxy-hydrogen flame, and, by manipulating the oxygen supply as the metal cools, to produce a fairly good button. However, for better results, Swanger suggests the following procedure:

First, clean rhodium sponge is pressed into pellets in a steel form, then heated and cooled in hydrogen. These pellets, now fairly firm, are next melted in vacuum in the high-frequency induction furnace. The ingots thus obtained have a smooth silver-white surface. These ingots are then remelted on lime with the oxy-hydrogen flame, and forged or swaged while very hot. In this way ductile wire of small size can be obtained.

Iridium. It is possible to melt iridium with the oxy-hydrogen torch, but the melting point is so near to the temperature of the flame itself that the process calls for great patience. Iridium melts more readily in the hotter oxy-acetylene flame, and if the acetylene-oxygen ratio is well adjusted, workable metal can be obtained. That is, metal that is workable at white heat. Even the best iridium so far produced cracks and crumbles when worked cold. Iridium has also been melted in the high-frequency induction furnace. Thoria crucibles were used, as with rhodium, and satisfactory results were obtained.

Ruthenium and Osmium. According to Atkinson and Raper, there seems to be no definite reason to exclude the possibility of melting and working these metals, in spite of their high melting point and volatile oxides, by modern powder metallurgy technique, using high temperatures and excluding air. Deville and Debray melted very small quantities of ruthenium with the oxy-hydrogen torch, but were unable to fuse osmium. Because of their rarity and restricted industrial application they have not received as much study as their sister metals, and the literature gives few details.

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PARTII. MELTING GOLD AND SILVER

Men who carry out the acid refining of gold are usually called upon to perform a number of related tasks, such as melting clean scrap into buttons for re-use, making up new karat golds, making castings, and the like. They may also have to choose the furnace and arrange its placement, purchase and care for crucibles, fluxes, ingot molds, and other equipment. Some of these matters have already been touched upon from time to time in this book.

SOURCES OF INFORMATION

To cover all the aspects of the gold melter's art would require a volume much larger than this one. Fortunately the literature is ample, so we shall call attention to some of the more valuable books and discuss here only a few points, including some that have been the subject of recent questioning or controversy. In Chapter E of this Appendix the reader will find descriptions (and in many cases prices) of many books and magazine articles, certain of which should be in the hands of every melter. We mention the following as outstanding: E. A. Smith's book *Working in Precious Metals*, (1934); Edward A. Capillon's paper *Melting and Casting Some Gold Alloys*, (1930); Leach and Chatfield's paper *Manufacture of Sterling Silver and Some of Its Physical Properties*, (1928); Daniel L. Ogden's paper *Melting Fine Silver in High Frequency Induction Furnace*, (1932); George S. Overton's book *How to Make Jewelry*, (1927); T. K. Rose's book *The Metallurgy of Gold*, (1937); Eugene W. Skinner's book *The Science of Dental Materials*, (1937) ; Thomas B. Wigley's book *The Art of the Goldsmith and Jeweller*, (1911); Tracy C. Jarrett's paper *Effect of Composition on Color and Melting Point of 10-K, 12-K, and 14-K Gold Alloys*, (1939); the same author's *Effect of Composition upon Physical and Chemical Properties of 10-K Gold Alloys*, (1939); and E. M. Wise's paper *High-Strength Gold Alloys for]ewelry, and Age-Hardening Phenomena in Gold Alloys*, (1929). This by no means exhausts the list of helpful publications.

MELTING THE FINE GOLD POWDER

The fine gold powder produced in acid refining is normally melted in a sand crucible in a gold-melting furnace. The purpose is to remove any residual impurities and to obtain a button that will be as near 1000 fine as possible.

Refiners often speak of this as one of their pleasantest tasks. The pure gold melts tranquilly to assume a sort of luminous transparency, very beautiful even through the melters' goggles, and it can be poured without spitting or turbulence into a shining yellow ingot.

As we say, it cools without spitting. That is because it does not absorb oxygen, even when molten. It might be well for us to pause here and recall a few facts that may offer an understanding of metal behavior. Most metals, such as copper and iron and nickel, unite with oxygen to form stable oxides; they unite slowly at ordinary temperatures, rapidly at high temperatures, and the oxides do not decompose on cooling. Platinum and palladium, as we have just seen, occlude oxygen when molten, only to give it up on cooling. Silver resembles the platinum metals in this respect, and the well-known spitting and crabbing of fine silver, when poured, is due to this peculiarity. But fine gold differs from all of these in that it does not absorb, or unite with, or take up oxygen, even when molten.

This characteristic is the basis of "fire" refining. It means that if oxygen is introduced into molten gold it will unite with any base metals that may be present, to form stable base-metal oxides. If these oxides can be floated or fluxed away, the gold will be purified.

This was brought out in Chapters V and XV of this book, to which the reader is referred. When nitre or saltpetre is heated strongly it releases oxygen gas; that is why we add a pinch of such a salt to the molten gold. We also add some borax, in which the base-metal oxides dissolve and are floated or fluxed away.

Chlorine is another gas which when hot forms stable compounds with base metals, but not with gold. Accordingly we can purify gold by introducing chlorine. This is the basis of the Miller process described in Chapters XXI and XXII; also of the practice of adding a little mercuric chloride, or ammonium chloride, or copper chloride, to the melt when purifying gold that is almost fine.

If platinum group metals are present in small amount in such gold, they can be removed by repeated treatments with nitre, passing off in the fumes. This fact is undoubtedly related to their tendency to take up oxygen when molten. Their removal by this means is not suggested as a method of separation, as there is no easy way to capture the volatilized metal. Chlorine and chlorides do not remove the platinum metals.

MELTING LEMEL

In Chapters V, XII and XVIII of this book, we mentioned the procedure for melting filings (lemel) into a button for subsequent acid refining. The purpose here is merely to get all the metallic particles into one lump, without regard to karat or working qualities. It is customary, but not essential, to carry out a few preliminary steps, such as the removal of iron with a magnet, and the burning out of grease and paper. In most shops the melting is done in a tall sand crucible in a gold-melting furnace, with calcined borax as a flux.

(There are on the market some prepared fluxes that are described as capable of “refining” lemel or dirty filings, meaning that they can remove certain of the impurities and produce a button that can be hammered and rolled. Such a button might be of approximately the same karat as the original metal, but on the other hand it might be much higher or much lower, depending upon circumstances that might change with every melt. It is obvious that such “refining,” while often a useful procedure, is quite different chemically from acid refining, in which fine gold is obtained, free from silver or other alloying element.)

As we said, this work is traditionally done in a gold-melting furnace. But if the reader has a platinum-melting torch, he is urged to consider the following letter, written by a veteran refiner of unusual skill:

"I used to melt my gold filings in a gold-melting furnace, using a big sand crucible and considerable flux. When you count the cost of the crucible, which can be used only once, and running the blower and gas for two or three hours, it is rather expensive. I find it is better to use the Hoke oxy-gas torch. Here is the idea:

"First burn the filings and take out iron with the magnet. Sometimes I use nitric acid, but not always. Use a large cut-down crucible, the same as for platinum, or break a cracked gold-melting crucible down low on one side. If using a new crucible, dip it into water first, as this prevents the crucible from breaking easily as moisture will be evenly distributed.[3]

"Rub boric acid inside the crucible to prevent sticking. Let the crucible stand in a clean iron tray while you melt, in case it tips over or any filings blow out. Put in only a little material at first and use a gentle flame, not much oxygen, gradually adding more material and using a harder flame as it runs into a button.

"After all the filings have been melted down, run the flame around the sides of the crucible, starting at the top, to melt down any little metal particles that may cling to the wall.

"Let the melt cool somewhat, then grasp the crucible with round tongs and turn it upside down and the button will fall out. If not, loosen it gently with a sharp tool, so as not to damage the crucible, which generally can be used several times.

"This plan is much cheaper than the old way, and takes no more than twenty minutes."

MELTING CLEAN SCRAP

When clean gold or silver scrap is melted down for re-use, every effort is made to keep the fineness and the working characteristics as nearly as possible the same as before. The process therefore is much more exacting than the melting of filings or scrap as a preliminary to acid refining, and it is not surprising that the process should have received considerable attention in the literature. Capillon's paper *Melting and Casting Some Gold Alloys*, and E. A. Smith's book *Working in Precious Metals*, are particularly helpful in this connection.

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[3] Note: Many experienced workers will disagree with this. In general every effort is made to keep crucibles as dry as possible.

Usually the scrap, after careful preliminary cleaning, is melted in a gas-air furnace or in an electric furnace, and boric acid is a popular flux, with or without powdered charcoal. It is well known that repeated remeltings may change the karat of gold alloys, by driving off part of the alloying elements, especially zinc. The temperatures of fusion and pouring are important, and the size and shape of the ingot molds have their influence on the success of the operation. All these details are discussed fully in the paper and book mentioned above.

Fine silver, in common with the platinum metals, absorbs considerable oxygen when molten, and expels it on cooling, with conspicuous spitting and crabbing. The same tendency to lesser degree is observable in Sterling silver and in gold alloys that contain much silver. The logical way to avoid this gas absorption is to use an electric furnace and melt in a vacuum or in an inert gas, but so far this practice has not become general. At present the most convenient way to avoid this gas inclusion, which is prone to cause blisters and brittleness, is to add a deoxidizer to the melt just before pouring.

DEOXIDIZERS

There are several substances which, when added in small amounts to gold and silver alloys, will take up the oxygen and pass it into the slag. They are sometimes called scavengers, or oxide-removers. Among the more successful ones are phosphor-copper and phosphor-magnesium-copper. Calcium boride is a third, suggested for gold alloys by E. M. Wise and tested by Capillon, who describes it as well as several others, in the paper referred to.

We sometimes hear stories of mysterious substances, which when added to gold alloys, to Sterling silver, aluminum bronze or other metals, have a magic effect and produce amazingly good results. Sometimes a workman will conceal this mystery treatment and demand extra compensation because of his secret knowledge. In almost every instance the magic is simply a good deoxidizer, properly used.

The amount needed is very small. Thus, one ounce of phosphor-copper is sufficient for a 100 *pound* melt; or $^1/_8$ of an ounce for a 200 ounce melt. It should be added ten minutes or less before the charge is pulled from the fire. It should be introduced in the form of small grains, and pushed under the surface and forced to mix well with all parts of the melt. The phosphorus unites with the oxygen and passes off as fumes or slag; the copper goes into the melt. In exact work, this small additional weight of copper must not be forgotten.

These deoxidizers should not be used with platinum, as the phosphorus will unite with it, instead of going off into the slag or escaping in the fumes.

FLUXES

The word *flux* comes from the root meaning to *flow*, but it has now come to apply to a wide variety of substances that are added to molten metals for one purpose or another.

Fluxes may be divided into four groups. Those (1) that introduce oxygen are used in removing oxidizable impurities from fine gold. Potassium nitrate (called saltpetre or nitre) and sodium nitrate (called Chile saltpetre) are the best of this group. The reducing agents (2) are those that remove oxygen by reacting chemically with oxides that are already present. To this class belong the many carbonaceous and organic materials—charcoal, sugar, dry sodium carbonate (called soda ash), argol, dry potassium carbonate (called pearl ash), potassium cyanide, and so on. Next we have those (3) that neither add oxygen nor take it away, but which form a coating that excludes it. Borax and boric acid are the commonest of these, and they further dissolve and flux off any base-metal oxides that may be present. To this same group belong fluorspar and powdered glass. Then (4) come the so-called tougheners—ammonium chloride, mercuric chloride and copper chloride, used in purifying gold that is almost fine.

These materials can have a powerful influence for either good or evil, and have commanded considerable attention in the literature. They have been mentioned often in this volume; in E. A. Smith's book, for example, several pages are devoted to the occasions and manner of their use; and the dealers in crucibles and supplies for metal workers are generous with helpful practical advice.

CASTING PRECIOUS METALS

The *cire perdu* or *lost wax* process of casting is very old, as one may learn by visiting any art museum. It consists of making a wax pattern, setting it in some material such as plaster of paris (called the investment), then heating the investment until the wax melts and runs away, and finally pouring molten metal into the cavity thus provided.

The modern dental laboratory has done much to transform this old art into a science—a science by means of which intricate designs can be reproduced accurately in metals of high melting point. Investment materials capable of withstanding high temperatures have been developed, and many tricks of technique have been learned. Platinum and high-karat gold jewelry (as well as dentures) are being cast to-day, in forms that were once considered impossible, by special processes described as economical and artistically satisfying. Patent applications cover different phases of this technique, about which more can be learned from dealers in metals and manufacturers of melting equipment.

MAKING UP NEW ALLOYS

This is the most exacting and the most interesting of the gold-melter's tasks. Within the last generation a host of new alloys have been made—white golds, pink golds, high-temperature dental golds, and others. Perplexing problems of manufacture and manipulation have arisen. The formulas of the different alloys, the conditions under which they are melted, poured, annealed and machined—all these have received deep study, as can be seen by a glance at the literature, to which the reader is referred. One of the best sources of information is E. A. Smith's book *Working in Precious Metals*, but later articles, appearing in the technical magazines, bring the subject up to date.

NEW LIGHT ON OLD METALS

The precious metals have been known to mankind for at least 5,000 years, and the melting and working of them was an art even in the days of King Solomon. But the recent studies on these metals have brought to light a wealth of new facts—facts that will grant wider scope to the artist, increased precision to the scientific worker, financial advantage to the wholesale producer, and increased responsibility to the man in the furnace room.

The craftsman of the past, hammering each article by hand, could tell by the feel of the metal when it was time to anneal, and if different articles responded differently, no harm was done. But with modern machine production, there must be no individual variation. We must know exactly when to anneal, and to what temperature, and all pieces will be treated the same. Color, karat, hardness, springiness, resistance to tarnish, and so on—all must be regulated and understood. A much more intimate and scientific knowledge of the nature of our metals and alloys is now demanded.

This intimate knowledge could not have been secured without certain useful tools, notably the microscope, the pyrometer, and the X-ray. The story of what they have revealed constitutes modern metallurgy.

When old-timers pick up a volume of modern metallurgy they are at first repelled by the technical terms and scientific diagrams. However, if they will start at the beginning and follow the author's train of thought, they will have the happy experience of recognizing old truths in a new dress. They will find explanations of facts that they had themselves learned by accident or experience. They will be able to say: "Why, that is something I knew all along but could not quite explain!" And finally, of course, they will see how to turn these new facts to their own advantage.

CHAPTER B

HAZARDS

The National Safety Council. Comparison of chemical and heat burns. First aid. First aid treatment for chemical eye burns. Neutralizers. Alkalies or caustics. Hydrochloric or sulphuric acid. Hydrofluoric acid. Nitric acid. Nitrous fumes. When handling sulphuric acid. Shower baths. Cyanide poisoning. Mercury. Hazards of the melting room; hazardous arrangement; crucibles; oxygen cylinders. Stains on the skin. Gas masks. Some articles to read.

* * * *

Several of the most potent chemical agents known to man—strong acids, caustic soda, and the deadly cyanide—are used in the refining of precious metals. Fumes such as sulphur dioxide, ammonia, chlorine, mercury vapor, and the brown gases produced by nitric acid, every one of which is a man-killer if present in sufficient concentration, must be handled and disposed of safely. We also have the hazards of the melting-room—the white hot crucible, the molten metal, and the terrific temperatures of the oxygen flame.

However, it is a fact that one hears only rarely of a serious accident in this work. Probably that is because precious metals are rarely entrusted to irresponsible workers. Possibly, also, their very preciousness makes for a sobriety of mind and builds up a psychology of carefulness. But the beginner must understand these hazards and their avoidance. Hence this chapter.

The National Safety Council, Inc., is a non-profit association devoted to the study of safety measures in industry. Among other activities it publishes pamphlets on the hazards connected with different processes, and recommends measures for their avoidance. The association maintains offices at 20 North Wacker Drive, Chicago, Ill., and all employers of labor should be familiar with its efforts.

We are indebted to the Council for its permission to quote the following paragraphs, taken from its copyrighted pamphlet *Chemical Burns, Their Nature and Treatment.*

“Chemical burns are often thought to be similar to heat burns, but this is true only in that both may cause destruction of body tissue. The object causing a heat burn may cool, or the person may withdraw from the object, and destruction of the tissues ceases. When contact is made with a chemical substance, the contact continues as long as the agent is present in sufficient concentration to destroy the tissue. Absorption must also be considered in treating chemical injuries, as this may cause illness or even death.

“The severity of chemical burns depends upon: (1) the concentration of the chemical, and (2) the duration of the contact. Generally, the first factor cannot be controlled, but the second may, and proper first aid rendered immediately is of outstanding importance.

“The successful handling of chemical burns calls for the complete removal of the irritating agent, or the administration of such treatment as will render the chemical inert.

“The importance of *immediate* first aid for chemical burns is indicated by the following experiments to test the action of several acids at different strengths:

“Four tests were made using a 70 percent nitric acid, a 76 percent sulphuric acid, a 37 percent hydrochloric acid, and a 99 percent acetic acid on three persons. In each case the burning could be noticed in five to fifteen seconds. Using the same acids in 25 percent concentrations, no burning was noted.

“To compare the effects of neutralization (using a 5 percent solution of sodium carbonate) with those of water, extensive tests indicated that the use of water, either in a large tank or from a running tap, was considerably better in treating acid burns than neutralization.

“If a patient’s clothing becomes soaked with corrosive fluid, burning will continue until the clothing is removed. Clothing should therefore be removed immediately, but efforts should be made to keep the injured person warm. The acid or alkali that remains on the skin should be removed by flushing copiously but gently with large quantities of water—warm if possible. Shock will be lessened if the water is warm, but speed is of greater importance, and if possible a stream of running water should be directed onto the burned area so that all the chemical may be washed away. The burned area may then be treated as any heat burn and covered with any suitable protection, preferably a water-soluble jelly.

FIRST AID

"Persons giving first aid often make the mistake of first applying an antidote. This treatment is not nearly so important as proper flushing with water. The immediate use of a neutralizing agent on an *unwashed* burn may *increase* the injury.

"According to some authorities, one of the most effective agents to combat burns is tannic acid. (This applies mostly to third degree or very serious burns. Sterile vaseline or anhydrous lanolin are often recommended for burns of lesser degree.) Many doctors are now using gentian violet in the form of a jelly for first, second, or third degree burns.

FIRST AID) TREATMENT FOR CHEMICAL EYE BURNS

"The seriousness of an eye injury is determined by (I) the strength and character of the chemical, (2) the length of time before treatment, and (3) the type of the first treatment. The importance of immediate first aid should be stressed. The mechanical removal of the chemical is very important. This can best be accomplished by careful washing. Water may be poured from a cup onto the bridge of the nose and allowed to run over the eyeball, which is kept exposed by holding the lid open, to flush out the inner surfaces of the lids. Do not pour water directly onto the eyeball. If a hose is used, be sure to use a slow stream so that the chemical may not be driven farther back under the eyelids.

NEUTRALIZERS

"There has been considerable controversy relative to the neutralization of acids and alkalies with suitable neutralizers. Recent research indicates that the best results may be obtained by the use of large quantities of plain, clean water. It is impossible to use too much water. The use of a soothing ointment or jelly (as recommended by the medical director or physician) in the after treatment has proven

Remember: For chemical burns, wash immediately with plenty of plain water.

beneficial. While the washing is going on, have the physician on his way to the scene, that he may give any treatment that he may deem necessary.

"The following paragraphs give brief descriptions of some important corrosive agents and suggestions for further first aid treatment—remembering always that flushing the burned area with water is the important first treatment, and that a doctor should be brought upon the scene as soon as possible.

ALKALIES OR CAUSTICS

"Here too, experiments have indicated that thorough washing with water, as a first aid remedy, is more effective than neutralization. No time should be lost before washing. Bathe freely with water, then apply a 2% solution of acetic acid, weak vinegar, or lemon juice. (Use care when making up caustic mixtures; for example the solution on page 17 with which you removed shellac from filings. Add the lye or potash slowly, and stir to avoid local overheating. Use similar care when ammoniating an acid solution, or acidifying an alkaline one—work slowly, stir well; and if the mixture spatters on skin or clothing, wash it off immediately with much plain water. —Ed.)

HYDROCHLORIC OR SULPHURIC ACID

"Bathe freely with water and apply a saturated solution of bicarbonate of soda.

HYDROFLUORIC ACID

"Bathe freely with much water. Apply powdered sodium bicarbonate or a 5% solution of ammonium carbonate. Boric acid is also recommended. Hydrofluoric acid is a violent corrosive, and skin burns heal slowly.

NITRIC ACID

"Bathe freely with water, then apply a saturated solution of bicarbonate of soda. One doctor advises scrubbing until as much as possible of the yellow pigment is removed, using soap, ammonia, and water.

NITROUS FUMES

"The fumes referred to are the red (or brown) fumes present when nitric acid is being manufactured or used. Beware of them. Don't think, even if you are big and healthy, that you can take chances with them. Don't think for one minute that you can get used to them. If you do get caught in them and have a suffocating cough, see a doctor.

WHEN HANDLING SULPHURIC ACID

"Never pour water into strong sulphuric acid. To dilute the acid, pour it into the water, slowly, and with constant stirring. Keep the acid away from combustible materials (such as wood or paper); it may start a fire. Keep acid containers away from heat, and out of the sun, to prevent building up pressure in them. Empty containers should be flushed out with water to prevent burns to those who handle them. Keep plenty of fresh water near at hand with which to wash acid off the body in an emergency."

* * * *

SHOWER BATHS

Laboratories and plants that handle acids in quantities are equipped with shower baths under which a worker can quickly step in case of emergency; a good type is one with a valve that operates when the worker steps on a platform. In most plants it is thought to be enough if a tub or barrel of water is available.

CYANIDE POISONING

The R. & H. Chemicals Department of the du Pont Company publishes a trade paper called *Modern Metal Finishing*, in the June 1936 issue of which a new antidote for cyanide poisoning is given. We quote:

ANTIDOTE

"Always have on hand a liter (quart) of a 1 percent solution of Sodium Thiosulfate and a carton of Amyl Nitrite Pearls. Directions for treatment:

1. Have patient inhale content of an amyl nitrite pearl.
2. Cause vomiting by giving soap water or mustard water.
3. Give 500 cc (about a pint) sodium thiosulfate solution by mouth.

"Repeat the above procedure every fifteen minutes. If necessary give artificial respiration until physician arrives.

"The rapidity of death from cyanide poisoning has been justly emphasized, for most patients die within 30 to 60 minutes. On the other hand, many linger for several hours; one lived over three hours. As long as the victim's heart still beats, the clinician should consider the case hopeful and treat it without delay.

"Be sure that cyanide never comes in contact with open wounds or skin abrasions. Always wash the hands well with running water after handling cyanide. Food should never be stored, handled, or consumed during cyanide operations. Keep cyanide away from all acids. Keep the container tightly closed when not in use; cyanide is weakened by exposure to air."

* * * *

MERCURY

Mercury poisoning can develop when mercury or amalgams are handled or heated, and when corrosive sublimate (mercuric chloride) is used as a flux in the melting of gold. The fumes appear at a low temperature and are extremely poisonous. They are heavy, so heavy that they are not carried off by a weak draft or a small exhaust fan; instead they settle to the floor, and seep through the crevices of the furnace or flue, and accumulate in the building The exhaust system must be designed with this fact in mind.

For five cents the Superintendent of Documents, United States Government Printing Office, Washington, D. C., will send a 4-page pamphlet entitled *Mercury Poisoning, Its Cause and Prevention,* issued by the United States Department of Labor. This is a concise statement explaining how mercury poisoning occurs, the signs and symptoms and what to do about it, and preventive measures. Any person who works with mercury, its salts or its amalgams, should obtain copies and post them where they will be read frequently.

To the precious metal refiner, the greatest hazard from mercury is probably that involved in opening the retort; see Chapter XVI. When the retort is opened it may still contain some mercury vapor. Unless the operator thoroughly understands this situation, he may receive enough mercury to cause poisoning.

Bare hands should not be used when handling mercury-bearing materials. Men should not smoke when there is a possibility of mercury fumes in the air, and food should not be eaten at a retort plant.

HAZARDS OF THE MELTING ROOM

Hazardous Arrangement. The National Safety Council estimates that hazardous arrangement is the principal mechanical cause of all serious injuries. Unsafe clothing and failure to use proper goggles can be included in this grouping. Unsafe planning or work, and unsafe methods and processes, are most frequently mentioned. For example, it is bad management to place the ingot mold so far from the furnace that the operator will have to walk many steps carrying a crucible full of molten gold. It is bad practice to leave obstructions on the floor of any factory, most especially ones in which hazardous materials such as strong acids or molten metals have to be carried about. It is bad practice to omit the guard crucible or other device to catch molten material in case a crucible breaks or molten flux boils over inside a furnace. It is bad practice to place gas cocks, electric switches, or other controls where they cannot be easily reached in an emergency. It is bad practice to leave off asbestos gloves and protective shin-guards and foot-gear when making large castings. Instances of bad practice can be multiplied indefinitely, but a little intelligent planning on the part of individual shop foremen, and vigilance on the part of the workmen, can reduce them to a minimum.

Crucibles. Many of the hazards of the melting room are connected with crucible failure. In Chapter A of this Appendix we mentioned the Crucible Manufacturers' Association, and their very informative pamphlet *How to Cut Crucible Costs*, which gives many safety suggestions. As we said before, this pamphlet may be had without cost from your crucible dealer, or from the Association at 90 West street, New York, N. Y.

Crucible users should realize, says this pamphlet, that a crucible is made of a material that undergoes certain changes under the influence of heat; that it must do work that no metal is capable of doing—that is, when the metal is molten and the crucible itself is at almost a white heat, it must still be strong enough to hold the heavy liquid metal and carry it safely to the mold. And it must do this over and over again. Therefore it is entirely within reason to say that a crucible must be handled carefully at all times, and particularly so when it is new. Suggestions on the handling of crucibles are given, some of which have already been mentioned in Chapter A. Proper storage with precautions against dampness are important. The use of properly shaped tongs is important. The reader is advised to have this pamphlet posted in a prominent place, and to refer to it often.

Oxygen Cylinders. The oxygen gas used when melting platinum is compressed in steel cylinders. The Interstate Commerce Commission regulations governing the conditions under which tanks can be shipped are such as to remove practically all hazards connected with tank construction. In addition, most cities have Fire Department regulations on the storage and handling of these tanks. If these regulations, and the suggestions offered by the oxygen dealers, are followed, the user need have no fears. It will be recalled that oxygen tanks can be found in almost every hospital that treats pneumonia, asthma, heart ailments, and some other disabilities; hence it is clear that such tanks bear a reputation for safety.

Cylinders are provided with a safety disc that will release the pressure in case the cylinder becomes unduly heated—as for instance if the building should take fire—and the gas itself is not poisonous. Keep tanks in a fairly cool place, not in the direct sun nor too close to a radiator; use no oil on any part of them; follow the advice of the dealer and you will have no hazard.

The regulators (pressure-reducing valves) used to regulate the oxygen flow, if handled as directed by the seller will work well for many years. Use no oil on any part of the regulator, torch, tubing, cylinder, or any connection or piping that carries compressed oxygen. This is important, because compressed oxygen can combine with oil to form an explosive mixture.

Pressure reducing valves have been known to rupture under abusive mismanagement. When this happens all the oxygen escapes. However, properly designed instruments are so made that there is no hazard to the user.

STAINS ON THE SKIN

Shortly after handling a solution that contains gold, the worker is almost sure to find purple stains on his fingers. Even a minute amount of dissolved gold will make a conspicuous and characteristic stain. Platinum and silver solutions cause unsightly black stains. Nitric acid produces a yellow stain. These stains themselves offer no special hazard to the worker, but ill-advised efforts to remove them can be dangerous.

Careful rinsing and scrubbing of the hands while the work is in progress will minimize these stains, all of which, once formed, are difficult to remove and usually remain until the outer layer of skin has been replaced.

Some foolhardy workers remove the purple gold stains by rubbing the spots with a lump of wet cyanide. This is unwise for two reasons: first there is the obvious danger of absorbing the poisonous cyanide through the skin; second, cyanide is sufficiently caustic to cause the skin to chap and peel, and it leaves the hands so roughened as to be rather worse off than before, both in appearance and in susceptibility to poisons and infections.

Different people respond differently to cyanide poisoning, but all authorities agree that it can be absorbed through small abrasions or tiny sores in the cuticle. Hence the worker is advised to use every care to avoid these metal stains, rather than to use drastic methods of removal.

GAS MASKS

The small shop, especially if it is equipped with a proper hood, will have little need for a gas mask. ~~A wet handkerchief draped over the face like a highwayman's mask will serve most purposes~~. The large plant, however, will probably want one. The chemical supply houses provide several designs for use with the various chemicals encountered in this work. In general it is well to depend upon fans and blowers, rather than to permit fumes to collect in such concentration as to suggest the need for a mask.

SOME ARTICLES TO READ

Publications of the National Safety Council, Inc., 20 North Wacker Drive, Chicago, Ill., especially CHEMICAL BURNS, THEIR NATURE AND TREATMENT.

CYANIDE POISONING. Modern Metal Finishing, issue of June, 1936; published by the R. & H. Chemicals Dept., E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.

MERCURY POISONING; ITS CAUSE AND PREVENTION. U. S. Department of Labor. Price 5¢. On sale by the Superintendent of Documents, Government Printing Office, Washington, D. C.

MERCURY POISONING. Pages 36-40 of the Information Circular No. 6966, U. S. Bureau of Mines, "Occurrence and Treatment of Mercury Ore at Small Mines," by M. W. von Bernewitz. This is out of print, but copies can be seen at many public libraries.

HEALTH HAZARDS IN CHEMICAL INDUSTRIES. By Henry F. Smyth, Jr., of the Industrial Toxicological Department, Mellon Institute of Industrial Research, Pittsburgh, Pa. Published by THE CHEMIST (bulletin of the American Institute of Chemists, 233 Broadway, New York), issue of April, 1939.

HOW TO CUT CRUCIBLE COSTS. Obtainable gratis from the Crucible Manufacturers Association, 90 West St., New York City.

CARE OF OXYGEN, ACETYLENE, AND OTHER COMBUSTIBLE GAS CYLINDERS. Distributed by the Air Reduction Sales Co., which has offices in many cities. General Office, 60 East 42nd St., New York City.

CHAPTER C

LAWS AND REGULATIONS

Federal Licenses for handling gold. Regulations concerning Government purchase of precious metals. National stamping law covering gold, silver and their alloys. Laws for stamping platinum. The Commercial Standards. Local ordinances. Standards in foreign countries.

* * * *

FEDERAL LICENSES FOR HANDLING GOLD

Shortly after the United States went off the gold standard in 1933, the Treasury Department instituted regulations for the licensing of persons who acquire, transport, melt or treat, export, import or earmark gold, or hold it in custody for foreign or domestic accounts. This obviously is of interest to the jeweler and dental technician handling gold. No fee is charged for these licenses, and the legitimate dealer or manufacturer has no difficulty in obtaining one.

At present writing, the person holding only small amounts of gold at a time requires no license; however, the regulations are subject to change without notice, and the reader is advised to obtain copies of the current regulations from time to time. These may be had from any Federal Reserve Bank, or from any Mint or Assay Office.

No federal license is required for the handling of platinum or silver.

In addition to the Federal license, some States and a few municipalities require local licenses of buyers of old gold, of pawnbrokers, dealers in second hand jewelry, and the like.

REGULATIONS CONCERNING GOVERNMENT PURCHASE OF PRECIOUS METALS

The United States Mints and Assay Offices will purchase gold, and usually silver as well. They are not authorized to buy platinum metals, and if these metals happen to be included with shipments of gold or silver, no payment will be made for them, and the refining charge may be increased by their presence.

The forms in which deposits will be accepted, the prices paid, etc., are all subject to change. At present deposits will be received in amounts of not less than one Troy ounce of gold, and the material must run at least 200 fine by assay. A copy of current regulations can be obtained for the asking from any Mint or Assay Office. Because the Government does not seek a profit on these operations, the price it pays is generally higher than that obtainable from commercial refiners. However, there is a wait of several days before the payment is made, and the conditions mentioned above are such as to exclude some kinds of materials.

NATIONAL STAMPING LAW COVERING GOLD, SILVER AND THEIR ALLOYS

The fact that gold and silver are used as money has meant that their stamping or marking has been regulated by law for many centuries. Such laws are usually thought of as a protection to the purchaser of jewelry or silverware, but at the same time they are a protection to the jewelry manufacturers as a group, since they tend to sustain public confidence in the industry.

Handy and Harman, precious metal dealers of Bridgeport, Connecticut, have published a book called *Handy Book for Jewelers* in which some of these laws are quoted in full.

The United States National Stamping Law, forbidding the importation, exportation, or interstate commerce of falsely or spuriously stamped articles of merchandise made of gold or silver, or their alloys, was enacted June 13, 1906. The full text of the act may be found in the *Handy Book* and in almost any law library or big public library. Ask for Rev. Stat. U. S., vol. 34, pt. 1, p. 260, 59th Cong., 1st Sess., Public Law 226. A summary quoted from the *Handy Book* covers its main provisions, as follows:

Gold. If an article is made of gold and is stamped gold, it must also bear a quality mark such as “10 karat” (10-K), “14 karat” (14-K).

If an article of gold is given a quality mark, the fineness by assay must not be lower than:—

Watch Cases and Flatware .... 003 less than stamped quality.
Other articles, not including solder .. .0208 (½ karat) less than the stamped quality.

However, the assay of a complete article, including solder, must not be more than .0417 (1 karat) under the stamped fineness per karat.

For example, the gold in a 14-karat watch case, free from solder must be at least .5803 by assay. The entire case, including solder, must assay at least .547 (13 karat). A gold ring, not soldered, stamped “14-K” must assay at least .5625 (13½ karat). The gold in a brooch stamped “10-K” must assay at least .3958 (9½ karat) and the entire brooch, solder and all, must assay at least .3750 (9 karat).

Silver. The silver in any article stamped “Sterling Silver” should assay .925, and the silver in an article marked “Coin Silver” should assay .900. The silver in an article, not including solder, must not be less than this by more than .004. For example, an article marked “Sterling Silver,” free from solder, must assay at least .921.

Soldered parts must not reduce the assay of the entire article, including solder, by more than .010 under the standard assays of .925 and .900, respectively, for sterling silver and coin silver. *For example*, an article marked sterling silver when melted, including solder, must assay at least .915.

Gold and Silver Used with Inferior Metals. An article made of an inferior base metal combined with gold may be marked “Rolled Gold Plate,” “Gold Plate,” “Gold Electroplate” or “Gold Filled” as the case may be. If any mark is used to indicate the fineness of the gold, it must be accompanied by one of these terms.

For example:—“10 K. Rolled Gold Plate,” “14 K. Gold Filled.”

The words “Sterling” or “Coin” alone or in combination with other metals cannot be used to describe a plated article.

For example:—“Sterling Plate” is prohibited.

Penalties. Violators may be fined up to $500 or be imprisoned up to three months, or both, at the discretion of the court.

LAWS FOR STAMPING PLATINUM

For some years after the introduction of platinum as a jewelry metal there was confusion regarding its marking, and much misbranding, adulteration and fraud took place. Three of the States in which considerable platinum jewelry was manufactured—New Jersey, New York, and Illinois—passed laws regulating the stamping of platinum and its alloys. And finally, on June 20, 1938, the National Bureau of Standards made effective a series of regulations, based on these State laws, that covers the entire nation. The full text of the New York State law will be found in the *Handy Book.* Copies of the new National Standard, known as Commercial Standard 66-38, may be obtained from the Superintendent of Documents, Washington, D. C., for 5¢. Briefly its main provisions are as follows:

Articles may be stamped “platinum” or “plat,” provided all parts of the article purported to be of platinum shall constitute at least 985/1000 parts platinum. If platinum assaying 985/1000 parts pure has been combined with gold the article must be stamped with the karat mark indicating the fineness of the gold in conjunction with the word or abbreviation of platinum, as “14K & Plat.” When platinum is alloyed with iridium, palladium, ruthenium or osmium, these articles must be marked in fractions designating the content of these metals. Merchandise bearing quality marks must also be stamped with a registered trade mark.

THE COMMERCIAL STANDARDS

The National Bureau of Standards, in co-operation with members of the precious metal industries, has formulated several other “Commercial Standards” that may be of interest to the reader. These Standards have their origin in the Bureau, rather than in the halls of Congress or the State Legislatures, and are a crystallization of established trade practices rather than any sort of governmental regimentation. They are subject to amendment when the interested industry feels that changes are advisable, and they are enforced with the co-operation of the Federal Trade Commission. Copies of the texts may be obtained from the Superintendent of Documents, Washington, D. C., price 5¢. Other standards may be proposed and possibly adopted in the future; the following are now effective:

Marking Articles made of Silver in Combination with Gold—Commercial Standard 51-35.

Marking Articles Made of Karat Gold—Commercial Standard 67-38.

Marking of Gold Filled and Rolled Gold Plate Articles other than Watchcases—Commercial Standard 47-34, with amendments of February 25, 1939. Bulletin TS-1942, of July, 1933, defines the terms “Gold Filled” and “Rolled Gold Plate.”

LOCAL ORDINANCES

In efforts to improve trade practices and to discourage traffic in stolen goods, a number of cities and states have passed laws of interest to the precious metal worker. Some of these regulate the sale of second-hand jewelry, especially second-hand watches. Others apply to itinerant buyers of old gold. Others require licenses of watch repair men or regulate the handling of jewelry “on memorandum.” Information on such local ordinances can usually be obtained from the local Chamber of Commerce, or from the National Better Business Bureau in the Chrysler Building, New York, N. Y.

STANDARDS IN FOREIGN COUNTRIES

E. A. Smith gives the following facts in his book *Working in Precious Metals,* page 395. We quote:

Platinum. For platinum the standard 950/1000 has now found general acceptance in most countries for the purpose of a quality standard for jewelry. (The International Jewelers’ Congress at Rome, May 5-7th, 1933, confirmed 950/1000 as the International Platinum Standard. See report in *Goldsmiths Journal,* June 1933, page 257.)

Gold. For coin the gold standard in most countries is 900, exceptions being Great Britain, which has adopted 916.6. This higher standard is also in use in Brazil, Chile, India, Newfoundland, Peru, Portugal and Turkey, whilst Egypt is 875.

For gold plate and jewellery the most universal standards are 750 and 585 (or 583).

Lower standards of 375 are used by Great Britain, Esthonia and Tunisia, and 333 by Germany, Italy, Bulgaria and Portugal

Silver. The standard of 900 is very general for silver coin In Great Britain the standard is 925 (temporarily lowered to 500).

In some countries lower standards are in use, especially for subsidiary coins.

For silver wares various standards are in use. The 925 standard is the one current in the British Empire and the United States, the so-called Sterling silver. The silver exported by England, too, is generally of this standard.

France manufactures 950 in larger objects for the home market, and frequently 800 in smaller articles.

The Scandinavian countries, the Netherlands, Czecho-Slovakia Austria, Portugal, Egypt and Bulgaria use standards between 850 and 830.

Germany manufactures 800 for the home market as well as for export; and in many countries, owing to German influence, the 800 standard is current. Manufacturers in Germany, however, are discussing a change from 800 to 835 as the lower quality alloy tarnishes somewhat readily. The 835 on the contrary is regarded as satisfactory.

* * * *

The Canadian Precious Metals Marking Act is quoted in the *Handy Book.* The magazine *The Manufacturing Jeweler* for January 4, 1940, page 7, gives a helpful summary of the principal provisions. Complete copies of the Act may be obtained from the King's Printer, Ottawa, Canada; price 10¢.

CHAPTER D

A LIST OF DEALERS

Buyers of precious metals. Dealers in chemical apparatus and supplies.
Dealers in supplies for Jewelers. Dealers in special
equipment and machinery.

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This list is by no means complete. There are many reputable dealers in addition to these few. Several of the firms here listed have branches in other cities. The telephone Red Books, and the trade catalogues mentioned in Chapter XX, will provide many more names.

Buyers of Precious Metals

With few exceptions, the firms listed below also sell gold, silver and platinum in one form or another, for industrial or scientific use. The reader is advised, before shipping precious metals, first to confirm these addresses, and second, if dealing with persons not on this list, to ask his bank for a report on their credit rating.

CALIFORNIA

Pacific Platinum Works, 814 So. Spring St., Los Angeles.
Wildberg Brothers Smelting & Refining Co., 635 So. Hill St., Los Angeles.
Shreve and Co., Post and Grant Sts., San Francisco.
S. B. Gracier & Sons, 212 Stockton St., San Francisco.
Western Gold and Platinum Works, 589 Bryant St., San Francisco.
Wildberg Brothers Smelting & Refining Co., 742 Market St., San Francisco.

CONNECTICUT

Handy & Harman, Bridgeport.
J. M. Ney Co., Hartford.

ILLINOIS

Thomas J. Dee & Co., 55 East Washington St., Chicago.
Goldsmith Bros. Smelting & Refining Co., 58 East Washington St., Chicago.
Kilgallon & Co., 31 North State St., Chicago.

LOUISIANA

H. Schmidt & Son, 208 Chartres St., New Orleans.

MASSACHUSETTS

Attleboro Refining Co., Union St., Attleboro.
John Hood Co., 178 Tremont St., Boston.
Eastern S. & R. Co., 107 West Brookline St., Boston.
Glines & Rhodes, North Attleboro.
Jewelers' & Silversmiths' Co-operative Refining Co., North Attleboro.

OHIO

Cincinnati Gold and Silver Refining Co., 523 Elm St., Cincinnati.
Peter Henry & Son, 439 Race St., Cincinnati.
G. W. Seifried Co., 127 Opera Place, Cincinnati.

MICHIGAN

C. L. Pratt, Jr., 15 Gratiot St., Detroit.

MINNESOTA

General Refiners, Inc., 27 No. Fourth St., Minneapolis.
Spyco Smelting & Refining Co., 55 So. Third St., Minneapolis.

NEW JERSEY

Irvington Smelting and Refining Works, Nye Ave., Irvington.
American Platinum Works, 225 N. J. Railroad Ave, Newark.
Balbach Smelting & Refining Co., 580 Market St., Newark.
Baker & Co., 54 Austin St., Newark.
Clinton Refining Co., 91 East Kinney St., Newark.
Enright Refining Co., 42 Marshall St., Newark.
L. Lelong & Bro., 449 Washington St., Newark.
H. A. Wilson Co., 97 Chestnut St., Newark.

NEW YORK

Hoover & Strong, Inc., 119 W. Tupper St., Buffalo.
Williams Gold Refining Co., 2978 Main St., Buffalo.
Sigmund Cohn, 44 Gold St., New York.
Joseph B. Cooper & Son, 26 John St., New York.
Dentists' Supply Co., 220 West 42, New York.
Goldsmith Bros. Smelting & Refining Co., 74 West 46, New York.
Moe Hamerschlag, Inc., 174 Park Row, New York.
Handy & Harman, 82 Fulton St., New York.
J. F. Jelenko & Co., 136 West 52, New York.
Johnson Matthey & Co., 15 West 47, New York.
Kastenhuber & Lehrfeld, 24 John St., New York.
Kushner & Pines, 21 West 46, New York.
Orange Bros., 40 John St., New York.
I. Stern & Co., Inc., 218 West 40, New York.
Charles W. Williams, 106 Fulton St., New York.

PENNSYLVANIA

J. Bishop & Co., Malvern.
T. B. Hagstoz & Son, 709 Sansom St., Philadelphia.
Masel Dental Laboratory, 1108 Spruce St., Philadelphia.
S. S. White Dental Co., 211 S. 12, Philadelphia.
Dentists' Supply Co., York.

MARYLAND

Gilbert Cummins & Co., 1 North Eutaw St., Baltimore.

RHODE ISLAND

Geo. M. Baker Co., 91 Page St., Providence.
Conley & Straight, Inc., 236 Eddy St., Providence.
Pease & Curren, 780 Aliens Ave., Providence.
Horace Remington & Son Co., 91 Friendship St., Providence.

TEXAS

Southwest Smelting & Refining Co., 1809 Main St., Dallas.
Southwest Smelting & Refining Co., 108 E. 10th St., Fort Worth.

WASHINGTON

Speyer Smelting & Refining Co., Medical & Dental Bldg., Seattle.

Dealers in Chemical Apparatus and Supplies

In addition to the following large organizations, there are many small chemical supply houses throughout the country, most of which carry in stock the chemicals and equipment used in refining, or can obtain them on short notice. It is advisable wherever possible to purchase from a local dealer, since transportation costs are often a large part of the cost of chemicals.

CALIFORNIA

Braun Corporation, 2250 East 15th St., Los Angeles.
Braun-Knecht-Heimann Co., 576 Mission St., San Francisco.
Justinian Caire Co., 268 Market Street, San Francisco.

COLORADO

Denver Fire Clay Co., Box 5510, Denver. (Branches in Salt Lake City and El Paso.)

ILLINOIS

Central Scientific Co., 1700 Irving Park Blvd., Chicago.
E. H. Sargent & Co., 155 East Superior St., Chicago.

MARYLAND

Gerald K. Heller, Eagle and Smallwood Sts., Baltimore.
James B. Ferguson, 1642 Warner St., Baltimore.

MASSACHUSETTS

Central Scientific Co., 79 Amherst St., Cambridge.
Macalaster Bicknell Co., Washington and Moore Sts., Cambridge

MISSOURI

Heil Corporation, 210 S. Fourth St., St. Louis.

NEW JERSEY

New Jersey Laboratory Supply Co., 235 Plane St., Newark.

NEW YORK

Buffalo Apparatus Co., 180 Main St., Buffalo.
J. & H. Berge, 145 Hudson St., New York.
Eimer & Amend, 18th St. and Third Ave., New York.
Emil Greiner Co., 161 Sixth Ave., New York.
Palo-Myers Inc., 81 Reade St., New York.
Will Corporation, Rochester.

PENNSYLVANIA

Arthur H. Thomas Co., West Washington Sq., Philadelphia.
Fisher Scientific Co., 709 Forbes St., Pittsburgh.

VIRGINIA

Phipps & Bird, Inc., 915 E. Cary St., Richmond.

WEST VIRGINIA

B. Preiser Co., 109 Washington St., Charleston.

CANADA

Fisher Scientific Co., 898 St. James St., Montreal.
Central Scientific Co. of Canada, 119 York St., Toronto.

Dealers in Supplies for Jewelers

For a much more extended list of dealers, the reader is referred to the *Jewelers Buyers Directory*, published biennially by the Jewelers' Circular-Keystone, 239 West 39, New York City; and to the *Jewelers Handbook*, published annually by Walter B. Frost & Co., 42 Weybosset St., Providence, R. I.

CALIFORNIA

Friedman-Gessler Co., 220 W. 5th St., Los Angeles.
E. W. Reynolds Co., 315 W. 5th St., Los Angeles.
Justinian Caire Co., 268 Market St., San Francisco.

COLORADO

Denver Fire Clay Co., Box 5510, Denver. (Branches in Salt Lake City and Utah.)

FLORIDA

Clifford R. Maxwell, 117 N. E. 1st St., Miami.

GEORGIA

Ewing Bros., 5 Plaza Way, Atlanta.
Jewelers Supply Co., 84 Peachtree St., Atlanta.

ILLINOIS

C. & E. Marshall Co., 1445 West Jackson Boulevard, Chicago. (Branches in Detroit, Duluth, Columbus, New Orleans, Houston, Dallas, Oklahoma City, St. Paul, Milwaukee, Los Angeles, Kansas City, Minneapolis.)
Swartchild & Co., 29 East Madison St., Chicago. (Branch in New York City, Boston, and Dallas.)
Henry Paulson & Co., 37 S. Wabash Ave. Chicago.
J. Henri Ripstra, 5 S. Wabash Ave., Chicago.

INDIANA

Bardach & Gran, 448 N. Capitol Ave., Indianapolis.
Indiana Jewelers' Supply Co., 15 East Washington St., Indianapolis.

KENTUCKY

Geo. Katzman Co., 3rd and Walnut Sts., Louisville.

LOUISIANA

New Orleans Jewelers Supply Co., 208 Chartres, New Orleans.

MARYLAND

John A. Tschantre, 25 N. Liberty St., Baltimore.

MASSACHUSETTS

Kirby & Co., 387 Washington St., Boston.
Wm. J. Orkin, 373 Washington St., Boston.
Travis, Farber Co., 373 Washington St., Boston.

MICHIGAN

Michigan Jewelers' Supply Co., 1022 Michigan Bldg., Detroit.

MISSOURI

Clark Tool & Material Co., 925 Grand Ave., Kansas City.
Edwards-Ludwig-Fuller Co., 1115 Walnut St., Kansas City.
Meyer Jewelry Co., 11th and Grand Ave., Kansas City.

NEW JERSEY

William Dixon, Inc., (tools, supplies, equipment, machinery, saws, buffs, materials,) 32 East Kinney St., Newark. (Branch in New York City.)

NEW YORK

Anchor Tool and Supply Co., 12 John St., New York.
Arrow Supply & Tool Co., 109 Lafayette St., New York.
Buhl, Peer & Keefe, (watch and jewelry supplies), 41 Maiden Lane, New York.
William Dixon, Inc., 36 West 47, New York.
Paul H. Gesswein & Co., 35 Maiden Lane, New York.
Hammel, Riglander & Co., (watchmakers' supplies,) 209 W. 14, New York.
M. J. Lampert & Sons, (watch and jewelry supplies) 35 Maiden Lane, New York.

OHIO

E. & J. Swigart Co., 32 West 6th St., Cincinnati.

PENNSYLVANIA

Wm. S. Waples, 727 Sansom St., Philadelphia.
Martin Gluck & Son, 313 Clark Bldg., Pittsburgh.

RHODE ISLAND

Z. Berberian Co., 147 Chestnut St., Providence.
Geo. L. Claflin Co., 156 Dorrance St., Providence.
Johnson & Raftery, 104 Point St., Providence.
Jewelers Supply Co., 1144 Eddy St., Providence.

TENNESSEE

Young-Neal Co., Chamber of Commerce Bldg., Nashville.

TEXAS

Jack Gould & Co., Santa Fe Bldg., Dallas.

VIRGINIA

Herr & Kline, 231 Granby St., Norfolk.

WASHINGTON

Butterfield Bros., 1504 Third Ave., Seattle. (Branch in Portland, Ore.)

CANADA

E. & A. Gunther Co., Ltd., Brantford, Ontario. (Branch in Vancouver.)

Dealers in Special Equipment and Machinery

Alberene Stone Corp. of Virginia, (hoods, sinks,) 419 Fourth Avenue, New York. (Quarries at Schuyler, Va.)
Alloys and Products, Inc., (deoxidizers,) Oak Point Ave., Bronx, New York.
American Cuttlefish Bone and Crucible Co., 75 Cliff St., New York.
American Gas Furnace Co., Elizabeth, New Jersey.
American Oil & Supply Co., (acids, crucibles,) 238 Wilson Ave., Newark, New Jersey.
American Seitz Filter Corp., (filtering equipment,) 480 Lexington Ave., New York.
H. J. Astle & Co., (blowers, polishing equipment,) 118 Orange St., Providence, Rhode Island.
Autovent Fan & Blower Co., 1805 No. Korstner Ave., Chicago, Ill.
Sigmund Cohn, (casting equipment,) 44 Gold St., New York.
DeBothezat Ventilating Equipment Division, 100 Sixth Ave., New York.
Dentists' Supply Co., 220 West 42, New York.
Jos. Dixon Crucible Co., 233 Broadway, New York.
E. A. Eddy Machinery Co., (jewelry factory machinery,) 211 Eddy St., Providence, R. I.

General Ceramics Co., (acid proof stoneware,) 225 Broadway, New York.

J. Goebel & Co., (crucibles, tongs, fluxes, furnaces, casting equipment,) 95 Bedford St., New York.

W. Green Electric Co., (plating equipment and salts,) 192 Broadway, New York.

H. Henrich, Inc., (alloying materials,) 68 Fulton St., New York.

Hoke Incorporated, (oxy-gas torches and accessories,) 122 Fifth Avenue, New York.

H. E. Jacoby, (filter-presses,) 205 East 42, New York.

J. F. Jelenko & Co., (casting equipment,) 136 West 52, New York.

Jewelers Technical Advice Co., (information and advice, books on precious metals,) 123 William St., New York.

Maurice A. Knight, (chemical stoneware,) Kelly Ave., Akron, Ohio.

Laboratory Construction Co., (hoods, fume disposal equipment,) 113 Holmes St., Kansas City, Mo.

Laboratory Furniture Co. Inc., (hoods, tables,) 37-18 Northern Blvd., Long Island City, N. Y.

Lapp Insulator Co., Chemical Porcelain Division, (ceramics,) 400 Gilbert St., LeRoy, N. Y.

Leiman Brothers, (dust collecting equipment, jewelers' benches,) 23 Walker St., New York.

McWilliams Mfg. Co., (rolling mills, driers,) 237 Eddy St., Providence, R. I.

The Merrill Co., (filter-presses,) 343 Sansome St., San Francisco, Calif.

Oliver United Filters, Inc., (filter-presses,) 33 West 42, New York.

Pangborn Corp., (dust control equipment,) Hagerstown, Md.

Research Corp., (Cottrell precipitation systems,) 405 Lexington Ave., New York.

E. H. Sheldon & Co., (hoods, laboratory furniture,) 720 Nims St., Muskegon, Mich.

T. Shriver & Co., (filter-presses,) 802 Hamilton St., Harrison, N. J.

D. R. Sperry & Co., (filter-presses,) Batavia, Ill.

Thermal Syndicate, Ltd., (quartz vessels,) 12 East 46, New York.

U. S. Stoneware Co., (ceramics, tanks, jars,) Akron, Ohio.

Van Dorn Metal Furniture, (hoods, tables,) 41 East 42, New York.

Western Precipitation Corp., (Cottrell precipitation systems,) 1016 West 9th St., Los Angeles, Calif.

CHAPTER E

BOOKS TO READ

The books and articles that are listed below are mentioned either because they are useful or because they are interesting to the worker in precious metals.

Several of the dealers in precious metals have published catalogues containing many facts of interest to the student and of practical use to the worker. Some of these trade publications are mentioned by name in Chapter X.

The large encyclopedias, and all text and reference books in chemistry give valuable information under the headings of "Gold," "Silver," "Platinum Metals," "Alloys," and so on.

The monumental BIBLIOGRAPHY OF THE METALS OF THE PLATINUM GROUP—1748 to 1917, by Dr. James Lewis Howe and H. C. Holtz, published by the United States Geological Survey, is of particular value to students of the history of these metals. See also the titles listed at the end of Chapter XVII.

Some of the magazines that cater to the precious metal industries also sell books, and take pleasure in advising their subscribers. Among such magazines are the following: *The Jewelers Circular-Keystone*, 239 West 39th St., New York City; *The Manufacturing Jeweler*, 42 Weybosset St., Providence, R. I.; *Horology*, 747 So. Hill St., Los Angeles, California; *The National Jeweler*, 531 So. La Salle St., Chicago, Ill., and *The Laboratory Technician*, 220 West 42nd St., New York City.

For books on gem stones, consult the Gemological Institute of America, 541 South Alexandria Avenue, Los Angeles. Associated with this institute are the American Gem Society, and the publication *Gems and Gemology*.

Several bulletins on the hazards connected with precious metal refining are mentioned at the end of Chapter B of this Appendix.

For laws, standards and regulations relating to the precious metals, see Chapter C of this Appendix.

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BOOKS

JEWELRY, GEM CUTTING AND METALCRAFT. By W. T. Baxter and Henry C. Dake. 224 pp. $2.50. McGraw-Hill Book Company, Inc., New York. 1938.

THE SCIENCE OF DENTAL MATERIALS. By Eugene W. Skinner. (Contains texts of American Dental Association Specifications for dental amalgam alloys; casting investment; impression compound; casting wax; inlay casting golds; mercury; wrought gold wire alloys; cementing medium.) 411 pp. $4.50. W. B. Saunders, Philadelphia. 1937.

THE METALLURGY OF GOLD. By Sir T. K. Rose and W. A. C. Newman. 561 pp. $15.00. Seventh edition. J. B. Lippincott Co., Philadelphia. 1937.

TESTING PRECIOUS METALS. By C. M. Hoke. (See Chapter 9 of this book.) 59 pp. $1.00. Jewelers Technical Advice Co., New York. 1937.

PLATINUM AND ALLIED METALS. With bibliography. 137 pp. Price 3s 4d. The Imperial Institute, Mineral Resources Department, South Kensington, London, England. 1936.

ANALYTISCHE CHEMIE DER EDELMETALLE. By Dr. Alfred Wogrinz. (Band XXXVI, die Chemische Analyse.) 141 pp. Price, paper, 13 RM; bound, 14.80 RM. Ferdinand Enke Verlag, Stuttgart, Germany. 1936.

HANDBOOK FOR PROSPECTORS. By M. W. von Bernewitz. 372 pp. $3.00. McGraw-Hill Book Co., Inc., New York. 1935.

THE METAL CLEANING HANDBOOK. By Robert W. Mitchell. 214 pp. $1.00. Published by the Magnus Chemical Company (manufacturers of cleaning materials), Garwood, New Jersey. 1935.

HANDBOOK FOR THE AMATEUR LAPIDARY. By J. Harry Howard. 140 pp. $2.00. Published by J. H. Howard, 504 Crescent Ave., Greenville, South Carolina. 1935.

WORKING IN PRECIOUS METALS. By E. A. Smith. 400 pp. $6.75. N. A. G. Press, Ltd, 26-34 Old St., E.C. 1, London, England.

1934. (Obtainable also from Henry Paulson & Co., 37 So. Wabash Ave., Chicago.)

PRINCIPLES OF ELECTROPLATING AND ELECTROFORMING. By William Blum and George B. Hogaboom. 424 pp. $4.50. McGraw-Hill Book Co., New York. 1930.

A LIST OF ALLOYS. By William Campbell. 65 pp. Paper bound, $1.50. Cloth bound, $2.00. American Society for Testing Materials, Philadelphia. 1930.

HOW TO MAKE JEWELRY. By George S. Overton. 298 pp. $3.00. Walter B. Frost & Co., Providence, R. I. 1927.

HANDBOOK OF NON-FERROUS METALLURGY. Edited by Donald M. Liddell, written by a staff of experts. In two volumes. (Chapters 28 and 29, in vol. 2, are of interest to workers in precious metals.) 1500 pp. $12.00. McGraw-Hill Book Co., New York. 1926.

CHASING AND REPOUSSE. By Albert Wehde. 24 pp. $1.00. The Tremonia Publishing Co., 621 Plymouth Court, Chicago. 1924.

THE PLATINUM METALS. By E. A. Smith. 120 pp. Sir Isaac Pitman & Sons, London. 1924.

A TEXTBOOK OF FIRE ASSAYING. By Edward E. Bugbee. 254 pp. John Wiley & Sons, Inc., New York. 1922.

HANDBOOK OF METALLURGY. By Carl Schnabel, translated by Henry Louis. Vol. 1, Copper, Lead, Silver, Gold. 1171 pp. $13.50. 1921.

GEM-STONES AND THEIR DISTINCTIVE CHARACTERS. By G. F. Herbert Smith. 314 pp. $3.00. Brentano’s, New York. 1920.

RECOVERING PRECIOUS METALS FROM WASTE LIQUID RESIDUES. By George E. Gee. 380 pp. $4.80. E. & F. N. Spon, Limited, 57 Haymarket, S.W.I. London. 1920.

JEWELRY MAKING AND DESIGN. By Augustus F. Rose and Antonio Cirino. 463 pp. $5.00. Metal Crafts Pub. Co., Providence, R. I. 1917.

SILVERWORK AND JEWELRY. By H. Wilson and Unno Bisei. 496 pp. $2.50. D. Appleton and Co., New York. 1912.

THE ART OF THE GOLDSMITH AND JEWELLER. By Thomas B. Wigley. 264 pp. $3.25. Chas. Griffin & Co., Ltd., London. 1911.

THE ELECTRO-PLATING AND ELECTRO-REFINING OF METALS. By Alexander Watt and Arnold Philip. 677 pp. $4.50. D. Van Nostrand Co., New York. 1911.

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ARTICLES

The reader will find that some of these publications are out of print, or difficult to obtain for other reasons. However, many libraries—for example the Engineering Societies Library, at 29 West 39th Street, New York City—are equipped to make photostatic copies, at a small sum per page, of any publication.

PLATINUM AND ALLIED METALS. By H. W. Davis. 11 pp. 5 cents. Chapter from Minerals Yearbook, Bureau of Mines. 1939.

EFFECT OF COMPOSITION UPON PHYSICAL AND CHEMICAL PROPERTIES OF 10-KARAT GOLD ALLOYS. By Tracy C. Jarrett. 9 pages. Metals Technology, October, 1939.

EFFECT OF COMPOSITION ON COLOR AND MELTING POINT OF 10-k, 12-k, and 14-k Gold Alloys. By Tracy C. Jarrett. 8 pp. Metals Technology, September, 1939.

NEW STONEWARE IN THE ELECTROCHEMICAL FIELD. By Percy C. Kingsbury. Transactions Electrochemical Society, pp. 303-310,1939.

DAS VERHALTEN DER EDELMETALLE UND IHRER KUPFERHALTIGEN LEGIERUNGEN GEGENUBER SAUERSTOFF in flüssigem Zustande und beim Glühen in festem Zustande. By E. Raub and M. Engel. Mitt. Forsch. Inst. Probieramts Edelmetalle, pp. 1-12, June, 1939. (Comprehensive review.)

ELECTROLYTIC SILVER REFINING. By Edmund Downs. (A general discussion.) The Metal Industry, London, pp. 543-546, vol. 54, May 19, 1939.

RECOVERY OF GOLD AND SILVER FROM PLATING SOLUTIONS. By Frank K. Savage. The Metal Industry, New York, p. 159, vol. 37, April, 1939.

REFINING $2,000,000 OF GOLD PER WEEK. By A. L. Entwistle. (Description of the treatment of crude gold bullion at the Royal Canadian Mint Refinery at Ottawa. See Chapter 22 of this book.) Canadian Metals and Metallurgical Industries, Toronto, Vol. 1, January, pp. 3-8; February, pp. 53-56, 1938.

THE RECOVERY OF SILVER, GOLD AND MERCURY FROM PRECIOUS METAL AMALGAMS. By C. M. Hoke. The Metal Industry, New York, pp. 22-23, January, 1938.

PROPERTIES OF THE PLATINUM METALS, II. Tensile strengths of platinum, palladium, and several of their commercial alloys at elevated temperatures, with a few .notes on high-temperature corrosion resistance of platinum. By E. M. Wise and J. T. Eash. Metals Technology, pp. 282-294, February, 1938. Also in Trans. A.I.M.E., Vol. 128, Institute of Metals Division, pp. 282-294, l938.

NEW PROCEDURE FOR THE ANALYSIS OF DENTAL GOLD ALLOYS. By Raleigh Gilchrist. Research Paper RP 1103, Journal of Research of the Bureau of Standards, Vol. 20, pp. 745-771, June, 1938.

A LIST OF LABORATORIES THAT MAKE ASSAYS, ANALYSES AND TESTS ON ORES, MINERALS AND OTHER SUBSTANCES. By C. W. Davis and M. W. von Bernewitz. 25 pp. Bureau of Mines Information Circular I.C. 6999. March, 1938.

RECOVERY OF GOLD FROM BALBACH-THUM SLIMES AT COPPER CLIFF, ONTARIO. By Frederic Benard. 5 pp. Metals Technology, February, 1938.

OCCURRENCE AND TREATMENT OF MERCURY ORE AT SMALL MINES. By M. W. von Bernewitz. 40 pp. Bureau of Mines Information Circular I. C. 6966, Oct., 1937.

PLATINUM IN THE WORLD'S WORK. By Lonnelle Davison. The National Geographic Magazine, Washington, D. C., Vol. 62, pp. 345-360. Sept., 1937.

PLATINUM AND ALLIED METALS. SOME POINTS OF INTEREST TO THE CHEMICAL ENGINEER. By C. Johnson and R. H. Atkinson. Trans. Institute of Chemical Engineers, London, Vol. 15, pp. 131-144, 1937. (See Chapter 22 of this book.) An abstract of this article was printed in The Industrial Chemist, (London), pp. 223-233, June, 1937. A shorter abstract was printed in The Chemical Age, (London), pp. 459-462, May, 1937-

JUST HOW MUCH PRECIOUS METAL IS LOST IN POLISHING? By Ernest A. Smith. The Manufacturing Jeweler, Providence, pp. 30-31, October 15, 1936.

SILVER: ITS PROPERTIES AND INDUSTRIAL USES. By B. A. Rogers, Irl C. Schoonover & Louis Jordon. Bureau of Standards, C412. 72 pp. 10 cents. October 2, 1936.

METALS OF THE PLATINUM GROUP. ORES, RECOVERY AND REFINING, FABRICATION AND USES, AND PROPERTIES. By R. H. Atkinson and A. R. Raper. Journal of the Institute of Metals, (London). Vol. 59, No. 2, pp. 179-210, 1936. An abstract of this paper appears in The Metal Industry, (London), pp. 114-116, January 15, 1937.

BULLION PARTING AT THE HOMESTAKE MINE. By Nathaniel Herz. (See Chapter 22 of this book.) Mining and Metallurgy, pp. 500-504, December, 1935.

A PROCEDURE FOR THE SEPARATION OF THE SIX PLATINUM METALS FROM ONE ANOTHER AND FOR THEIR GRAVIMETRIC DETERMINATION. By Raleigh Gilchrist and Edward Wichers. Journal of the American Chemical Society, Vol. 57, pp. 2565-2573, 1935.

STUDIES ON THE RECOVERY OF GOLD AND SILVER. By Ed. S. Leaver, M. B. Royer, J. A. Woolf, R. E. Head, B. W. Gandrud, R. E. Evans, and F. W. Thackwell. Bureau of Mines, Report of Investigations R. I. 3275. 65 pp., June, 1935.

PROPERTIES OF THE PLATINUM METALS. I. Strength and annealing characteristics of platinum, palladium, and several of their commercial alloys. By E. M. Wise and J. T. Eash. Trans. A.I.M.E., Vol. 117, Institute of Metals Division, pp. 313-328, February, 1935.

JEWELERS' LOW GRADE WASTES: AN ASSET OR A LIABILITY? By C. M. Hoke. (See Chapter 18 of this book.) The Metal Industry, New York, November and December, 1934.

PLACER MINING IN THE WESTERN UNITED STATES. PART II. HYDRAULICKING, TREATMENT OF PLACER CONCENTRATES, AND MARKETING OF GOLD. By E. D. Gardner and C. H. Johnson. Bureau of Mines Information Circular 6787. 89 pp., October, 1934.

A LIST OF PUBLICATIONS ON THE PLATINUM METALS. 9 pp. Bureau of Standards Letters Circular LC-426, October 1, 1934.

A METHOD FOR THE SEPARATION OF RUTHENIUM FROM PLATINUM, PALLADIUM, RHODIUM AND IRIDIUM. By Raleigh Gilchrist. Research Paper 654, Bureau of Standards Journal of Research, Vol. 12, pp. 283-290, Mar., 1934.

A NEW SYSTEM OF ANALYTICAL CHEMISTRY FOR THE PLATINUM METALS. By Raleigh Gilchrist and Edward Wichers. Publicado en: Trabajos del IX Congreso Internacional de Química Pura y Aplicado, Toma VI, Química Analitica. Madrid, Spain, 1934.

RECOVERY OF PRECIOUS AND SECONDARY METALS FROM ELECTROLYTIC COPPER REFINING. By M. A. Mosher. (See Chapter 22 of this book.) Trans. A.I.M.E., Vol. 106, pp. 427-440, 1934.

THE ROLE OF THE PLATINUM METALS IN DENTAL ALLOYS, III. The influence of platinum and palladium and heat treatment upon the microstructure and constitution of basic alloys. By E. M. Wise and J. T. Eash. Trans. A.I.M.E., Vol. 104, Inst. of Metals Division, pp 276-307, 1933.

ELECTROLYSIS OF SILVER-BEARING THIOSULFATE SOLUTIONS. By K. Hickman, W. Weyerts and O. E. Goehler. Industrial and Engineering Chemistry, New York, Vol. 25, pp. 202-212, February, 1933.

TREATING WASTE FROM SILVER MANUFACTURE. By Ernest A. Smith. The Metal Industry, New York, Vol. 32; pp. 272-273, 304-305, 341-342, August, September and October, 1932.

TREASURE TROVE IN LOWLY “SWEEPS.” Scientific American, p. 163, Sept., 1932.

THE RECOVERY OF PRECIOUS METAL FROM FACTORY WASTE. By John S. Isdale. The Brass World, pp. 138-139, July , 1932.

MELTING FINE SILVER IN HIGH FREQUENCY INDUCTION FURNACE. By Daniel L. Ogden. Trans. American Electrochemical Society, New York, pp. 221-223, I932. Reprinted in The Brass World, p. 144, July, 1932.

RECOVERY OF PRECIOUS METALS FROM ELECTROLYTIC COPPER REFINING AT THE CANADIAN COPPER REFINERS PLANT, MONTREAL EAST, QUEBEC. By C. W. Clark and A. A. Heimrod. Trans. American Electrochemical Society, pp. 437-450, 1932.

THE ROLE OF THE PLATINUM METALS IN DENTAL ALLOYS. I & II. By E. M. Wise, Walter S. Crowell & J. T. Eash. Trans. A.I.M.E., Vol. 99, pp. 363-412, 1932.

ASSAYING PLATINUM METALS. By Martin Schwitter. Metal and Mineral Markets, pp. 6-10, Jan. 21; pp. 6, 7, Feb. 18; pp. 6-11, Mar. 17, 1932. A reprint of this article under the heading REFINING PLATINUM METALS, will be found in the Brass World, Sept., Oct., Nov. and Dec., 1932.

A METHOD FOR THE SEPARATION AND GRAVIMETRIC DETERMINATION OF OSMIUM. By Raleigh Gilchrist. Research Paper 286, Bureau of Standards Journal of Research, Vol. 6, pp. 421-448, March, 1931.

FABRICATION OF THE PLATINUM METALS. By C. S. Sivil. Trans. A.I.M.E., Institute of Metals Division, pp. 246-261, 1931.

THE MAKING OF MIRRORS BY THE DEPOSITION OF METAL ON GLASS. Bureau of Standards Circular 389, 17 pp., 5¢, January 6, 1931.

FIELD TESTS FOR THE COMMON METALS. By George R. Fansett. 51 pp. University of Arizona, Tucson, Ariz., March 15, 1930.

MELTING AND CASTING SOME GOLD ALLOYS. By Edward A. Capillon. 20 pp. Mining and Metallurgy, February, 1930.

HIGH-STRENGTH GOLD ALLOYS FOR JEWELRY, AND AGE-HARDENING PHENOMENA IN GOLD ALLOYS. By E. M. Wise. Trans. A.I.M.E., Vol. 83, pp. 384-408, 1929.

MELTING, MECHANICAL WORKING AND SOME PHYSICAL PROPERTIES OF RHODIUM. By Wm. H. Swanger. Research Paper 127, Bureau of Standards Journal of Research. Vol. 3, pp. 1029-1040, December, 1929.

A GRAVIMETRIC METHOD FOR THE DETERMINATION OF RUTHENIUM. By Raleigh Gilchrist. Research Paper 125, Bureau of Standards Journal of Research, Vol. 3, pp. 993-1004, December, 1929.

PHYSICAL PROPERTIES OF DENTAL MATERIALS. By R. L. Coleman. Research Paper 32. Bureau of Standards Journal of Research, pp. 867-938. December, 1928.

PURIFICATION OF THE SIX PLATINUM METALS. By Edward Wichers, Raleigh Gilchrist and Wm. H. Swanger. (See Chapter 17 of this book.) 29 pp. Mining and Metallurgy, March, 1928.

REFINING AND MELTING SOME PLATINUM METALS. By J. O. Whiteley and C. Dietz. (Osmium is not included. This paper describes methods of refining dental and jewelry scrap and laboratory ware, in 100 ounce lots. See Chapter 17 of this book.) 9 pp. Mining and Metallurgy, March, 1928.

USE OF THE NOBLE METALS FOR ELECTRICAL CONTACTS. By E. F. Kingsbury. 19 pp. Mining and Metallurgy, March, 1928.

THE PLATINUM METALS AND THEIR ALLOYS. By Frederick E. Carter. 24 pp. Mining and Metallurgy, February, 1928.

MANUFACTURE OF STERLING SILVER AND SOME OF ITS PHYSICAL PROPERTIES. By Robert H. Leach and C. H. Chatfield. 13 pp. Mining and Metallurgy, February, 1928.

SAMPLING AND EVALUATING SECONDARY NON-FERROUS METALS. By T. A. Wright. 17 pp. Mining and Metallurgy, February, 1928.

GOLD, SILVER, COPPER ALLOYS. By Frederic E. Carter. 17 pp. Mining and Metallurgy, February, 1928.

MELTING STERLING SILVER IN HIGH FREQUENCY INDUCTION FURNACES. By Robert H. Leach. Trans. American Electrochemical Society, pp. 223-227, 1928.

THE GLOW TEST FOR METALS OF THE PLATINUM GROUP. By C. W. Davis. Journal of the Franklin Institute, pp. 679-700, May, 1927.

IRVINGTON SMELTING AND REFINING WORKS. By Adolph Bregman. (See Chapter 22 of this book.) The Metal Industry, New York, pp. 183-187, May, 1927.

ALLOYS OF PRECIOUS METALS AND THE HIGH FREQUENCY INDUCTION FURNACE. By Reginald V. Williams. The Metal Industry, New York, pp. 141-143, April; pp. 188-190, May, 1927.

SOME NEW ANALYTICAL REACTIONS OF THE PLATINUM METALS. By S. C. Ogburn, Jr. Journal of the American Chemical Society, Vol. 48, pp. 2494-2507, Oct., 1926.

ANALYSIS OF DENTAL GOLD ALLOYS. By William H. Swanger. Scientific Papers of the Bureau of Standards, No. 532. 10¢. Vol. 21, pp. 209-239, August, 1926.

For a discussion of the dangers connected with the heating of osmium, see *The Keystone*, Philadelphia, p. 92, January, 1924; *Chemical and Metallurgical Engineering*, p. 743, November 10, 1924; *Brass World*, Vol. 20, p. 242, 1924; *Jewelers' Circular*, May 28, 1924.

METHODS FOR THE RECOVERY OF PLATINUM, IRIDIUM, PALLADIUM, GOLD AND SILVER FROM JEWELERS' WASTE. By C. W. Davis. 14 pp. 5¢. Bureau of Mines Technical Paper 342, January, 1924.

THE PREPARATION OF PLATINUM AND OF PLATINUM-RHODIUM ALLOY FOR THERMOCOUPLES. By Robert P. Neville. Trans. American Electrochemical Society, pp. 125-136, 1923.

RECOVERY OF PLATINUM FROM USED CONTACT MASS AT THE OLD HICKORY POWDER PLANT. By A. L. Kibler. (See Chapter 22 of this book.) Journal of Industrial and Engineering Chemistry, Vol. 14, pp. 636-641, July, 1922.

THE METALLURGY OF PLATINUM. By Louis duParc, translated by Allen C. Redding and Geo. M. Nelson, with Frank Sanborn. A translation of Chapter XV of duParc's "Le Platine du Monde." Issued in *Mining in California*, a publication of the California State Mining Bureau, San Francisco, Vol. 18, pp. 158-172, April, 1922.

THE DETECTION AND ESTIMATION OF PLATINUM IN ORES. By C. W. Davis. 27 pp. Bureau of Mines Technical Paper 270. January, 1921.

BIBLIOGRAPHY OF THE METALS OF THE PLATINUM GROUP —1748-1917. By Jas. Lewis Howe and H. C. Holtz. 558 pp. (Out of print.) United States Geological Survey, Bulletin 694, 1919.

ELECTRODEPOSITION OF GOLD AND SILVER FROM CYANIDE SOLUTIONS. By S. B. Christy. 171 pp. 25¢. U. S. Bureau of Mines Bulletin 150, 1919.

TEXT BOOKS FOR THE JEWELER'S LIBRARY. By Clement W. Coumbe. (A bibliography.) The Jewelers' Circular-Weekly, pp. 123-129. Feb. 7, 1917.

HANDLING OF PRECIOUS METAL SCRAP, FILINGS, SWEEPS, ETC. By C. M. Hoke. The Keystone, Philadelphia, pp. 289-295, September, 1917.

ELECTROLYSIS OF LOW GRADE GOLD BULLION. By Theo. W. Bouchelle. Engineering & Mining Journal, January 25, 1913.

TREATMENT OF GOLD AND SILVER AT THE UNITED STATES ASSAY OFFICE IN NEW YORK CITY. The Brass World, pages 307-314, September, 1913.

ANNUAL REPORT OF THE DIRECTOR OF THE MINT FOR 1912. Treasury Department Document 2671, pages 44-52, 1913.

DE L’ANALYSIS DU PLATINE IRIDIÉ EMPLOYÉ PAR LA SECTION FRANÇAISE DE LA COMMISSION INTERNATIONALE DU MÈTRE À LA CONFERENCES DES PROTOTYPES. By E. H. Sainte-Claire DeVille and J. S. Stas. Procés-verbeaux, Comité International des Poids et Mesures. Annexe No. II, 1878.

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