ANAEROBIC TREATMENT

OF

SEWAGE AND WASTES

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ЪУ

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Library facilities were used at the Polytechnic Institute of Brooklyn; The Cooper Union; Engineering Societies Library; Columbia University, College of Physicians and Surgeons; and New York City Public Library.

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It is with sincere appreciation and grateful thanks that I acknowledge the guidance, help and cooperation of Professor Albert N. Aeryns, my thesis adviser; and the help and encouragement of my wife, Marian. ABSTRACT

In sewage treatment anaerobic digestion is the established method of stabilizing the organic material removed from the liquid wastes. Anaerobic treatment is also used to remove putrescible material from organic industrial wastes. This method has sometimes been adepted when the waste did not respond satisfactorily to other methods of treatment.

An attempt has been made to summarize the present knowledge of the anaerobic treatment processes. It was hoped that by assembling the data obtained from various investigators a pattern for the application of anaerobic treatment could be obtained and possibly a prediction as to the efficiency of application to various wastes, its limitations and the effect of variations in the process and environment could be made.

The first step of the investigation was to assemble a bibliography by standard library methods. This bibliography was continuously extended throughout the period of research as the fund of reference material was accumulated and consulted.

It soon became apparent that it would be necessary to limit the thesis to anaerobic fermentation for the production of methane, This being of greatest interest and application in the field of study indicated.

Anaerobic biological colonies may be utilized for the production of other substances. However, their range of

111

application is more limited, and the variation is one of degree and control rather than of method. The same might be said of anaerobic digestion of organic material from sources other than those indicated.

Anaerobic fermentation for the production of methane thus became established as a norm for discussion of the process. With the establishment of a norm, the result of deviation from that norm could be investigated.

It was found that factual knowledge of the process of anaerobic fermentation is rather meager. Laboratory isolation and investigation of methane -producing bacteria has been achieved. Contending theories do not yet completely explain the mechanics of methane production.

Collateral organisms liquify the solid and more complex organic material for utilization by the methaneproducing bacteria. These collateral organisms have yet to be enumerated and their contribution to the process evaluated.

The effect of environment on the biological colony is better known. Satisfactory operation may be predicated on operation within the established limitations of environment. Further information on the effect of certain environmental factors is necessary. It is not possible, with present information, to explain all the effects of environment; only to delineate a satisfactory environment.

At this time, data from all sources can not be correlated. Data on sewage sludge digestion is particularly difficult to correlate with information from the anaerobic treatment of other wastes. The bar to correlation is the differences in method of reporting results used by individual investigators. It is believed that if complete data on volatile matter content, volatile acids and the quantity of seed material were given in each report on anaerobic treatment relationship between the various data might be found.

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Sufficient knowledge is available to show that anaerobic treatment is feasible for most organic wastes. In any disposal problem full consideration should be given to anaerobic methods of treatment since satisfactory and economical solutions to the treatment problem may, thereby, ensue.

TABLE OF CONTENTS

PART I ANAEROBIC TREATMENT	Page
INTRODUCTION	1
HISTORICAL NOTES	1
ORGANIC MATTER INTEREST IN ORGANIC MATTER OCCURANCE OF ORGANIC MATTER Carbohydrates Fats Proteins INSTABILITY OF ORGANIC MATTER	4455566
ENZYMES AS CATYLISTS	9 9
BIOCHEMICAL OXIDATION	10
AEROBIC & ANAEROBIC OXIDATION	10
Oxidizing-Reducing Potential	11
THEORIES OF BIOCHEMICAL OXIDATION	12
Fermentation	13
CHEMISTRY OF BIOCHEMICAL OXIDATION	14
BACTERIAL METABOLISM RESPIRATION Respiration of Aerobes Respiration of Anaerobes DIGESTION Hydrolysis Role of Water DIGESTION OF ORGANIC MATTER Carbohydrates Fats Protein NUTRITIVE REQUIREMENTS	15 15 15 16 17 17 18 18 18
THE PURPOSE OF ANAEROBIC TREATMENT	20
PRODUCTS OF ANAEROBIC TREATMENT	20
THE PROBLEM OF ANAEROBIC TREATMENT	20
ENVIRONMENTAL CONDITIONS	21
UTILIZATION OF ORGANIC MATERIAL	21
LOSS OF OXIDIZABLE MATERIAL	23
BIOCHEMISTRY OF METHANE PRODUCTION THEORIES OF METHANE PRODUCTION Intermolecular oxidation Intramolecular Oxidation	24 24 24 24 26

vii

PRODUCTION OF SUBSTANCES OTHER THAN METHANE INTEREST IN PRODUCTS OF DECOMPOSITION	27 27
LIMITATION OF THESIS TO METHANE FERMENTATION UNIVERSAL APPLICABILITY OF METHANE FERMENTATION	28 28
NUTRITIONAL REQUIREMENTS OF THE ORGANISMS	29
THE MICROORGANISMS OF ANAEROBIC DIGESTION THE METHANE BACTERIA Isolation of Methane Bacteria THE OTHER ORGANISMS	30 30 31 32
THE ANAEROBIOSIS OF SEWAGE & SLUDGE THE STAGES OF ANAEROBIC DECOMPOSITION First Stage - Acid Production Second Stage - Acid Regression Third Stage - Methane Fermentation	33 33 35 36
ENVIRONMENTAL CONSIDERATIONS EFFECT OF TEMPERATURE EFFECT OF pH EFFECT OF PRODUCTS OF DECOMPOSITION Alkalinity Ammonium Carbonates Volatile Acids Chemical Products EFFECT OF SEEDING EFFECT OF MIXING Scum EFFECT OF AMMONIA NITROGEN EFFECT OF HEAVY METALS & OTHER TOXIC SUBSTANCES	3802334663579
ENVIRONMENTAL CONSIDERATIONS FOR THE METHANE BACTERIA TEMPERATURE REACTION NITROGEN SURFACE OBLIGATE ANAEROBES	60 61 61 61 61

PART II	
THE PRACTICE OF ANAEROBIC TREATMENT	D • C T
	PAGE
INTRODUCTION	63
TREATMENT OF SEWAGE: - PRECONCENTRATION OF ORGANIC MATTER	65
SEPARATE SLUDGE DIGESTION SYSTEMS FEEDING MIXING HEATING FLEXIBILITY TWO-STAGE DIGESTION TYPICAL INSTALLATIONS "Controlled Digestion" System Single Tank System Two-Stage Digestion System The Imhoff Tank	66 69 70 71 72 73 73 77 77
TREATMENT WITHOUT PRIOR CONCENTRATION OF ORGANIC MATTER THE SEPTIC TANK THE SEPTIC TANK ACTION Unheated Digesters	82 83 86 87
ANAEROBIC TREATMENT OF INDUSTRIAL WASTES	89
REQUIREMENTS FOR ANAEROBIC TREATMENT OF INDUSTRIAL WASTES NUTRITION ORGANISMS Acclimitization and Adaption WEDICAL METHODS OF ANAFEORIC TREATMENT FOR	89 89 90 91
TYPICAL METHODS OF ANAEROBIC TREATMENT FOR INDUSTRIAL WASTES Septic Tank Fermentation Wastes Strawboard and Fiberboard Wastes Yeast Wastes FILTER MEDIA RESULTS OF ANAEROBIC TREATMENT OF WASTE	93 93 93 94 97 100 100
COMPARATIVE COSTS OF ANAEROBIC AND AEROBIC WASTE TREATMENT	10 1

SUMMARY AND CONCLUSIONS

INTRODUCTION	Page 106
THE BIOLOGICAL COLONY FOR ANAEROBIC TREATMENT	107
THE ENVIRONMENT FOR METHANE FERMENTATION	107
RELATION OF FEED TO SEED MATERIAL	110
THE UTILITY OF METHANE FERMENTATION	114
CONCLUSIONS	114

ix

LIST OF FIGURES

F,TC	URE TITLE	PAGE
1.	The Nitrogen Cycle	7
2.	The Carbon Cycle	8
3.	Curves Showing the Chemical Changes, Changes in Flora and Fauna and Effects of Temperature, Inocculation and Reaction Control on Natural Anaerobiosis.	37
4.	Relation between Reduction in Volatile Matter in Digested Sludge and Detention Periods of Raw Wet Sludge.	50
5.	Relation between Total and Volatile Solids in Digested Sludge.	51
6.	Gas Production from Sludge Digestion.	52 [`]
7.	Effect of Temperatureing.Rate of Sludge Digestion	56
8.	Effect of Rapid Stirring.	56
9.	Relation between Volume Required in Digester and Detention in Days for Various Solids Content of Raw Sludge.	64
10.	Typical Two Tank Layout Suggested Digester Piping for "Controlled Digestion".	74
11.	Separate Sludge Digestion Tank.	78
12.	Two-Stage Digestion System.	79.
13.	Imhoff Tank.	80
14.	Relation Suspended Solids Removal and Volume of Accumulated Sludge, Septic Tank.	88
15.	Proposed Fiberboard Waste Treatment & Disposal Works.	95
16.	Pilot Plant for Anaerobic Digestion of Strawboard Wastes.	96
17.	Comparison of Units Required for Treating 200,000 gpd of Strawboard Waste	96
18.	Plan of Treatment Plant for Yeast Wastes	9 8

LIST OF TABLES

TABLE	TITLE	PAGE
I	Partial Table of Enzymes	10
II	Inhibition of Digestion by Various Ions	45
III	Summary: Chemical Content of Sludge Liquors.	47
ĪV	Effect of Ammonia-Nitrogen Concentration on Rate of Gassification of Cornstalks	57
V	Calculation of Amount and Nature of Domestic Sludge	67
VI	Comparative Results of Plain Sedimenta- tion and Septic Sedimentation	84
VII	Industrial Wastes Treated Anaerobically	102

· xi

PART I ANAEROBIC TREATMENT

INTRODUCTION

Since early in the nineteenth centruy man has been increasingly concerned with the treatment of the waste products of his mass metabolism and industry, that they may be disposed of without offense and with minimum nuisance to himself. These wastes are widely diverse in their natures and origins and are composed of both organic and inorganic matter. The bulk of them are organic, or at least, it is the organic wastes that are of primary concern since it is their decomposition which may be offensive to both sight and smell, and if of intestinal origin they may be carriers of the pathogenic organisms of various diseases.

HISTORICAL NOTES*

The first description of a device for the anaerobic treatment of sewage appeared in the French journal "Cosmos" in December, 1881. Described therein was the "Mouras' Automatic Scavenger", an air tight vault in which the solid matters in raw sewage were dissolved. It can not be said that the treatment was described as an anaerobic process at that date, although Pasteur had demonstrated his "life without air" and classified bacteria into aerobic, anaerobic and facultative.

W. D. Scott-Moncrieff did experimental work on the

^{*} Unless otherwise credited, source of historical notes is AMERICAN SEWAGE PRACTICE, vol III, by Metcalf and Eddy. 1st. Edition. pub. 1916 by McGraw-Hill Book Company.

liquification of solids without oxygen about 1890 and A. C. Houston in '92 and '93; their work and the difficulty of disposal of sludge from plain sedimentation tanks attracted attention to the "anaerobic tank". The 1894 report of the Massachusetts State Board of Health described the action in septic tanks without so naming them.

Donald Cameron of Exeter, England began, in 1895, the construction of a "septic tank" for that city. Cameron and his associates secured a United States patent on the process of septicization and other patents on methods. Litigation over these patents made engineers hesitant about adapting the "septic tank" process in this country, and American engineers turned to other methods to avoid conflict. The Imhoff Tank introduced to this country about 1906 showed much promise, and Dr. Imhoff was most cooperative to interested engineers, charging no fees for consultation except a moderate royalty. The two-story tank thus increased in popularity.

In 1899, H.W. Clark reporting on work at the Lawrence Experiment Station indicated, that since in septic tanks the stronger the applied sewage the greater the removal of organic matter, experiments had been started on passing sewage through ordinary settling tanks so constructed that the sludge settling to the bottom of these tanks could be flushed into a septic tank for treatment instead of treating the whole of a city's sewage by septic action. Thus was started separate

sludge digestion.

Baltimore, Maryland and Birmingham, England adapted separate sludge digestion on a municipal scale in 1912. In that same year Fuller* stated "Improvements due to the use of two-story septic tanks seem to have decidedly limited the extent of the development of this arrangement." The tanks at Baltimore and at Birmingham were operated on a batch system. The tanks at Birmingham were artificially heated by steam, during the winter months, to maintain a favorable temperature for digestion. (8)

In 1923, a continuous process separate sludge digestion unit was installed at Brownsville, Texas; probably the first of the modern type of separate sludge digestion installations. This was followed, in 1926, by the operation of the first plant designed to include heating and gas collection equipment for separate sludge digestion tanks. (8) The development and installation of this form of anaerobic treatment has progressed continuously since that time.

The practical application of certain basic requirements for successful anaerobic **transm**ent were appreciated at an early date. (8) The knowledge gained by experience and experiment was brought together by Schlenz in 1944 (121) and summarized by Buswell and Schlenz (20) (122) in 1947; these

^{*} page 500 SEWAGE DISPOSAL by G. W. Fuller. First Edition pub. 1912 McGraw-Hill Book Company, New York

indicated considerable advances, improvements and developments made since 1912.

The above historical outline is concerned principally in the field of sewage disposal; however it may be noted that in 1911 Bowles investigated the use of septic tank treatment for creamery (an industrial) waste (17). Industrial waste treatment has paralleled sewage treatment throughout its development. Investigation of the anaerobic treatment of organic substances continund; throughout the period of development, Buswell's work on the destruction of carbohydrate wastes being significant in its contribution to knowledge of the anaerobic processes. His work led to a patent on the production of methane in 1935. (24)

ORGANIC MATTER

Organic materials are products of the processes of life, synthesized from minerals and inorganic matter by the addition of energy. Organic material is unstable, continually seeking to return to its initially stable chemical constituents with the release of energy. In the cycle of life, some organic matter is continually being synthesized into new organic material while some is being utilized as a source of energy to effect the synthesis.

INTEREST IN ORGANIC MATTER

The community of man, as it is interested in its wastes, is concerned with the destruction of organic matter or its degradation to inorganic matter. Since chemically the synthesis of organic matter is a process of reduction, degradation may be effected by oxidation, releasing energy

in the form of heat or, biochemically, by allowing bacterial life to utilize the stored energy in its metabolism. The wastes of modern America, being water carried, are over 98% liquid making direct chemical oxidation impractical and bacteriological treatment is generally necessary. OCCURANCE OF ORGANIC MATTER

Organic matter occurs in sewage as carbohydrates, fats, proteins and their products of decomposition. Carbohydrates

All organic matter contains carbon. The carbohydrates contain carbon, hydrogen, and oxygen, with the oxygen atoms numbering one half the hydrogen atoms. Sugars, starches, and cellulose are typical carbohydrates. Chemically, starch consists of large molecules which may be represented as $(C_6H_{10}O_5)_x$; simple sugars (monosaccharides) dextrose, levulose, etc. as $C_6H_{12}O_{10}$; complex sugars (polysaccharides) by $C_{12}H_{22}O_{11}$; and cellulose by $(C_6H_{10}O_5)_x$. Carbohydrates are of plant or vegetable origin. They are compounded by plants from materials in the soil, air, and water; the energy required being obtained from the sun by the process of photosynthesis. Fats

Fats are also composed of carbon, hydrogen, and oxygen; however the number of atoms of hydrogen is always greater than twice the number of oxygen atoms. The general classification fats includes all ether soluble substances,oils, greases, soaps, etc. .

Organic fats may be of animal or vegetable origin. Few simple fats occur in plant or animal tissue; however the simple fats Glyceryl Oleate $C_{3}H_{5}(C_{17}H_{33}O_{2})_{3}$ and Tristemrin $C_{3}H_{5}(C_{18}H_{35}O_{2})$ will serve to illustrate the chemical formulae of fats. Potassium oleate is a typical soap, $C_{17}H_{33}$ ·COOK. Proteins

Protein is made up of carbon, hydrogen, oxygen, nitrogen and usually sulfur and phosphorus. About 16% of the compound is nitrogen and about 1% sulfur and other elements. The building blocks of proteins are the amino acids (42).

Chemically, egg albumin $C_{696}H_{1125}O_{220}N_{175}S_8$ and milk casein $C_{708}H_{1130}O_{224}N_{180}S_4P_4$ represent typical proteins. INSTABILITY OF ORGANIC MATTER

Organic material is unstable and as indicated in the life cycles, Figures 1 and 2 pages 7 and 8; is continually being utilized by higher organisms to build new living tissue or must decay. The object of treatment for sewage and wastes is to permit the decay to occur without nuisance. Decay is brought about by microorganisms; - yeasts, molds, bacteria and protozoa; thus it is inevitable that complete treatment must be a biological process. Bacteria are notmally considered as assuming the major role in sewage treatment.^{*}

* Pillai and Subrahmanyan, working with the isolated ciliate Epistylis Sp, claim this protozoa can bring about all the changes associated with aerobic purification. (99)



FIGURE 1



Microorganisms may look upon sewage and other organic wastes as a natural cultural medium for the promotion of their own growth and activities. The raw wastes may be considered as a chemical compound which is to be converted to another chemical compound. The microorganisms, through the agency of their enzymes, act as a catylist to propitiate the change.

ENZYMES

Enzymes are themselves protein molecules which are extremely specific in their action, being concerned with the decomposition or synthesis of a particular compound only. Table I, page lo, is a tabulation of some enzymes and the substances upon which they act.

ENZYMES AS CATYLISTS

Enzymes are true catylists not reacting chemically in the change they bring about; although there is evidence of a steady deterioration made up by the production of fresh enzymic material. ((5) page 43). Enzymes are of two types: hydrolases, generally secreted into the medium surrounding the cells which produce them; and desmolases, which remain within the cell producing them. The extracellular hydrolases convert insoluable substances into compounds of lower molecular weight which may diffuse into the cell and be oxidized by the desmolases for vital cell processes.

A yeast plant secretes invertase and zymase. In the presence of invertase and water, sugar is split into glucose and fructose. Zymase converts the simple sugars into

alcohol and carbon dioxide;

с₆н₁₂0₆--►2со₂ + 2с₂н₅ он

Table I

PARTIAL TABLE OF ENZYMES*

Enzyme	Substance Acted Upon	Product
Amylase	Fats	Dextrins and Maltose
Glycolase	Hexose sugars	Lactic acid
Sucrase (Invertase	Sucrose	Glucose and fructose
Inulase	Inulin	Fructose
Lactase	Lactose	Glucose and glactose
Maltase	Maltose	Glucose
Pepsin	Proteins	Proteosis, peptones
Rennin	Casein	Paracasein
Trypsin	Proteins, albumoses, peptones. peptides	Peptides, ammino acids
Urease	Urea	Carbon dioxide and ammonia
Zymase	Glucose, fructose, mannose, galactose	Alcohol (ethanol) and carbon dioxide

* Adapted from GENERAL CHEMIS TRY by H. N. Holmes pub. by MacMillan Company (1931)

BIOCHEMICAL OXIDATION

Biochemical oxidation proceeds through the agency of enzymes. Oxidation of a substance has occurred if oxygen has been added, hydrogen removed, and elctron lost or the valence increased.

AEROBIC AND ANAEROBIC OXIDATION

Biochemical oxidation which takes place in the presence of free oxygen is termed aerobic and the organisms

involved called aerobes. Bacterial respiration can take place in the absence of nascent oxygen and when this occurs the process and organisms involved are termed anaerobic. In anaerobic fermentation some of the organisms involved may be **faculative** aerobes, that is, able to carry on their metabolism with or without the presence of free oxygen.

More generally it might be stated that anaerobic organisms are injured by the presence of free oxygen. In respiration, when free oxygen enters the reaction, hydrogen peroxide may be produced. This is a bactericide and would harm the bacteria present if they were unable to destroy it. Aerobes, with some exceptions, produce the enzyme "catalase" to achieve this destruction.

Oxidizing - Reducing Potential

The division of aerobes from anaerobes by showing that the former produce catalase does not suffice as a complete explanation. Clark and his associates (see 5) have shown that the concentrations of electrons in the medium become a measure of the oxidizing or reducing potential of a biochemical system. Observations indicate there is no distinct division between aerobic and anaerobic conditions, rather a continuous shading from one to the other with certain organisms, or their active enzymes, showing a marked preference for a certain range of oxidizing-reducing potential in carrying on their activity.

Sewage or waste containing a mixture of inorganic

and organic materials and their products of decomposition have both oxidizing (having an affinity for electrons) and reducing (having a tendency to give up electrons) agents present simultaneously. The potential of each existing in the medium would determine the level of activity of the so called aerobes or anaerobes rather than the presence or absence of free oxygen,obligatory anaerobes prefering concentrations of electrons and the obligatory aerobes, at the other end of the scale, prefering to do without.

THEORIES OF BIOCHEMICAL OXIDATION

Warburg (145) considers biological respiritory oxidation as taking place through the catylitic transfer of oxygen to the substance being oxidized, - the iron compound "cytochrome" being alternately oxidized and reduced.

Wieland (150) considers biological oxidation to consist of the loss of hydrogen rather than the gain of oxygen. Hydrogen, activated by an enzyme, is transferred from one molecule (a "hydrogen donator") to another molecule (the "hydrogen acceptor"); or the transfer of the "activated" hydrogen may take place between different parts of the same molecule.

Molecular oxygen may function as the hydrogen acceptor as occurs in the oxidation of alcohol to acetic acid by the vinegar bacteria genus Acetobacter;

С2H50H ≠ 02 - → СH3COOH ≠ H20

Levine (61) describes the bacteriological oxidation of alcohol to acetic acid in the absence of free oxygen if methylene blue is present in the reacting mixture. Through the agency of the bacteria two hydrogen atoms are removed from the alcohol ($C_{2H_5}OH$) the methylene blue (which contains no free oxygen) acting as the hydrogen acceptor. The alcohol becomes acetaldehyde, $C_{2H_5}OH = CH_3COH + 2H$, which takes on a molecule of water to become hydrated acetaldehyde ($CH_3COH \cdot H_2O$) which in turn is dehydrogenated by the bacteria to acetic acid (CH_3COOH). The source of the necessary oxygen is the water **of** the solution. Nitrates and sulfates may also act as the hydrogen acceptor.

Quastel (101) considers that the intramolecular oxidations proceed by the activation of a carbon neucleus by an electrostatic force in the enzyme.

Such a multitude of theories indicates that no one theory can satisfactorily explain bacteriological oxidations undercall conditions, at this time. Buswell (31) after reviewing the theories of anaerobic fermentation makes the statement;

"Frequently two or more of these mechanisms may either operate simultaneously or in response to changing environmental conditions within the culture."

Fermentation

When nitrate, sulfate or other compound functions as the acceptor of the "**activated**" hydrogen atom, "catalase" is not necessary since hydrogen peroxide is not formed. This constitutes fermentation. The change of alcohol to acetic acid previously described is a fermentation process.

CHEMISTRY OF BIOCHEMICAL OXIDATION

-1

Buswell (20) has summarized the chemistry of the biochemical oxidation of organic matter by representing the chemical constituents of organic matter with C for carbon, H for hydrogen, and X for the relatively small amounts of the other few chemical elements that enter into organic compounds. By his symbolism organic material becomes CHX.

Aerobic decay may they be represented as:

 $CHX + 02 = CO_2 + H_{20} + X$

which would indicate the complete reduction of the organic material.

Anaerobic purification can be represented by:

 $CHX + H_2O = CO_2 + CH_4 + X$

in which the organic material is eliminated from the substrate by oxidizing the carbon to carbon dioxide and through the formation of methane gas which escapes from the liquid.

When sulfates are present (and they may be decomposition products of proteins) the following reaction may occur:

 $CHX + SO_4 = CO_2 + H_2S$ or RHS

RHS representing any complex carbon-hydrogen radical. Hydrogen sulfide is of course foul **smelling** and the mercaptans and other carbon-hydrogen compounds may be even more so.

Dr. Buswell has, of course, neglected the oxygen which is also present in organic matter but this in no way affects the simple illustration he has produced.

BACTERIAL METABOLISM

RESPIRATION

Life is carried on by the utilization of energy. Living things obtain this energy by the oxidation of organic material. Respiration is the oxidation of food in the living cell. Respiration may be of three types: gaseous, intermolecular, or intramolecular.

In general, bacterial respiration utilizes oxygen, the three types of respiration correspond with the oxidation-reduction potential within the media.

Respiration of Aerobes

Gaseous respiration is the perogative of the aerobes and occurs when the substrate contains gaseous oxygen. Respiration of the Anaerobes

At lower oxidation potentials of the media intermolecular respiration occurs; without free oxygen to accept the "activated" hydrogen atoms nitrates, nitrites or sulfates (in that order) will become the hydrogen acceptors. In sewage all three of the above compounds will be present to some extent. Nitrates and nitrites may be reduced without creating offensive products; however the reduction of sulfate leaves as a product of the decomposition hydrogen sulfide, with its offensive odor. In sewage practice, the level at which hydrogen sulfide production begins is normally considered as the start of anaerobic decomposition. This is of course a purely arbitrary definition.

At a lower oxidation potential, organisms which obtain energy by intramolecular respiration become active. The previously described fermentation of glucose to alcohol is a simple illustration of what occurs:

 $C_{6}H_{12}O_{6} = 2CO_{2} + 2C_{2}H_{5}OH$

In glucose there is sufficient oxygen to oxidize the hydrogen to water or the carbon to carbon monoxide. In the reaction illustrated one third of the carbon has been completely oxidized leaving alcohol, with a greatly lowered oxygen ratio. The yeast obtains energy for its metabolism.

DIGESTION

Digestion is the breaking down of complex molecules of food into simpler molecules that they may diffuse through cell walls. In anaerobic digestion, by bacteria, digestion is mainly an extracellular function garried on by the enzymes secreted by the cells. Enzymic action may continue after the organisms secreting the enzymes have been destroyed. The process of digestion may be one of fermentation or hydrolysis. Hydrolysis

The hydrolytic action of the enzymes makes use of the oxidative power of the hydroxl ion and the reductive action of the hydrogen ion in a divided molecule of water. In the hydrolysis of a typical carbohydrate, cellulose, the **chemi**cal reaction may be noted as follows:

 $(C_{6}H_{10}O_{5}) + x(H_{2}O) = x(C_{6}H_{12}O_{6})$

In this manner a complex molecule is reduced to a simple sugar. Similarly fats can be reduced to fatty acids and glycerin: $C_{3}H_{5}(C_{18}H_{35}O_{2})_{3} + 3H_{2}O = 3(C_{17}H_{35} \cdot COOH) + C_{3}H_{5}(OH)_{3}$

Tristearin + Water = Stearic Acid + Glycerin Other substances may be similarly decomposed. In the reaction, illustrated above, water itself becomes the oxidizing agent. Role of Wat¥r

It should be noted that for anaerobic decomposition water is necessary not only as a disbursing medium but is a necessary adjunct to the chemical reactions taking place.

Langford° reports the following comments by Dr. H.

Bach:

".... in order to be decomposed, sludge particles must be totally immersed in water, allowing the bacteria an unrestricted supply of this essentially indespensible liquid; for, as he observes, the bacterial body itself consists of far more than 90 per cent water. He further emphasized the importance of protecting the bacteria from the access of oxygen in order to insure the true anaerobic action, his thought being that only this kind of bacterial action results in breaking up the sludge particles in their depths, as compared to aerobic action, which is to his mind confined to the surface of particles and therefore may be employed only in cases where undissolved suspended matters if at all present, are at least in minute amounts, and in minute particle sizes. Another point emphasized by Bach is the necessity of protecting the bacterial actions, as a refuse of the bacterial cell or as a result of splitting action of bacteria on a substance. His thought is that carbon dioxide is especially poisonous to bacteria of any kind."

DIGESTION OF ORGANIC MATTER

Carbohydrates

The simple sugars, such as glucose, are readily soluable and available to the microorganisms as food. More complex carbonaceous material like starch, inulin and some cellulose materials are hydrolysed first to complex sugars by splitting the

• Page 38 reference ((78))

large molecules; simpler carbohydrates and ultimately simple sugars result from further hydrolysis. Some carbohydrates are extremely stable; lignocullulose, for example, being very resistant to putrefaction, however, in general carbohydrates are readily available food material.

Fats

Fats, ether soluble, are hydrolysed to fatty acids (water soluble) and glycerol as previously shown in the illustration of hydrolytic action. The ultimate products include methane, carbon dioxide gas and ammonia.

Proteins

Proteins always exist as large molecules. Proteoses, still of large and complex molecular structure, will result from the first splitting; continued splitting into smaller molecules will eventially produce amino acids and various carbonaceous materials. Amino acids, in general, are soluble. Protein, since it contains sulfur and nitrogen, in its putrefaction releases hydrogen sulfide, mercaptans, indol, skatol, etc. as products of decomposition. These substances cause the odors often associated with anaerobic fermentation.

NUTRITIVE REQUIREMENTS

Bacteria require (in amounts varying with the species) potassium, sodium, calcium, magnesium, iron, chlorine, sulfur and phosphorous for their metabolism. Metabolism may be divided into anabolism, the building up of the protoplasm of the bacterial cell and the formation of chemical compounds for active growth, and catabolism which is the breaking down of substances within the cell or in the media surrounding the cell.

The nutritive requirements vary with the species of the organism. Some bacteria obtain nitrogenous substances by breaking down protein; others have the ability to oxidize ammonia to nitrates and nitrites. In digesting, anaerobically, fresh solids containing 4 or 5 percent nitrogen it has been found that ammonia nitrogen accumulates, indicating that more nitrogen is present than is required for the metabolism of the organisms. On the other hand, if sufficient nitrogen in a usable form is not present digestion may be inhibited. (24)

When bacteria capable of utilizing albumin were isolated and placed in a pure culture containing albumin alone they could not digest it; however, when peptone was added the necessary enzymes were developed and the albumin was attacked and destroyed. (5)

Autotropic bacteria obtain energy for their growth from simple chemical compounds, meeting their carbon requirements with carbon from carbon dioxide or simple carbonates; heterotropic bacteria utilize more complex organic material.

THE PURPOSE OF ANAEROBIC TREATMENT

The purpose of anaerobic treatment is primarily to stabilize organic wastes so that they may be disposed of without offense.

PRODUCTS OF ANAEROBIC TREATMENT

The products of decomposition will, of course, be influenced by the materials being decomposed and the bacteria which are active. Under the usual conditions of waste disposal by-products are only incidental to the process; and so long as they create no nuisance are not controlled, except as their control may contribute to the efficiency of the process.

The products usually obtained from anaerobic decomposition are methane and carbon dioxide gases and a humuslike sludge. The desirable characteristics, and those usually obtained from domestic sewage, are that this sludge have only slight inoffensive odor and while it may continue to decompose, that this decomposition be benthal in nature.

Anaerobic fermentation may also be used for the production of alcohol (6) (151); Buswell (20) points out the possibility of concentrating acetic, propionic and butyric acids under favorable conditions; and Laigert (77) has produced petroleum in the laboratory.

THE PROBLEM OF ANAEROBIC TREATMENT

The problem of anaerobic treatment is one of maintaining a proper habitation for the desired flora and fauna, in which they may obtain the foodstuffs they desire and need for their metabolism and have an optimum environment for carrying on their life processes. It is essential that sufficient quantities of carbon, hydrogen, oxygen and at least traces of sulfur and phosphorus be present. In domestic sewage the required elements are present and in about the proper ratio for balanced life; with industrial wastes this may not be true, and to maintain anaerobic treatment processes it may be necessary to supply the elements which are lacking or are deficient in quantity. ENVIRONMENTAL CONDITIONS

Environmental conditions include temperature, oxidationreduction potential, acidity or alkalinity, concentration of organic and inorganic materials, reaction and the actual organisms present. End products that are detrimental to the bacterial population must be eliminated or avoided. The availability of food includes proximity to the organisms as well as its presence in the substrate.

Rudolfs (109) considers the essential conditions for bacterial development as food supply, reaction, temperature and removal of waste products. Langford (78) indicates that investigations show temperature is more important than pH.

UTILIZATION OF ORGANIC MATERIAL

Living organisms utilize organic material for synthesis of their own structure and for energy to effect the synthesis. Biochemical stability has been achieved when the organic material is no longer available as a foodstuff. When this has occurred the purpose of treatment has been gained, oxidizable material may remain, as in the humus-like sludge of domestic sewage, but since it is not immediately available as a food it is biochemically stable.

Phelps (5) page 40), using the data from Butterfield's work indicates that <u>B. aerogenes</u> in a peptone-sugar solution, while utilizing 3.0 milligrams of oxygen per liter of medium, produced 1.2 milligrams of dry bacterial substance per liter and oxidized 4.5 milligrams of organic material. With a total of 6.5 milligrams of organic matter utilized, about 21 per cent was synthesised to new material and 79 per cent consumed for energy of living and growing.

Considering the energy content of the new material formed and comparing with the energy of the food consumed, only about 3 per cent of the energy in the food is available in the new growth.

These values are not the same for all organisms. Experimental work with other organisms and different media would and do show entirely different results. Zobell and Grant (152) wobking with several strains of bacteria in media containing small concentrations of glucose and ammonia phosphate or peptone found 60 to 70 per cent of the organic substrate was oxidized to the balance being converted to bacterial protoplasm.

Pasteur's experimental data (5) on the fermentation of dextrose to alcohol and carbon dioxide (an intramolecular reaction:- $C_{6H_{12}O_6} = 2C_{2H_5}OH + 2CO_2$) shows 100 parts of sugar to yield 48.5 parts of alcohol. Theoretically the yield should be 51.1 parts; therefore only about 2.6 percent of the initial weight of the sugar can be converted to new organic material (yeast), and of this amount some is lost to small quantities of by-products which appear with this biochemical reaction.

In this case the heat of combustion of the glucose is 3.74 kilogram calories per gram, and an equivalent amount of alcohol to that obtained from the fermentation of the glucose would give 3.63 calories. The carbon dioxide has no heat of combustion; therefore at most 0.11 calories can be left in the new organic matter.

LOSS OF OXIDIZABLE MATERIAL

Pasteur found that 80 to 90 grams of sugar were required to synthesize one gram of yeast anaerobically and only 8 or 9 grams of sugar were required to produce one gram of yeast when aerobic conditions prevailed (31). In this same reference Buswell and Neave indicate that 328.6 calories per gram may be obtained by the complete oxidation of alcohol to carbon dioxide and water, but if the alcohol is fermented anaerobically the reaction yields only 43.5 calories. The oxidation obtained anaerobically is, however, not complete, the end products being methane and carbon dioxide. Methane is only slightly soluble in water, and if it escapes from the solution (with its high heat of combution) considerable oxidizable material may be considered as removed.
BIOCHEMISTRY OF METHANE PRODUCTION

Many organic materials are capable of being decomposed anaerobically to carbon dioxide and methane. The limited group of bacteria able to bring about this change will be discussed later. The chemical breakdown of various organic substances to methane and carbon dioxide is illustrated by the following equations (25) (any intermediate steps are ommitted):

For sugard and starches,

 $C_{6H_{10}O_{5}+H_{2}O} = 3CO_{2} + 3CH_{4}$

For fats (the decomposition of stearin is illustrated),

 $4C_{57}H_{11006} + 106H_{20} = 65C0_{2} + 163CH_{4}$

For proteins (the decomposition of casein is illustrated), $C_{148H_{233}O_{48}N_{37}S + 524H_{2}O = 1366O_2 + 308CH_4 + 148NH_4(HCO_3) + 4H_2S$ THEORIES OF METHANE PRODUCTION

There are two contending theories attempting to explain the biochemistry of the production of methane in anaerobic fermentation. Buswell and Neave (31) believe that the food media is the direct source of methane, whereas the European concept followed by Barker (81) contends that the methane results from the reduction of carbon dioxide acting as the acceptor for "activated" hydrogen.

Intermolecular Oxidation

It has been demonstrated (81) that hydrogen-carbon mixtures introduced into digesting sludge disappear in

accordance with the formula:

 $CO_2 + 4H_2 = CH_4 + 2H_2O$

the sludge acting as a catalyst for the reaction.

Levine (81) states that Barker (10) demonstrated, that at least in the first stages of anaerobic fermentation of alcohol in the presence of carbon dioxide, acetic acid and methane are produced, - the amount of methane being proportional to the amount of carbon dioxide utilized and the amount of acetic acid proportional to the amount of alcohol. Buswell and Sollo (33), using the isotrope C^{14} to trave the formation of methane, found that the methane formed contained but small amounts of the tagged atom, indicating that the methane was not directly formed from the carbon dioxide. Stadtman and Barker (132), repeating the work of Buswell, to confirm it, found that when working with impure cultures of the methane bacteria little of the C^{14} was present in the methane produced; but with the fermentation of acetic acid by Methano Bacterium Omelianski, in the presence of labeled carbon dioxide, the carbon dioxide was directly used.

Barker indicates that for the impure cultures the carbon dioxide supplied may be utilized in an intermediate step, but that the methane must result from the reduction of carbon dioxide. This concept of methane production concurs with accepted theories of the biological reduction of Carbonates (CO₃), Nitrates (NO₃) and Sulfates (SO₃) being in nature a similar function. It was previously presented (page 15) that oxygen, nitrates and sulfates will act as hydrogen acceptors, and if present they do so in that order.

Heukelekian (60) attributes the following demonstrations of the chemistry of these reductions to van Niel: $4H_2A + H_2SO_4 = 4A + H_2S + 4H_2O$ representing the reduction of sulfates and $4H_2A + H_2CO_3 = 4A + CH_4 + 3H_2O$ representing the production of methane.

The H2A represents any compound (organic or inorganic) upon which the bacteria act. In either case the bacterial enzymes activate the hydrogen in this doner. The "activated" hydrogen then reduces the sulfate, in one case, or the carbonate in the other. The end products are, (as illustrated) water, an organic or inorganic residual and either methane or hydrogen sulfide.

Intramolecular Oxidations

Buswell and Neave, in their concept, consider that the acetic acid formed in the substrate is decomposed by intramolecular oxidation:- the methane produced being chiefly derived from the methyl group and the carbon dioxide coming from the carboxyl group. The carboxyl group (COOH) in the acetic acid (CH3.COOH) is first oxidized to CO₂ and the "activated" hydrogen released to reduce the remainder of the molecule to methane (CH₃+H = CH4). Buswell and Sollo found confirmation for this theory in the anaerobic fermentation of acetic acid in the presence of labeled carbon dioxide.

PRODUCTION OF SUBSTANCES OTHER THAN METHANE

At present the anaerobic treatment of sewage and wastes is almost entirely concerned with those fermentations which result in the production of methane. The production of alcohols (151) are achieved through the inocculation of the media with cultures of specific bacteria and have been limited to the treatment of specific wastes. Acid production may be achieved by special manipulation of the media being processed. Buswell (20), working with the methane bacteria, has produced concentrations of acetic, propionic and butyric acids as high as 7,000 parts per million by the addition of alkali (as lime or sodium hydroxide) to the substrate in the laboratory. Other by-products, which may be obtained, are achieved by similar methods.

INTEREST IN THE PRODUCTS OF DECOMPOSITION

It has previously been stated that the purpose of waste treatment is to reduce the organic material to relatively stable inoffensive matter with a minimum of nuisance to the community of man. To this it may be added, it is desired to effect this reduction at a minimum of cost and expense. The products of decomposition are of interest if their commercial value may help defray the cost of treatment and secondly if their control will increase the efficiency of the treatment process.

LIMITATION OF THESIS TO METHANE FERMENTATION

This thesis will be restricted to those anaerobic treatment processes which produce methane or are capable of so doing. Limitation is necessary in order to keep the project within reasonable bounds. Methane production is of most general and practical interest, Fermentations to produce other products would make an interesting separate topic. All biochemical treatment processes require that a suitable environment be maintained for the bacteria and/or other organisms whose work is desired. It is corollary, for any biochemical process, that undesired organisms or products should be excluded or discouraged.

UNIVERSAL APPLICABILITY OF METHANE FERMENTATION

Boardel (Buswelli (22) indicates that data available in the various publications show that, with the exception of hydrocarbons, practically all carbonaceous substances can be converted quantitatively to methane and carbon dioxide, if fermented long enough and under proper conditions. "Even lignin yields slowly to this action." It is generally accepted that nitrogenous substances are readily digested anaerobically. The same investigator (27 & 29) attributes the gases from two-stage digestion as resulting principally from the fats, soaps and proteins in the substrate.

Examination of the chemical formulae for typical organic substances, which have been given on page 24, will show: that starches and sugars, when completely digested,

will yield equal parts of carbon dioxide and methane; that fats, have slightly varing compositions, but will yield gas which is 62 to 75 per cent methane and 25 to 38 per cent carbon dioxide; that with proteins the percentages of carbon dioxide and methane in the gas will vary from 25 to 35 per cent carbon dioxide and 65 to 75 per cent methane, depending upon the proportions of the chemical elements contained in the material being decomposed.

NUTRITIONAL REQUIREMENTS OF THE ORGANISMS

While studies have been made to determine what substances may be fermented anaerobically, only in a general way is it known what elements are required by the organisms present for their metabolism. Thus Buswell and Boruff (24) found that in the fermentation of carbonaceous materials, ammonia-nitrogen, added to the solution so as to maintain concentrations of 23.8 to 600 parts per million, stimulated the production of methane.

Schlenz (121 & 123) indicates that the addition of ammonia-nitrogen has a beneficial effect on the digestion of sewage sludge, especially on scum accumulations. Heukelekian (58) modified Barker's media for culture of methane bacteria to promote more rapid growth. He also found that there was an optimum concentration of organic substrate that promoted growth.

Studies on the nutritional requirements of the anaerobic organisms, similar to those undertaken at MIT by Helmers and others for aerobic types, might supply much

THE MICROORGANISMS OF ANAEROBIC DIGESTION

THE METHANE BACTERIA

Some progress has been made since Professor Barker

stated in 1936 (11):

"There is probably no important group of bacteria so poorly known as that group which is made up of the methaneproducing organisms.

Although the formation of methane is a phenomenon of common and wide-spread occurance in nature and is of increasing importance in sewage purification and disposal of waste products with the simultaneous production of fuel, the existing knowledge of the causative agents of this fermentation is still very slight. This is evident from the fact that not a single representative of the group is listed in the standard works on bacterial taxonomy."

The work of Barker (10 & 11), Buswell (20), Heukelekian (58, 59, 60, 61) and others has done much to improve this knowledge since the time of the above statement.

Barker indicated that the following four species of bacteria appear to be most important in methane fermentations:

Methano sarcina methanicii

A coccus. 4 or 5 mu in diameter. Usually in packets of 4 or 8. Ferments acetic and butyric acids with production of methane, but not ethyl or butyl alcohol.

Methano coccus Mazci

A micrococcus. Less than 1 mu in diameter. Singly or in slimmy aggregates. Ferments acetic and butyric acids but not ethyl or butyl alcohols.

Methano bacterium Omelianskii

A bacillus. Ferments ethyl alcohol to acetic acid and butyl alcohol with methane fermentation. This same organism probably also ferments butyric acid to acetic acid. Acetic acid is not fermented.

Methano bacterium Sohngenii A bacillus. Ferments acetic and butyric acids but not ethyl alcohol. A thermophilic organism described by Coolhous is considered by Barker to be a variety of <u>Methano</u> <u>bacterium</u> <u>Sohngenii</u>.

These organisms have the following common characteristics (20) they are gram negative, non-motile, and non-spore forming. They are strict anaerobes capable of using ammonia as a source of nitrogen. They have a very slow rate of development and seem to require a certain amount of surface for their propogation. Both Buswell (20) and Heukelekian (58) used shredded asbestos for added surface in the substrate, in their laboratory cultures.

Isolation of Methane Bacteria

Although methane production from decomposing vegetable matter was recognized in 1776 and Sohngen studied methane producing bacteria in 1906, not until about 1936 was a pure culture obtained. Barker by using a medium in which the only source of food was ethyl alcohol succeeded in isolating <u>Methano bacterium Omelianskii</u>. In 1947 Buswell (20) reported having obtained an apparently pure culture of <u>Methano sarcina</u> <u>methanicii</u>.

The isolation of the pure cultures was hailed as opening the way for developing artificially active inoculum material which would shorten the period for starting digestion. However, Heukelekian (60) has found that the methaneproducing bacteria are not capable of utilizing complex substances and that sewage sludge must be liquified by other bacteria. He suggests that liquifaction and methane production might properly be separated.

THE OTHER ORGANISMS

The words of Lackey (75) may be used to sum up the present status concerning the organisms present in anaerobic treatment:-

"Better comprehension of the process would be possible if the kinds and numbers of bacteria actually at work were known."

Surveys have been made (see 75) but at present there is no comprehensive listing or indication of probable numbers that may be expected of bacteria or yeasts for anaerobic processes. The protozoa present have been tabulated but their role is not completely known, although Rudolfs states (110) "....it is evident that by sheer force of their numbers they may be an important factor under certain circumstances."

Quantitatively, under direct microscopic examination, relatively few organisms (motile bacteria, yeasts, filamentous fungi, actinomycetes or protozoa) are found (75). Cultures do give large counts but this would be expected. Photomicrographs taken of cultures from sludge digesting in a satisfactory manner show a satisfactory development of methanebacteria forms, contrary to cultures from unsatisfactory digesters which show poor development (20).

Lackey (75) made the following statement concerning the biology of sewage treatment, which may be repeated and underlined for the anaerobic processes:

"Things that must be known are: first, more precise information on the species of each group of organisms working in the treatment plants; second, the relative abundance of each, so that no important (numerically or volumetrically) organism is neglected; third, the range - not the optimum, but the range - of environmental conditions under which the organism works; and fourth, the work accomplished - whether a small segment of the purification process, or a large one."

THE ANAEROBIOSIS OF SEWAGE AND SLUDGE

When the organic material in sewage or sewage sludge decomposes in the absence of sufficient oxygen to maintain aerobic conditions, the anaerobic decomposition occurs in three stages. Any concentration of organic matter might, in general, follow the same stages in its anaerobic degradation. However, the chemical composition or concentration of carbonaceous and nitrogenous material would have an influence on this.

THE STAGES OF ANAEROBIC DECOMPOSITION

These stages of anaerobic decomposition have been recognized for many years and are generally described as:

- 1. Septic or acid production stage.
- 2. Acid regression or acid digestion stage.
- 3. Alkaline fermentation or methane digestion stage. First Stage - Acid Production

In the absence of a sufficient supply of oxygen, the first stage will begin to develop almost immediately. The usual physical sign of the onset of this stage is the production of hydrogen sulfide odors. The production of these odors is, of course, dependent upon the presence of sulfur and the sulfur-bacteria. Heukelekian has investigated hydrogen sulfide production in sewage (56).

The production of hydrogen sulfide is only a symptom of the first stage of anaerobic decomposition. When anaerobiosis starts under the condition of insufficient oxygen (as it will naturally), the organisms attack the most readily available food substances first. These are the carbohydrates - sugars, starches and simpler celluloses, and soluable nitrogenous compounds. The products of decomposition will be carbon dioxide from the carbohydrates (see page 24), and the nitrogenous material that is attacked will, in breaking up, permit formation of organic acids, hydrogen sulfide and some carbonates.

It should be noted that the reaction of most of these products will tend to make the substrate more acid. Walker (144) notes that the solubility of a gas is proportional to its partial pressure in the atmosphere in contact with the solution. An examination of the equations previously given (page 24) for the complete decomposition of sugars and starches indicates that the gas formed will be fifty per cent carbon dioxide and fifty per cent methane. Thus in the first stage of anaerobic decomposition the concentration of carbon dioxide (which is much more soluable in water than methane) will be very high, and large quantities of carbonic acid will be formed.

In the early stages the principal component of the escaping gas is carbon dioxide and some hydrogen sulfide.

High acid concentrations inhibit and may almost stop the bioligical activity.

4

Stage one lasts about two weeks in natural anaerobic decomposition of sewage and sewage sludge. The actual duration depending upon temperature and other factors. In this stage the pH of the solution may drop to 5 or below.

As the concentration of carbohydrates is reduced, the fats and protein substances are more strongly attacked. Examination of the formulae of their complete reduction (page 24) will reveal that carbon dioxide makes up only twenty-five to thirty-eight per cent of the gas from their degradation; in addition the break-down of the proteins allows formation of ammonium bicarbonate, a salt which remains in solution. The products of decomposition thus tend to form less acid and even to neutralize acids that may be present. The Second Stage - Acid Regression

Stage two lasts about three months. The odors become more offensive due to formation of such compounds as indole, skatole and mercaptans from the decomposing protein substances. Gas production falls off, but contains a higher percentage of hydrogen. The sludge is grey in color and becomes sticky; entraped gases may cause it to become foamy and some of it to ride to the surface (cases have been reported where all the sludge has risen). The pH in this period slowly rises.

The Third Stage - Methane Fermentation

Stage three, alkaline fermentation, starts when the pH reaches about 6.8. Methane and carbon dioxide gas is given off. The volume of methane exceeding the volume of carbon dioxide. The pH may continue to rise and go slightly above the neutral point. Acids are broken down as soon as they are formed. In the first stage they were accumulating mainly from the breakdown of the more easily digested carbohydrates. The nitrogenous material is attacked as soon as acid accumulation stops (110), evidenced by the production of ammonia-nitrogen early in the second stage.

Stage three continues with the production of methane, the sludge becomes humus-like with a slight tarry odor and without the addition of new material, the digestible matter is exhausted and gasification ceases in about thirty days. Stage three is well buffered and inoculated with the organisms and their enzymes desired for the satisfactory fermentation of the material being digested; it is required that this stage of digestion be maintained if satisfactory anaerobic treatment is to be achieved.

Figure 3, page 37, includes curves that summarize the chemical changes occuring in the digesting material during the period of "natural" anaerobiosis. These curves trace the path of "natural" anaerobiosis previously described. Also included on this figure, are curves to indicate the quantitative change of the organisms present during the period





of digestion.

ENVIRONMENTAL CONSIDERATIONS

Studies of the individual organisms present, the work each performs, and the optimum habitat or conditions affecting the useful or efficient existance of each in the substrate are almost unknown. However, many investigators have studied the effect of environment upon the biological colony as a whole. Buswell and his associates at the Illinois State Water Survey; Rudolfs, Heukelekian and others at the New Jersey Agricultural Experiment Station; Fair and Moore (40) (41) and Rawn (103) have contributed much through their investigations of environmental conditions and their effect upon anaerobic treatment. This does not list all those who have contributed; others will be referred to throughout the text.

EFFECT OF TEMPERATURE

Bacteria and other organisms are generally affected by temperature. Extreme high temperature has the effect of sterilization, - ten minute exposure at 55 to 58 degrees Centigrade killing most bacteria excepting those which can form spores and moist heat at 120 degrees Centigrade killing all bacteria and spores. Tolerance to low temperatures is better, activity decreases with temperature to a point where the organisms may become completely dormant. In general, organisms have an optimum temperature, or narrow range of temperature, at which most rapid growth occurs, a maximum temperature above which there will be no further growth and a minimum temperature below which no growth occurs.

Bateriologists classify bacteria according to their growth at different temperatures as:

- Psychrophilic. Optimum temperature 15 to 20 degrees Centigrade. Minimum 0°C. Maximum 30°C.
- Mesophilic. Optimum temperature 37° C.-5° to 10° on either side of this temperature their growth is inhibited.
- Thermophilic. Optimum temperature 50° to 55° C. Minimum 25° to 45°C. Maximum 85° C.

It will be noted that the above temperature ranges overlap, - some bacteria in each group being facultative or having the ability to grow throughout an extended range of temperatures.

Fair and Moore (40)(41) made extensive studies of the effects of temperature on sludge digestion. Figure 7, page 56, reproduced from their work indicates the relationship between temperature and the time required for digestion of sewage sludge. This figure clearly shows the increased activity which occurs in the mesophilic and thermophilic temperature ranges. These men went further and formulated the rates at which digestion processes take place, determining the velocity constants which are dependent upon the temperature of the reaction.

Rudolfs investigated the effect of temperature on certain aspects of the anaerobic digestion process. Figure 3, page 37, includes curves summarizing the effect of temperature upon the reduction of volatile matter, gas production, and number of organisms present during "natural" anaerobiosis. Rudolf's work did not, in this case, include the thermophilic temperature range; however, while the numbers of organisms present seems to decrease with temperature, there is a definite peak in volatile matter reduction and gas production at mesophilic temperatures. This is in full agreement with the work of Fair and Moore.

EFFECT OF pH

Methane production does not occur at a pH much below 6.8 or above 8.8. The reaction of satisfactorily operating anaerobic treatment is in the neighborhood of the neutral point. Many investigators feel that the total alkalinity or organic acids (reported as acetic acid) are a better criterion than pH and also more accurately determined under the usual conditions of operation (51)(121). Observations on the control of pH by the addition of alkaline material (usually lime) have been made under many conditions and at many plants (45). Very often the addition of lime has been made to control the pH and attempt to shorten the break-in period of Imhoff and separate sludge digestion tanks. Schlenz (122) and Buswell (20) have questioned that this is the most satisfactory expedient to use. Buswell indicates that by the addition of alkali it is possible to build-up concentrations of acids of 7,000 p.p.m., but the production of acid and the production of methane can

not be simultaneous processes.

Schlenz (123) explains that when a highly ionized condition is induced by the addition of lime the formation of acetic acid from organic material tend to continue to the aceta**te** upon which the methane bacteria do not work. He gives the following chemical formula to explain the difference in reaction: - $2(CH_3 \cdot COOH) + Ca(OH)_2 = Ca^+ + 2(CH_3COO)^+ + 2H_2O$ indicating the meaction with lime present. Without the presence of lime the acetic acid breaks down as follows:--



Heukelekian (60), when working with the methane bacteria, found when the reaction of "natural" anaerobiosis was controlled by the addition of lime that certain undetermined agents which inhibited the later action of the bacteria were either neutralized or not produced. His work included the inoculation of previously prepared culture media with methane bacteria colonies. He determined that gas production occured sooner and in larger quantities when the substrate had the acid fermentation stage controlled by the addition of lime, even though the pH of both media were the same when inoculation was made. At the present time discussion of pH control by the addition of chemicals is still active. (143). Opinions range from that of Schlenz (122) that pH is the result of proper digestion conditions and the control of pH alone will not obtain these conditions, to the idea that a little liming well applied will help.

In general bacteriology it is considered that a pH of less than 2 or more than 11 will act as a disinfectant, with a corresponding inhibiting effect occuring as these limits are approached. The methane bacteria themselves have an optimum range near 7.0. It would appear that, if other factors may be controlled so that an acid environment does not develop, this would be more desirable than attempting to control acidity by the addition of chemicals.

EFFECT OF PRODUCTS OF DECOMPOSITION .

There are formed, during the course of anaerobic fermentation, many products of the decomposition; the hydrolysis of some substances to other materials, the higher organic materials being split to less complex compounds, etc. The stages of digestion products, for the materials present in sewage sludge, is relatively unexplored. Some work has been done determining the products formed during the anaerobic fermentation of certain specific materials (134)(135). The effect of certain substances, such as alkalinity, volatile acids and certain carbonates, is also known.

Alkalinity

The alkalinity, as calcium carbonate, of raw sewage varies from 400 to 1200 parts per million and of thoroughly digested sludge is between 3,000 and 3,500 parts per million (51). Alkalinity, as such, probably can not be termed a product of decomposition; however the change in alkalinity certainly reflects the accumulation of products of decomposition or possibly the utilization or reduction of certain materials. Haseltine (51) suggests, that since for digesting sludge alkalinity may be determined as easily and more accurately than the pH, the path and control of digestion might be ascertained more effectively if alkalinity tests were substituted for routine pH analysis. A minimum alkalinity of 2000 parts per million, in the digester, is required for satisfactory methane production.

Ammonium Carbonates

Ammonium carbonates are products of the decomposition of proteinaceous material. Ammonium bicarbonate (NH₄HCO₃) was previously mentioned under the first stage of "natural" anærobiosis, page 35, where it was mentioned that this salt is formed and remains in solution. This salt contributes to the alkalinity of the substrate and within the limits of alkalinity of 2,000 to 3,000 parts per million may be considered as beneficial. Snell (129) reported difficulty in digesting undiluted human excreta, due to the formation of large amounts of ammonium carbonate, $(NH_4)_2CO_3$. During his experiments he found that urea, $CO(NH_{4})_{2}$, and ammonium carbonate in concentrations of 4,300 parts per million (as Nitrogen) completely prevent the digestion of seeded feces; the same strength of ammonium bicarbonate retarded digestion 25 to 50 per cent.

Snell experimented with the inhibitory effect of some other ions, with the results tabulated in Table II, page 45. He found that sulfate ion (1.4%) in combination with sodium or ammonium ion was completely inhibitive even when the pH was adjusted to neutral. He thought that ammonium, calcium and similar ions were not so inhibitive as the stronger alkaline ions such as sodium and potassium.

It can not be said that the work in this field is anywhere near complete.

Volatile Acids

Volatile acids are present in raw sewage to some extent and they are a major product of the break down of higher organic substances. Their presence in the substrate is necessary to the production of methane by the methane bacteria that have been isolated. In excessive amounts however they are detrimental to the production of methane. Schlenz (121) suggests that acidity be controlled by "volatile acid" determinations. Methane production falls off when the concentration of volatile acids (as acetic acid) rises much above 2,000 parts per million. Buswell (20) suggests that, for control, the upper limit should be between 2,000 and 3,000 parts per million.

TABLE II

INHIBITION OF DIGESTION BY VARIOUS IONS

Chemicals Employed in Inhibition Experiments with Seeded Feces*

Exp. No.	Chemical Employed	Initial Concen. **	pH Adjusted to	Remarks	
Series A.			250 c.c. bottles		
e b c d	Urine Urea (NH _U)2CO3 NH4HCO3	3000 3000 3000 3000	Unadjust. Unadjust. Unadjust. Unadjust.	No digestion No digestion No digestion Normal digestion	
Series B.			4 liter bottles		
19. 20. 21. 22. 23. 24. 25. 26. 27.	(NH ₄)2SO ₄ NH ₄ C1 NH ₄ HCO3 (NH ₄)2CO3 Na2 BO 4 NH ₄ NO3 CO(NH ₂)2 KOH for pH Blank	4280 4280 3960 4280 4280 4280 4280 0	7.0 7.6 8.7 7.2 7.0 7.9 8.2 7.05	No digestion Rate 25% of blank Rate 50% of blank No digestion No digestion No digestion Above pH 8.2-8.5 digestion almost stops Digests rapidly	
	Series C		41iter bottles		
52. 57. 58. 59. 60.	NH4HCO3 NH4HCO3 ditto ditto ditto	6 710 1420 2820 4260	Unadjust. ditto d ů tto ditto ditto	107 *** 100 105 94 81	

* From "Anaerobic Digestion III. Anaerobic Digestion of Undiluted Human Excrets." by J.R. Snell. In Sewage Works Journal vol. 15 page 679 (1943)

** Initial concentration in whole mixture (p.p.m. as nitrogen). ***Liters of gas per kilogram volatile solids per hour.

Chemical Products

Chemical products, of the anaerobic digestion process, have been determined by Rawn and others (103). The effect of each of these products on the progress of decomposition has not been studied in detail and only the effect of some is known in general. The digestion tanks upon which the observations were made are compartmented and the digesting material follows a continuous path through the compartments. For purposes of study, this has the effect of dividing the period of digestion into stages so that the variation of the chemical products with time could be determined.

Reproduced in Table III, page 47, are the results of Rawn's analysis.

EFFECT OF SEEDING

Seeding consists of adding digested or digesting sludge to the new material to be treated. Its effect is so important that in reality the process should be regarded as one of adding new material for digestion by the developed media. Only in this manner can the desired third stage of "natural" anaerobiosis be maintained. If the addition of new material is not controlled, interference with the satisfactory methane fermentation will occur and the process will retrogress to the unsatisfactory second or first stage. Without proper seeding each batch of organic matter to be treated will pass through the progressive stages of anaerobic fermentation. Seeding eliminates the first two stages.

47.

SUMMARY: CHEMICAL CONTENT OF SLUDGE LIQUORS IN PARTS PER MILLION Sew- Seed Mix-Number of Days detention** S'ge ture 2.6 5.2 Description age 7.9 9.2 32.2 *** Fixed Solids 1016 1085 Volatile Solids 1815 1687 Ammonia as N Volatile Acids as acetic Bicarbonate HCO3 2124 3059 -- 1306 Silicon SiO2 Phosphate POL Sulfate SOL August October (155) Chloride, Cl ---------Calcium, Ca Magnesium, Mg Sodium, Na -_ _ -----Potassium, K -Iron, Fe 6.93 pH *** 7.06 7.14 7.26 -----6. ------Organic Nitrogen, N

TABLE III *

* From "Multiple-Stage Sewage Sludge Digestion" (103) by Rawn et al., Proceedings ASCE vol 63 pg 1673

** Original paper listed stages instead of detention time of sludge when sampled,

*** These values were computed, not obtained by analysis

The volatile organic acids, reported as acetic, were tentatively analyzed as being composed of:

Acid	Perc	entage
Formic Acetic Propionic Butyric Valeric		• 0 • 63 • 33 • 6 •1 • 4

Without regard to the unsatisfactory products of nuisance that will occur without seeding, it would be justified merely by the saving in time which it engenders. On Figure 3, page 37, it is graphically shown that not only is the time of digestion reduced to twenty per cent of that for unseeded material but the peak volume of gas is also increased.

Seeding introduces into the material a balanced culture of the organisms necessary to its proper digestion. It also contains the extracellular enzymes of these organisms ready for immediate attack upon the digestible matter. Equally important, it may be considered well buffered in that it contains those products of decomposition which keep the pH near the neutral point. The ammonia present is ready to combine with the carbon dioxide, which may be liberated, to form ammonium carbonates. The ammonium carbonates contribute to the alkalinity, for if they could not be formed, the dissolved carbon dioxide would increase the acidity of the substrate.

There is no clearly established minimum or optimum ratio between the quantity of new material added and the quantity of digesting material required for adequate seeding. Rudolf's (119) indicates that the usual volatile matter loadings for sewage sludge are about 5 per cent of the volatile matter content of the seed sludge. He found, when working with **soluble** yeast wastes, that they could be digested at about this same loading, as can chewing gum and penicillin wastes. Rudolfs suggests that there is a universality of results here, which indicates that the digestible portion of many wastes (regardless of nature or source) will be acted upon by the organisms of the seed at the same rate.

Rankin (102) made a study of the operating records of some twenty sewage treatment plants, culled from the reports of about fifty plants. The rest were discarded because the records were considered incomplete or insufficient to supply the necessary data for the study. He found that there was no correlation between the amount of dry solids fed to the digester and any other factor. He did find that certain information could be correlated against the volume of raw sludge feed divided into the volume of the digester. This, of course, gives the theoretical liquid displacement time in the tank.

Rankin's curves for "Relation between Volatile Matter Reduction and Wet Sludge Detention", "Relation between Total and Volatile Solids in Digested Sludge and Reduction in Volatile Matter", and "Gas Production from Sludge Digestion" are reproduced as Figures Numer 4, 5 and 6 on pages 50, 51, and 52.

He records plants digesting sewage sludge with as little as ll days and a maximum of 62 days detention, - these plants being included in his study. The one with eleven days detention fell below the curve of reduction in volatile



14.15 (N 12 A.



From: DIGESTER CAPACITY REQUIREMENTS by Rankin: Sewage Works Journal Vol. 20 pg.486



matter vs. days detention. It will be noted that he stopped his curves at fifteen days detention, the evidence of the eleven day plant possibly indicating that they fall sharply to zero a short distance below this point so that it would be dangerous to extrapolate them further.

Rudolfs (119) observed, with yeast wastes, that efficiency of digestion was constant with a given load, regardless of whether it is applied as a strong material for a long detention period or more dilute material for a shorter period. He suggests that daily or monthly applied load, in terms of biochemical oxygen demand or volatile matter, would be a better yardstick than detention time.

The present lack of uniformity in reporting makes comparisons between anaerobic treatment of different wastes most difficult.

Rudolfs and Fontenelli (111) found an optimum digester loading, with sewage sludge, occurred at 0.1 pound of volatile solids (dry weight) per day per cubic foot of effective primary digester capacity at 82°- 84°F.

EFFECT OF MIXING

At one time it was generally considered that the ebullition of gas within the digesting material would provide the necessary mixing action to bring the feed material into contact with the seed material. Experience and experiments have proven that this natural mixing is insufficient to obtain maximum digestion efficiency and positive mixing is now

considered necessary. An immediate effect of positive mixing is an improved and more uniform production of gas (49).

Mixing insures that the benefits of inoculation will be obtained. It brings the biological colony into contact with the food material, which is necessary if fermentation is to take place, and it assures that the buffering action of the substrate is available throughout the tank and not localized. Mixing also aids in establishing a uniform temperature throughout the tank contents. Without it the danger of local pockets of raw unseeded material or low temperature is always present. These pockets, in which digestion may revert to Stage I, endanger the operation of the entire tank; for the spreading products of acid digestion may arrest digestion in adjoining areas until the entire tank is affected and the tank must go through the long period of acid regression associated with Stage II before alkaline fermentation can be reestablished.

Trubnick (140) indicates that in the treatment of yeast wastes a reduction of 85 per cent of biochemical oxygen demand could be effected in three days if the waste was constantly agitated, but without the agitation twenty-five days were required for the same reduction. Hillis (63) eliminated a scum problem by recirculation.

Buswell and Boruff (24) include in their patent on a "Method of Producing Methane" the statement,

"We found, however, that if the fermentation vessel is arranged with flexible connections or otherwise so that it may be inverted from time to time,.....fermentation proceeded smoothly and at a rapid rate."

Buswell and Boruff were working with carbonaceous material and experienced difficulty with the formation of a floating mat. With sewage sludge which always contains a certain amount of grease that is immiscible with water and therefore floats to the top, mat and scum formation may become pronounced without positive mixing. The fats, in such a mat, are readily digestible if they are brought into contact with the seed material.

Scum

Some of the first work in agitating the contents of a fermentation tank was attempted in order to relieve scum formation. To a certain extent it was successful. Schlenz notes (121) that the addition of ammonia-nitrogen is also helpful in relieving a difficult scum problem that resists stirring.

Scum may indicate a dangerous condition in that it represents a concentration of organic matter that is not completely submerged in water, it may be practically unbuffered and hydrolysis of the material near the furface in contact with the fermenting liquid may lead to concentrations of volatile acids sufficiently high as to interfere with proper digestion. In short, it constitutes a localized pocket which may upset the entire digestion process if not continuously controlled.

Figure 8, page fifty-six, graphically summarizes the improvement that may be attributed to the beneficial effects of stirring or mixing. These results were reported from the



operation of municipal treatment plants.

EFFECT OF AMMONIA NITROGEN

Ammonia nitrogen seemingly is necessary to the bacteria for the building up of their own structure. The presence of ammonia nitrogen, reported in analysis, may not mean that it is in a form available to the bacteria. In fact, as indicated by the work of Snell (see page 44), in association with certain ions it may be deleterious.

Buswell and Boruff (24) in their patent make the following statement:

"The regulation of the ammonia content of the liquor is also an important part of our process. When the ammonia is too low, the rate of gasification decreases and the amount of volatile fatty acids increases. This is illustrated in the following table:....." (Table IV, below, is reproduced from their work)

TABLE IV*
EFFECT OF NH, # N CONCENTRATION ON RATE OF GASSIFICATION
4 OF CORNSTALKS
(All other variables kept as near constant as possible)
Volume of Digestion tank
Cornstalks fed, lbs. per day (dry) 6 to 10
During an 18 day period (low NH ₁ - N content)

	Maximum	Minimum	Average
NH ₁ - N (p.p.m.) Volatile Acids as acetic (ppm Gas per day (cu. ft.)	28.0) 494. 8.9	4.2 275. 3.5	15.1 377. 6.8
During a 51 day perio	d (NH) - N	content re	gulated)
	Maximum	Minimum	Average
NH ₁ - N (p.p.m.) Volatile acids as acetic (ppm Gas per day (cu.ft.)	123.9) 364 68	23•8 95 24	59.0 228 34.2

* From "Method of Producing Methane," by Buswell and Boruff (24)

The same authors state further:

"The necessary concentration of ammonia ion for efficient gassification of the material is maintained by adding a predetermined quantity of a suitable ammonia containing compound, such as sewage; stable urine, and the like, are also available as a source of ammonia and any of these may be added in suitable amounts as required to the liquor in the digestion tank."

"..... It will be understood that an excessive ammonium hydroxide content is to be avoided, since the resulting alkalinity would impair and ultimately destroy the activity of the fermenting bacteria. Similarly, an excessive concentration of ammonium salts would so increase the osmotic pressure of the solution as to have a detrimental effect upon the bacteria. In general, the concentration of NH₁-N may be increased to as high as 600 p.p.m. with corresponding higher rate of gasification before any ill effects are noted."

The above quotation is from a work dealing with the methane fermentation of carbonaceous material, in which nitrogen is not a major chemical constituent. Schlenz (121) has also noted a beneficial effect from the control of ammonium nitrogen in the digestion of sewage sludge. It is indicated to be particularly helpful in the control of scum and in the operation of digesters that might be considered as overloaded.

He states that Fuller at Olean, N.Y. successfully controlled scum in sewage sludge digestion tanks by addition of 40 p.p.m. of ammonia salt to the scum layer and circulation of the digester liquor. This reduced a persistant stiff six foot deep layer to a soft songy layer about two feet thick.

Schlenz further reports on his experience in promoting successful digestion of sewage sludge in tanks in which previous attempts had failed. His results were achieved by the addition of ammonium sulfate and recirculation of the digester liquore over the scum layer. Ammonium sulfate was added in an ammount equivalent to 35 p.p.m. of available ammonia nitrogen in the entire tank volume, although subsequent analysis showed 1,422 p.p.m. of ammonium nitrogen in the tank.

Buswell (28) indicates that approximately 7 milligrams of ammonia nitrogen are required for each gram of carbohydrates and related compounds decomposed.

It would appear that this is an open field for investigation. It is accepted that nitrogen is a required element in the metabolism of bacteria. The addition of peptone or ammonia nitrogen to the substrate is accepted practice in the development of bacteriological cultures; however desirable concentrations for optimum anaerobic fermentations are matters for conjecture, as is the most desirable form. Methods of introducing the desired nutrient without introducing undesirable ions should also be investigated. EFFECT OF HEAVY METALS AND OTHER TOXIC SUBSTANCES

Copper, chromium, the arsenates and similar substances are known to be toxic to biological organisms and they, of course, have ill effects when introduced into anaerobic fermentations. Investigations, as those of Pagano (96), of the effect of toxic materials are concerned with the concentration of the toxic substance that the active biological colony can withstand before it is destroyed.
ENVIRONMENTAL CONSIDERATIONS FOR THE METHANE BACTERIA

The methane bacteria which have been studied by Barker and others have exhibited only a limited tolerence to environmental conditions. Since the production of methane is a desired correlary to the anaarobic treatment of sewage and organic wastes, special consideration should be given to obtaining an environment suitable for their active growth. This is not inimical to any of the objectives of anaerobic treatment, except possibly the volume of residual sludge drawn from the digester might be adversely affected. This may be a minor consideration in that the residual sludge from a satisfactorily operating tank drains well. Therefore, while the initial volume may be higher due to the slightly increased water content, the final volume of humus to be disposed of will be the same and possibly less if the environment during fermentation has led to improved liquification. Walker (144) indicates that generally the optimum condition for methane production are the same or closely the same as those for liquification and stabilization of organic matter. Satisfactory results are being obtained in this regard in many plants which are not operating for optimum methane production.

In reality the increased moisture content of the residual sludge should not be completely charged to methane production, since it results from the active continuous mixing of the digester contents. This is desirable for the entire biological colony, although it is included here because Heukelekian's work (59) indicated greater numbers of the methane bacteria in the sludge than in the supernatant liquor which points out the desirability of circulating the sludge for inoculation as well as its previously mentioned buffering action.

TEMPERATURE

The temperature range of the methane bacteria is 68° to 118°F. with an optimum range of 80°F. to 95°F., the greatest activity occurring near the latter figure. Reference to Figure 7, page 56, shows that this is optimum for the mesophilic bacteria.

REACTION

The pH range is 6.5 to 8.5 with an optimum range between 6.9 and 7.2.

NITROGEN

Nitrogen requirements are satisfied with ammonia nitrogen.

SURFACE

As was previously mentioned, page 31, which the methane bacteria seem to require a certain amount of surface for their propogation. This is apparently not pecular to them, as it has been noted with other bacteria, particularly with low food concentrations (153).

OBLIGATE ANAEROBES

The methane bacteria have been found to be strict anaerobes with extreme sensitivity to the presence of oxygen. This indicates that rigorous measures should be taken to exclude oxygen or otherwise raise the oxidization potential of the substrate.

THE PRACTICE OF ANAEROBIC TREATMENT

INTRODUCTION

The practice of anaerobic treatment may be divided into two general categories:

(1). The destruction of organic matter collected or concentrated by other treatment.

(2). A treatment process for the whole waste, sometimes followed by other treatment methods. The septic tank and certain other devices exemplify this category.

It does not appear that anaerobic treatment of sewage or wastes is economical, usually, for concentrations of organic matter of less than one per cent dry weight* due to the large tankage required (22). Figure 9, page 64, from the work of Rankin (102) indicates the increases in tank volume necessary for dilute wastes. There is no upper limit of concentration although above three per cent evaporation and drying may permit recovery of valuable by-products from industrial wastes (19).

Anaerobic treatment usually produces an effluent that is dark and somewhat foul. For reasons as yet obscure, a final effluent comparable to that from aerobic treatment can not be obtained and the effluent from anaerobic treatment has a relatively high Biochemical Oxygen Demand. (19). *Trubnick (139) states, "..... that wastes containing less than one per cent organic solids cannot be economically treated by digestion is losing validity. Digestion of wastes with as low a concentration as 1000 ppm solids and 500ppm BOD is now feasible,....."



TREATMENT OF SEWAGE: - PRECONCENTRATION OF ORGANIC MATTER

In the disposal of municipal sewage, anaerobic treatment is most generally utilized to destroy organic matter which has been concentrated from the waste by other treatment. This is the first class of anaerobic treatment mentioned previously. Included in this class are Imhoff Tanks which concentrate the material and digest it in the same tank, but in results are the same as those plants in which these operations are carried on in separate structures.

Sewage treatment is, today, normally referred to as primary or secondary; chemical precipitation is sometimes termed intermediate treatment.

Primary treatment is simply removal of that portion of the pollutional matter which will settle out while the sewage remains quiescent for one or more hours. Plain sedimentation tanks and Imhoff tanks are primary treatment devices. Chemical precipitation carries this process a step further by inducing greater removal of suspended material through the agency of a chemical floc formed in the sewage, by the addition of chemicals as it enters the sedimentation basin. Secondary treatment achieves greater clarification of the influent sewage by passing the effluent from the primary tanks into additional devices where it is subjected to the action of an aerobic biological colony. By this means most of the remaining suspended matter is removed, as are some of the dissolved impurities.

In primary treatment the sludge from the settling basins is usually removed to anaerobic sludge digestion tanks for destruction of the organic matter, as is also the case with the sludge from chemical precipitation tanks. In secondary treatment some of the organic matter removed is utilized by the zoogloeal colony in its own metabolism. Imhoff and Fair (page 185, reference 3) indicate that this amounts to about one-third of the non-settleable solids which reach trickling filters and five per cent of the non-settleable solids reaching activated sludge units. The usual sewage treatment plant thus relies upon anaerobic treatment for the destruction of organic matter. Table V, page 67, reproduced from this reference outlines the results which may be anticipated from various combinations of treatment devices.

SEPARATE SLUDGE DIGESTION SYSTEMS

Current design and operation of units for the separate digestion of sewage sludge recognizes most of the principles required for the satisfactory production of methane gas. In particular installations, however, some of the principles may be overlooked or neglected. This neglect may, in part, result from a tendency to regard the anaerobic digestion units only as a necessary adjunct to the other treatment devices; whereas, in the removal and destruction of organic material the other treatment units are really a part of the anaerobic treatment process.

Schlenz (121) indicates that too often the digestion

TABLE V

CALCULATION OF AMOUNT AND NATURE OF DOMESTIC SLUDGE

Values are expressed in grams per capita daily.

Treatment Process	Total Solids	Organic Solids	Mineral Solids	Specific Gravity
(A)	(B)	(C)	(D)	(E)
Suspended solids in sewage				
Total suspended solids Settleable solids Non-settleable solids	90 54 36	65 39 26	25 15 10	1.20 1.20 1.20
I. Plain Sedimentation (p	rimary)			
Solids removed = Fresh sludge Solids digested	54	3 9 - 26	15 +6	1.20
Digested sludge	34	13	21	1.596
II. Trickling Filtration®				
Non-settleable solids affected Solids digested during	36	26	10	1.20
Solids to be removed Solids removed	-12 24 13	-09 17 9	- 3 7 4	1.21
Combined I and II = Fresh sludge mixture Solids digested Solids remaining =	67	48 - 32	19 +8	1.21
Digested Sludge mixture	43	16	27	1.60
III. Activation ¹				
Non-settleable solids affected Solida digested	36	26	10	1.20
during activation ⁴ Solids to be removed	- 2 34	- 2 24	10	1.23
solids removed = Fresh activated sludge5 Solids digested	31	21 -14	10 +4	1.23

Treatment Process	Total Solids	Organic Solids	Mineral Solids	Specific Gravity9
Solids remaining = Digested activated sludge	21	7	14	1.67
Combined I and III = Fresh sludge mixture Solids digested ¹	85	60 _40	25 +10	1.21
Digested sludge mixtur	e 55	20	35	1.60
fresh activated sludge	65	34	31	1.40
IV. Chemical precipitation				
Solids removed ⁶	72	52	20 + 6	
Solids precipitated Solids digested ⁸	7 8	52 31	26 + 8	1.25
after digestion	55	21	34	1.59

TABLE V - continued

•If filters are operated at high rates, in stages or with recirculation of effluent, suitable adjustments must be made. •If primary sedimentation is curtailed or eliminated suitable adjustments must be made.

1 2/3 of organic solids, 1/4 becoming mineralized. 2 1/3 of solids. 3 55% of solids to be removed. 4 5% of solids. 5 90% of solids to be removed. 6 80% of suspended solids. 7 30 p.p.m. of FeCl3 converted to Fe(OH)3 (80 gal. of sewage). 8 60% of organic solids, 1/4 becoming mineralized. 9 Assuming specific gravity of organic matter equals 1 and aposific gravity of organic matter equals 1 and

specific gravity of mineral matter equals 2.5,

Specific gravity =
$$\underline{B} = \underline{2.5B}$$

 $\underline{C + D}$
 $\underline{1 2.5}$ = $2.5C + D$

Adapted from: SEWAGE TREATMENT by Imhoff and Fair pub. by John Wiley & Sons, New York (1940) tanks have been called upon to accomodate the optimum schedules of the other portions of the treatment system without regard to proper operation of the digester. Maintenance of the desired biological colony, and its welfare, demand that consideration be given the environmental conditions under which it is being made to function.

FEEDING

One of the weak links of the anaerobic chain is in the initial transfer of the sludge to the digestion system. A bacteriological colony operates most efficiently if supplied with foodstuffs continuously. Imhoff (68) indicates that many of the advances in all types of sewage treatment installations has resulted when a continuous flow process has been developed to take the place of a fill-and-draw device. The transfer of sludge from settling tanks is not readily adapted to continuous flow; the best that can be accomplished at this time is the frequent transfer of small amounts. A collection system that makes this difficult or impractical, may seriously influence the digester operation, even though it is not considered as a part of the digester system.

At this point, also, oxygen may be permitted to enter the anaerobic system, - a condition which is not desired.

Refering to Figure 9, page 64, the effect of large volumes of water on the capacity requirements of the dig-

estion units may be seen. This figure shows the desirability of feeding raw sludge containing as little water as possible. Reducing the volume of water reduces the investment required in fermentation tanks, or permits longer retention of digestable material in the tank capacity which has been installed. MIXING

Positive mixing devices are usually provided. Some stir the entire tank contents, others circulate only the supernatant liquor. Heukelekian (59) found the greatest number of methane organisms in the digesting sludge, whereas Buswell (27) found the greatest numbers of all active organisms in the supernatant. Buswell's work, being earlier, does not show the functional desirability of the organisms found. The present lack of knowledge about the work accomplished by the various organisms prevents factual evaluation of the results obtained through circulation of the supernatant. Each system has advantages, and if circulation of the supernatant is accomplished in a manner that brings the new material into active contact with the organisms present in the tank and keeps the mixture well buffered, it probably equals complete stirring in efficiency.

HEATING

The advantages of heating have become so well established that even the very small plants are designed to include heating equipment. (9). Various means of heating sludge have been attempted with various success (133),

(47), (124); hot water heating coils and heat exchangers within the digester, see Figure 11, steam injection into the sludge (9), and heating the circulating supernatant in an external heat exchanger, see Figure 10. Recently radient heating, by means of coils buried in the digester walls, has been proposed. Each method has advantages and disadvantages. The mechanics of heating can not be discussed in this thesis and might well be made a separate topic.

The provision of heating equipment does not guarantee that the digesting material will be maintained at the optimum temperature desired. (122). To be most effective, the optimum temperature should prevail throughout the contents of the tank. It has been found, however, that often spots 10 to 15 degrees lower than the recorded temperature actually existed in operating tanks. In other cases, the tanks temperature is materially lowered during periods of sludge transfer, thus subjecting the biological colony to more or less shock.

Adequate insulation might be mentioned in connection with heating. While insulation will not serve as a cure for other heating ills, a lack of, or insufficient, insulation will multiply any defects apparent or inherent in the heating system.

FLEXIBILITY

Figures 10 and 11, pages 74 and 78, are taken from equipment manufacturers' literature and represent typical

modern installations for separate anaerobic digestion of sewage sludge. Anaerobic digestion can be accompished successfully in a single tank; but, whene ver the size of the plant is sufficient to make division of the required tank capacity into two or more units ecomonically feasible, flexibility is gained. Flexibility of operation is desirable in any sewage treatment device. The treatment process is in continuous operation, as the operator has no control over quantity and quality of the influent to the plant, when difficulty in operation is experienced, he is harassed by the continuing flow of more sewage to be treated. Flexibility may permit the ingenious operator some latitude to meet the unexpected or the unusual problems that arise during the continued operation of the plant.

TWO STAGE DIGESTION

The stirring of the contents of a single digestion tank sometimes makes it difficult to draw clear supernatant liquor from the tank, the decanted liquor having a high solids content and Biochemical Oxygen Demand. Two-thirds of the gas produced during digestion is produced in the first five to eighteen days (depending upon temperature and other factors). Attempts have been made to improve the digester supernatant by completing the process in two stages.

The first stage, lasting six to eight days, is carried on in a conventional digestion tank. The sludge from the first stage is transferred to a second stage tank

and retained there the necessary time to complete digestion. No positive stirring takes place in the second stage, and since two-thirds of the gas has been evolved in the first stage, little stirring is caused by the ebullition of gas. Therefore, in the second stage, concentration of the sludge takes place in the bottom of the tank, a clearer supernatant may be drawn, and the sludge when removed has a lower water comtent. Two stage digestion has given satisfactory results in many plants. Often, to reduce the plant investment, the second stage has been made of simple construction with both stirring and heating equipment eliminated.

Greater flexibility of operation ensues if the tanks are so constructed and piping arranged that they may be operated either in series or parallel. Schlenz (121) points out the desirability of piping so that the sludge from the secondary can be back-circulated to the primary in the control of volatile acids.

TYPICAL INSTALLATIONS

"Controlled Digestion" System

Figure 10, page 74, is adapted from a Pacific Flush Tank Company drawing No. 4 - D - 940.1. This drawing is a titled, - "Typical Two Tank Layout, Suggested Digester Piping for - "Controlled Digestion"".

Schlenz makes the following remarks concerning "controlled Digestion" (123) in describing the controls given to the operator to enable him to obtain".....the



utmost in digester control,":

"(1) Automatic and close control of digestion tank temperature.

(2) Effective scum control by(a) Digester liquor recirculation.
(b) Selective heating of scum zone.
(c) Ammonia nitrogen control.

(3) Volatile acids control by the provision of back circulation of the digester liquor from a secondary digester to the primary digester."

(4) Selection and uniform withdrawal of digester liquor.

(5) Utmost in flexibility of operation so that raw solids may be added to any tank in the digestion system and be initially seeded by being added to the recirculated digester liquor."

This system of digester installation has been developed by a manufacturer, of many years experience, in the field of sewage treatment plant equipment. It may be considered as one attempt to obtain the utmost in digester efficiency through the application of present knowledge and operating experience. Figures 11 and 12, which will be described later, may also be viewed in this way and represent a somewhat different answer to the same problem.

Mr. Schlenz (122) describes this system in the following manner:

A circulating pump is provided (see plan) to circulate digester liquor from a zone above the best digested sludge, with a discharge point in the center of the tank at the high liquid level. The discharge of this active seeding material unto the scum layer tends to soften the scum and bring it into intimate contact with the active liquor. Liquor should be circulated at a rate which will overturn the upper two-thirds of the tank contents every 24 to 48 hours.

Optimum and uniform temperature is maintained throughout the entire tank by passing the circulating liquor through an external heat exchanger. Raw sludge is heated to the tank temperature by being pumped into the circulating liquor where it is intimately mixed with the active material and passed through the heat exchanger before being discharged into the digester at any of the points shown.

A small chemical mixing tank and pump, with discharge into the circulated liquor line, makes possible the addition of ammonia nitrogen or other mutrients.

The circulating or transfer pumps may be used to transfer material of one volatile acid content to a tank whose contents have a different volatile acid content. In this way the volatile acids may be controlled.

The supernatant selector system indicated permits continuous withdrawal of supernatant at a slow uniform rate, by employing a slotted tube that extends throught the depth of the tank in the section where supernatant is most likely to be located, and a calibrated gauge control device. With this arrangement the selection and withdrawal of supernatant is automatic, with but little attention required from the operator.

Single Tank Digestion

Figure 11, page 78, is adapted from a publication of the Dorr Company. It shows an installation for separate sludge digestion in a single tank. It may be noted that mixing is accomplished by a propeller in the tank powered by an external motor. Heating is done by coils around the walls of the tank. The floating cover permits some flexibility in the addition of raw sludge and the withdrawal of supernatant, it being unnecessary to balance the addition and withdrawal while either operation is taking place. The discharge ports being placed some distance above the bottom permit some concentration of the denser sludge in the bottom before it is withdrawn. The remainder of the tank contents are circulated.

Two-stage Digestion System

Figure 12, page 79, is also adapted from a publication of the Dorr Company. In this figure a two-stage digestion system is shown. Stirring, by means of a propeller, and heat exchangers are provided in the primary stage; the secondary stage is without this equipment, although heating coils are shown as optional equipment. The second stage serves as a holding tank in which a portion of the sludge gas is collected and the sludge is concentrated before withdrawal for drying.

Imhoff Tank

Figure 13, page 80, is a typical cross section





TWO-STAGE DIGESTION SYSTEM

Adapted from: Bulletin No.6261 pub.by the Oorr Company.

Figure 12



through an Imhoff Tank. Introduced into this country about 1906, many installations have been made with various variations in the layout of the plant. Means of heating and gas collection have been developed for these tanks (3) but have rarely been used in this country. In general, installation is now limited to the smaller community with limited funds for construction of a treatment plant and even more limited funds for its operation.

Satisfactory treatment is obtained with an Imhoff Tank; however, there are certain limitations, particularly in the anaerobic digestion process, in this device. Heating is rarely economical so that digestion proceeds at less than optimum temperature, ebullution of gas from the digesting sludge is the only sturring so that, at best, the highest efficiency cannot be anticipated. The lack of sturring, in any tank, can have an accumulative effect in that if gas production decreases so does the sturring action, which may lead to a further reduction in gas production.

The lack of heating equipment means that the rate of digestion will be lowered (see Figure 7, page 56). In northern climates the temperature may be so far below optimum during some periods of the year that digestion ceases or nearly so. During these periods deposition of organic matter continues so that when the temperature rises a superabundance of foodstuffs is available to the organisms present. The over-abundance of organic material may permit volatile acid production to become so great that methane fermentation is inhibited. Much of the discussion (143) supporting the use of lime in anaerobic treatment comes from those experienced in the operation of Imhoff Tanks. Their experience has proven it to be beneficial. Heukelekian (60) found in the laboratory that the methane bacteria attack more readily decomposition products from the first stage of anaerobiosis when the reaction has been controlled with lime. This should not be taken as an indication that lime should be indiscriminately used for the control of all anaerobic fermentations. Control of Imhoff tanks with other materials was not discussed in the literature consulted.

TREATMENT WITHOUT PRIOR CONCENTRATION OF ORGANIC MATERIAL

It was previously mentioned (page 63) that the application of anaerobic processes in the treatment of organic wastes may be divided into two general classes. In this division, the treatment of the entire wastevolume was placed in the second category. Historically this use of anaerobic treatment would be in the first division; since it was the observation of the reduced amount of solids removed from the tanks in which sewage and its deposited sludge were held, without air, that led to the further investigations of the anaerobic digestion of sewage solids.

The limitations of anaerobic treatment (see page 63) confine its use at this time to the treatment of very strong industrial wastes or to installations having only a small

volume of waste toobe treated. In the treatment of sewage, septic tank installations are used for dwellings, schools and institutions in unsewered areas; also for the very small municipality, 1500 persons or less (142). Anaerobic treatment sometimes followed by other devices, is being increasingly used for industrial wastes (see Table VII), (page 102). THE SEPTIC TANK

The septic tank is a tank (either open or closed) through which the waste is permitted to flow. There is a moderate detention period for the volume of liquid flowing. The deposited solids are retained for a sufficient time to complete the process of anaerobic digestion. Considerations of the spetic tank often overlook the fact that the colony of anaerobic organisms has an opportunity to act upon the dissolved and suspended, as well as on the sttleable, organic material present. Early investigators were interested in the change in ammonia-nitrogen and other changes in the effluent from the septic tank. Table VI, page 84, compares the effluents of plain sedimentation and septic tanks.

Disappointment in the anticipated results obtained with large scale septic tanks, and possibly the litigation over patents, discouraged some of the early interest in the device. The public demand upon industry for pollution abatement, has forced a continued search for economical methods of treatment; this has led to some development and interest in the anaerobic processes, a seemingly increasing TABLE 11 *

COMPARATIVE RESULTS OF PLAIN JEDIMENTATION FOR 24 HOURS AND JEPTIC JEDIMENTATION FOR 21.6 HOURS

'n

	•	Sedime	. uayopu	Septie	Efflant
	Screened Sewage	Praly-	Reduction per cent	Prusly- 515	Reduction percent
Rmmonical nitrogen	46.5	7.64	ý	52.7	/3'
RIDUMINOID Difrogen	0.0/	4.0	10	80	20
Total Organic Difrogen	19.2	6.71	20	17.4	18
Total introgent Kieldahl)	67.2	6:09	N	20.8	ر م
Oxugen consumed of 27°C. at once	238	19.7	17.2	6.61	16.4
Osugen Consumed at 27°C. in 4 hrs.	1.001	75.5	23	0.77.0	23
Solids in suspension	215.0	93.9	56	95.7	55

1 Increase

Adapted from AMERICAN SENERAGE PRACTICE. VOLITI by Metruts and Eddy 15% Ed. Pub: McGraw His Book Co., New York , 1916

interest at this time.

The early disappointments caused an almost complete dismissal of the septic tank for sewage treatment;-except for those installations where no other known device was practical. This regard of the septic tank as a second rate treatment method has, of course, caused it to have second rate consideration regarding design, installation, and investigation;- an unhappy situation leading to even further abuses. Seventeen million persons are estimated to be served by septic tanks and soil absorption systems of sewage disposal (148). Nearly all the forty-eight states publish standards on domestic septic tank installations; yet there seems to be an almost complete lack of factual investigation on even this one form of septic tank installation.

Most states require that domestic septic tanks have a length at least twice but not more than three times the width, and usually a minimum depth of liquid of about four feet. The reason for these dimensions may have become somewhat obscure. Nottingham and Ludwig (84)(85)(95) report experiments on long shallow tanks which gave superior removal of settleable and suspended solids over the conventional shape. The fact that experience has shown one type to give satisfactory results does not preclude the possibility that another type might not be more satisfactory. The U.S. Public Health Service is now engaged in an investigation of the septic tank - soil absorption system of domestic sewage

disposal (148).

THE SEPTIC TANK ACTION

In theory the septic tank is a treatment device capable of methane fermentation. In operation, it often operates in the acid fermentation or acid regression stage of anaerobiosis. Commonly space for sludge storage is provided at the bottom and scum storage at the top. That acid fermentation will exist during long periods of operation may be predicated from the operating conditions. Sewage is detained, quiescent, in the tank for a period of three to twenty-four hours, suspended material settles, and grease and the lighter material float; ' both are retained in the tank. Operating temperature is the temperature of the sewage and usually well below the optimum for the methane bacteria.

When the tank is "ripe", gasification takes place in the settled sludge. Gas collects in some of the sludge particles and they float to the top of the tank; as the hydrostatic pressure decreases some of the gas bubbles are released, permitting the sludge to settle to the bottom again. During periods of rapid gas ebullition the effluent may have a higher solids content than the influent. Some of the rising sludge may become enmeshed in the grease at the surface adding to the scum layer.

During periods of low temperature bacteriological activity may almost cease. The organic material accumulated during these periods may contribute to acid production when activity resumes, to be followed by periods of rapid gas formation, during which the accumulated sludge is unloaded. Figure 14, page 88, shows the relationship between suspended solids removal and sludge accumulation in two experimental septic tanks.

The mixing which occurs is due solely to the ebulition of gas. Some seeding of the scum layer may occur, but conditions are adverse to digestion in this layer (see page 55).

In spite of its handicaps, in normal operation the septic tank manages to achieve about 25 to 30 per cent reduction in the weight of solid matter collected. Since the sludge is generally stored in the tank for long periods without much mixing action, a great degree of compaction may be obtained. The volume of sludge removed from a septic tank runs about 25 per cent of the volume removed from plain sedimentation tanks. (4)

Unheated Digesters

Some small communities (142), in order to eliminate some of the disadvantages of the septic tank, have installed plain sedimentation basins from which the sludge is removed to unheated tanks for digestion. The advantages are gained by increased investment and operating cost. The unheated digester cannot be expected to produce the same results as the methane digesters previously described.





Figure 14

pub .: Factoral Jeanny Reney, Cincinnat. (1950)

88.

ANAEROBIC TREATMENT OF INDUSTRIAL WASTES

Treatment of organic industrial wastes by anaerobic processes ranges in practice from lagoons and septic tanks through plants to recirculate the anaerobic biological colony. In its simpler applications it has sometimes been adapted as an expedient, in other cases it has been selected after laboratory investigations and pilot plant operation have demonstrated that the method produces a desired end result in the most economical manner.

The literature contains many reports of laboratory investigations on the anaerobic fermentation of various substances and particular wastes (see 28). Much less information is available on plant scale treatment of various wastes, anaerobically.

REQUIREMENTS FOR ANAEROBIC TREATMENT OF INDUSTRIAL WASTES

The basic requirements for maintaining a biological colony must be met for successful treatment of an industrial waste. The waste must be a biological food and non-toxic, the desired organisms must be present, and their nutritional and environmental requirements satisfied.

NUTRITION

In the treatment of sewage the material received probably constitutes more nearly a balanced food for the microorganisms than do most wastes. Wastes may be made up almost exclusively of a single substance, and therefore be deficient in materials for the growth of the organisms, or excessive amounts of certain substances may accumulate to a degree to inhibit the activities of the organisms.

In treating carbonaceous material sufficient nitrogen may be lacking for the building of the bacterial cell. If the ratio of carbon to nitrogen is in the range of 40: 1 to 50:1 nitrogen will be deficient (54); when the ratio is decreased to 10:1 or 20:1 the appearance of ammonia in the substrate may indicate an excess of nitrogen (93). In fermenting carbonaceous material Buswell and Boruff show an improved gas yield with a ratio of ammonia-nitrogen to volatile acids (as acetic) of 1:4 above the yield when the ratio is only about 1:25 (24). A more general discussion of nutritional requirements will be found on pages 18 and 57. ORGANISMS

With sewage the organisms necessary for its anaerobic fermentation are already present; maintaining proper environmental conditions, more or less, insures the development of those types which are desired for the process. The ripening of a septic, Imhoff or separate sludge digestion tank is the period when the organisms of the active biological colony are developing in numbers and becoming acclimatized to the food supply and environment in which they are to work.

In the destruction of organic wastes no single organism can be made responsible for accomplishing all the changes associated with the process. Pure cultures are used in industrial fermentations, as for the production of alcohol and penicillin; but it should not be expected that the most efficient destruction of wastes can be achieved in this manner. To produce alcohol (151) manipulation of the waste is required to make it a satisfactory media for the culture of a specific organism; and the process, in effect, ceases to be primarily one of destruction and becomes one of recovery, i.e., the destruction of organic matter becomes incidental to the production of alcohol.

In anaerobic treatment the inoculum material is usually sludge from a sewage sludge digester. Buswell and Boruff, in their patent, indicate that inoculation is not always necessary; however, if previous manipulation has caused sterilization of the material the biological colony must be introduced into the fermentation vessel.

Acclimitization and Adaption

The experience of Singleton (126) and Buswell and Sollo (34) in acclimatizing sewage sludge to the anaerobic treatment of other substances may be taken as more or less typical. One was dealing with a fiberboard waste (carbonaceous) and the other with wool scouring wastes (having a high grease content). Both used digested sewage sludge for inoculum, after this was placed in the digestion unit small quantities of the waste to be treated were added daily (the amount controlled by the volatile acids concentration in the unit). After a period of about fifteen days the sludge had reached a stage at which the maximum loading could be applied

without cessation of the production of gas.

Heukelekian (54) emphasis that many mechanisms are at work during this period of "acclimatization" and "adaptation". First, certain species of the mixed colony are better suited to the food and environment and consequently they become the dominent forms. Since they may be small in numbers originally, an extended lag may occur before the maximum digestion rate under the prevailing conditions may be obtained. Second, certain species subjected to unfavorable toxic conditions may in time adapt themselves to the conditions by a process of selection brought about by the survival of the more tolerent varieties of the species. The ultimate in the process of acclimatization and adaption would be a mutation or production of a new variety or species. Examples of mutations are numerous in the literature of bacteriology (54); however, with mixed cultures it is difficult to separate mutation from selection. Heukelekian indicates that in the biological treatment of phenolic and other wastes containing inhibitory substances a striking adaptation of the flora and fauna may be noted.

There are, of course, limits to the amount of adaptation that the organisms may be expected to achieve in the matter of nutrition and toleration of toxic substances. Some wastes will require the addition of nutrients and others the neutralization of toxic substances, in the manner of treating penicillin wastes (55), before any form of biochem-

ical treatment may be attempted.

TYPICAL METHODS OF ANAEROBIC TREATMENT FOR INDUSTRIAL WASTES

In adapting anaerobic treatment for industrial wastesseveral systems have been devised or proposed. The recommended system is influenced by the manufacturing process and condition of the waste as received for treatment. The waste can be high in solids (14), the organic material can be colloidal (92) or almost entirely dissolved (140). Residual sludge volume, therefore, can be very high (14) or almost nil (118). The wastes can be received hot or cold. Flow can be intermittent or continuous. All these factors must be considered in selecting a treatment system.

Septic Tank

The simplest application of anaerobic treatment to industrial wastes is by means of the septic tank. This method has the advantages of least cost of construction and operation. While it has the disadvantages mentioned on pages 86 and 87, in certain cases it may be capable of producing the desired end result (11)(12)(16).

Fermentation Wastes

Kraus (73), in one of the most successful and best reported large scale anaerobic treatment operations, treats the "beer slope" from a butanol-acetone plant. The digesters, in operation for about fifteen years (19), reduce the 17,000 p.p.m. Biochemical Oxygen Demand of the entering waste about 70 per cent in a ten day detention period. The anaerobic treatment is followed by activated sludge. Digestion is in the thermophilic range, the waste is received so hot that cooling to 134 degrees F. is a problem. Treatment at higher temperatures was not successful (73). The ebullition of gas is so rapid that stirring is unnecessary. Control is by volatile acids content. Kraus has proposed use of digester liquor as an aid to the activated sludge process (72) (74). Strawboard and Fiberboard Wastes

Figure 15, page 95, shows the layout of a proposed treatment plant for fiberboard wastes. This system of anaerobic treatment utilizes digestion tanks of the type shown in Figure 10. The raw waste will have a solids concentration of 12,800 p.p.m. and an initial B.O.D. of 5350 p.p.m. The planned reduction in B.O.D. is 80 per cent, although laboratory experiments indicated a possible reduction of 94 per cent. As an added source of nitrogen it is proposed to utilize anhydrous ammonia, laboratory work indicating additional nitrogen will be required. The lagoon will store the effluent during periods of low flow in the receiving stream. An additional twenty per cent reduction in the remaining B.O.D. will result if the effluent is held in the lagoon for ninety days. This reduction is predicated upon laboratory studies. The inoculum material for the laboratory work was digesting sewage sludge, which required over eleven days acclimitization before maximum loading could be obtained.

Figure 16, page 96, is another proposed plant for





Figure 15.


Adapted from: SEWAGE WORKS JOURNAL Vol. 21.

treatment of strawboard wastes. This design is based upon laboratory research and a study of existing equipment (43).

Pilot plant studies were in progress, but operation reports have not yet become available. It is anticipated that results equivalent to those described in connection with Figure 15 will be achieved. The equivalent results may be obtained at a saving in the volume of the units involved, as may be seen in Figure 17, page 96. Not indicated in the figure is the volume required for digestion of the excess sludge from the proposed unit. It should be noted that in this device return of the "active" sludge is planned. Yeast Wastes

Figure 18, page 98, is the layout of a plant for the anaerobic treatment of yeast wastes. The yeast wastes (which are typical of a great variety of solu ble organic wastes such as chewing gun, distillery and antibiotic (119)) are described as being highly hygroscopic, with the solids being almost entirely dissolved and colloidal; - suspended solids content rarely exceeding 200 p.p.m. The total solids content varies from 10,000 to 20,000 p.p.m., the five day B.O.D. between 2,000 and 15,000 p.p.m. and volatile solids between 7,000 and 15,000 p.p.m. (140)

This plant was evolved after an extended laboratory and pilot plant investigation. Anaerobic digestion and trickling filters were selected after investigations which included electrodialysis, chemical treatment and activated



Adapted from: SEWAGE WORKS JOURNAL, Vol. 21

Figure 18

sludge as well as the methods shown here.

The plant will produce a reduction of 94 per cent in suspended solids and 85 per cent in B.O.D. (119). It consists of two holding and equalizing tanks; a two-stage digestion system, designed on the principle of a continuous up-flow of the more concentrated liquid wastes through the sludge blanket (it was found that best results would be obtained if a rotary distributer were employed at the bottom of the tank((119); a hopper-bottomed circular settling tank for the retention of the **sludge carried over with the** digester effluent; a two-stage high rate trickling filter with a 1:1 recirculation ratio, which treats the digester effluent mixed with the dilute portions of the raw waste; and a settling tank for the final effluent.

The inoculum was ripe sewage sludge acclimitized over a period of six months before a maximum load was applied. It was found that a minimum volume of sludge equivalent to one eighth of the tank capacity was required for proper operation of the digesters at normal loadings. Larger volumes did not materially improve performance; when the sludge volume exceeded one half the tank volume excessive carry-over of the sludge occurred (119). Sludge accumulation was rather slow, amounting to only about 300 gals. of ripe sludge per million gallons of waste treated (117). Return of the sludge from the settling tank resulted in a detention period for the sludge of many months, so that a very high reduction of the

volatile matter content of the sludge resulted (117). FILTER MEDIA

The examples of anaerobic treatment plants for industrial wastes given here were selected as being typical of methods of application currently being employed. Certain variations may be found in adapting the method to a particular waste disposal problem.

No plants were found using a filter media to support the biological colony. In view of the evidence that the methane producing bacteria desire support this is rather surprising. Of course, unless the solids in the waste are dissolved there is always a certain amount of fiberous material available for support. One investigator (38) concluded as the result of his experiments that artificial support for the colony would be beneficial.

RESULTS OF ANAEROBIC TREATMENT OF WASTE

When organic wastes are treated anaerobically, with due regard to the requirements for satisfactory biological conditions, a reduction in biochemical oxygen demand of 70 to over 90 per cent may be achieved. The products of the process will be a conbustible gas and a humus-like solid. The composition of the gas and its amount, and the amount of humus-like solid will depend upon the material being decomposed (19). If woody carbonaceous material comprises the bulk of the original substance the residue may amount to 40 per cent, while simpler sugars, fats and proteins may be completely gasified. The effluent will not be completely stabilized and will require a high dilution or further (aerobic) treatment if offense is to be avoided. The dissolved and colloidal solids as well as the settleable solids will have been reduced, and the pH will have been stabilized near the neutral point.

Table VII, page 102, lists some wastes that have been treated anaerobically. This is not a complete listing; data on other wastes may be found by consulting the references in the bibliography. The wastes in Table VII were selected in an attempt to compile certain data about the treatment processes. The material in the bibliography was consulted; however, the manner of reporting did not permit including much of the data in this table.

COMPARATIVE COSTS OF ANAEROBIC AND AEROBIC WASTE TREATMENT

Few comparative cost estimates between anaerobic and aerobic treatment are available in the literature, and those available are rather old. In comparing the cost of treating milk wastes (28) simple covered tanks for anaerobic digestion were estimated at fifty cents per cubic foot. On the basis of a 95 per cent removal of the pollutional load when a dosage of one twenty-fifth of the tank volume were applied per day, it was computed 5.72 cubic-feet capacity would be required for each pound (dry weight) of milk solids. This amounted to two dollars and eighty-six cents per pound of milk solids treated. If the remaining 5 per cent of B.O.D.

TABLE VII

INDUSTRIAL WASTES TREATED ANAEROBICALLY

Waste	Reterence	Detention Time Days	Digester Loading B.O.D. Ibs/cu.ft/da.	In fluent B.O.D. p.p.m.	Reduction B.O.D. To	Volatile Solids ^{Ibs} /cuH/da.	Volatile Solids Influent p.p.m.
Yeast (Molasses) Compressed Yeast	19 19 119 119	9.9 3.9	.075 .10 .19	10,000 5,000	80 70 95 85	.108 .10 4	10,500 7,000
Beer "Slope" """" Distillery Penicillin	73 19 19 55	9.6 10 14.5 20	.072 .07 .02	11,500 17,000 16,000 6,680	78.2 69.8 90.0 81	.089 .114 .143	12,500 30,000 30,000
Milk Products Fiberboard Tomato Canning	62 30 34 35 3 5	6 5 .10 7.5	•00357 •00775	57 actor 380- 3,300 5,350 587 957	93 94 68.8 83.3		
" " Wool Scouring Natural Gums " "	35 26 83 83 92	5 20 10 5 5	.0106	854 10,000 2500- 4800 2,100 4,000	60.6 91.7 91.5 87.	•06	1.004 12,000
Tannery & Sewage Sludge	141						

were removed on trickling filters, the estimated total investment per pound of solids was \$8.70; if removed by sand filters, the investment became \$17.46 per pound of solids. The comparative cost for filtration without anaerobic pretreatment was \$116.80 per pound of solids on trickling filters and \$292.00 per pound of solids on sand filters. Presuming that the percentage relationships of the costs has remained approximately the same, for comparative purposes anaerobic digestion and trickling filters cost only 7.45 per cent of aerobic treatment using trickling filters alone and only 2.98 per cent of the cost of sand filtration alone.

It is not felt that the above comparison truly represents the cost of methane fermentation since the tanks apparently are more nearly septic tanks. The same reference contains an estimate on the cost of an anaerobic treatment plant for distillery wastes, as follows:

Digestion Tanks

4 - 280,000 ga. steel tanks @ \$4,200....\$16,800 4 - Agitators, installed @ 1,700.... 6,800 20, 140 sq. ft. heat insullation @40%... 8,100 4 - heating coils, installed @\$ 750.... 3,000 \$34,700

Pumps

2	-	70 gpm beer slop pumps, float control		
		@ \$170 \$	340	
2		200 gpm trickling filter pumps		
		with manual controls@ \$220	440	
2	-	250 gpm back circulation pumps		
		with manual controls@ \$220	440	
2	-	70 gpm heating water pumps \$140	280	
1	_	20 gpm sludge pump @ \$140	140	
				1,640

Miscellaneous Equipment

Valves and piping.....\$44,900 Water heater and controls.....1,200 Slop cooler and connections.....1,900 Pumphouse and pit.....1,000 Gas regulation and meters.....2,000 Total \$11,000 Total \$47,340 Contingencies, Engineering, Patents @ 20% 9,470 Total for digestion equipment....\$56,810

Trickling Filters

Trickling filters, complete.....\$26,400 Contingencies and Engineering @ 15%.....<u>3,960</u> \$30,360 Total cost of plant

To extend these figures so that a comparison of cost between anaerobic and aerobic treatment of this waste may be determined the following assumptions will be made: that 75 per cent of the B.O.D. removal is accomplished by the digesters (it is believed that this is a conservative estimate of the removal); and that the B.O.D. removed by the trickling filters remains constant with load (117).

With these assumptions, to treat the whole waste on trickling filters the filter capacity would have to be 100/25 or four times as large to remove 100 per cent of the B.O.D. instead of the 25 per cent estimated to be removed by them.

Using the figure above the estimated cost of the aerobic treatment plant would be:

105.

Trickling filters, complete 4 @ \$26,400.....\$105,600 Trickling filter pumps @ \$440..... 1,760 Beer slop pumps..... 340 1,000 Pumphouse and pit..... 3,000 Valves and piping..... \$111,700 Contingencies and Engineering @ 15%..... 16,700 Total for aerobic treatment plant (without provision for digestion of trickling \$128.400 filter sludge).....

This estimated investment of \$128,400 for an aerobic treatment plant is believed to be conservative. Using it as a comparison with the estimate above for anaerobic treatment it is found that the anaerobic plant costs 32 per cent less than treatment by aerobic methods only. If the per cent removal of B.O.D. by anaerobic fermentation is taken as 80 instead of the 75 per cent used in the computations, above, the cost of the anaerobic system would be 45 per cent less than the aerobic system.

The actual cost figures used in the previous computations are considerably out of date, but the percentage figures are substantially correct. Since the method of computation would favor the aerobic system, it may be safely stated that anaerobic treatment will often offer substantial savings over aerobic processes.

SUMMARY AND CONCLUSIONS

INTRODUCTION

The purpose of treating sewage and waste is to stabilize organic material so that it may be disposed of economically and without offense to the community of man. To achieve the requisite stabilization an oxidation process must be employed. With water carried wastes, biochemical oxidation (which is nature's own way of destroying waste) is a most practical method.

Biochemical oxidation requires a colony of living organisms. The colony may be aerobic or anaerobic depending on the source of oxygen utilized by the organisms in their metabolism. In the destruction of large quantities of organic material the anaerobic colony is frequently employed. In the treatment of sewage the actual destruction of the solid organic matter is, in the United States almost universally, achieved by anaerobic digestion. To a lesser extent, anaerobic treatment is used to stabilize organic industrial wastes.

Biological treatment requires that the proper biological colony be developed and maintained. Development of the colony means allowing those organisms best suited to the available food and enviornment to increase and achieve the balance required to permit continued satisfactory treatment. In certain cases, inoculation with the desired organisms may be necessary.

To have satisfactory treatment it is necessary

to maintain an optimum environment for the working organisms. The maintenance of a proper environment is of extreme importance in any biological process regardless of the type or species of organisms involved.

THE BIOLOGICAL COLONY FOR ANAEROBIC TREATMENT

Factual knowledge of the organisms employed in the anaerobic treatment of sewage and wastes is very meager. Methane-producing bacteria have been isolated and studied in the laboratory; however, the other organisms employed are almost unknown. Studies are needed to determine the species, numbers normally present, and work done by the other organisms. Isolation and study to determine the environmental conditions optimum for these organisms are sorely needed, as well as factual data on their nutritional requirements and the products resulting from their metabolism. Included in these studies should be the effect of concentrations of various ions on the organisms.

For industrial wastes particularly, studies of the adaptation and mutations of the various species to their environment would be most interesting.

While much work may still be done without a complete knowledge of the organisms, for complete control and development of the methods of anaerobic treatment this basic knowledge must eventually be obtained.

THE ENVIRONMENT FOR METHANE FERMENTATION

At present, the anaerobic treatment of sewage and

wastes is, in the ultimate, a process of liquification and methane fermentation. Anaerobic treatment may be carried on which is not presented as methane fermentation; however unless deliberate control is maintained to produce other products, in which case the process should be classified as . one of recovery rather than destruction, the most efficient treatment and destruction will ensue if the environment is maintained for methane fermentation. While factual data is not presented, it appears that the optimum range of the liquifying organisms is at or near the range of the methaneproducing bacteria.

In certain cases, economy may preclude the adaption of methane fermentation. Essentially this means eliminating from the design certain items necessary to maintain and control the environment for methane fermentation. The limitations of such an expedient should be recognized. Care should be exercised to minimize the undesirable products which may ensue and it should not be expected that, without creating the necessary environment for methane fermentation, the efficiency of that process will be obtained.

An established biological colony is affected by the temperature and pH of its environment. It is also affected by decomposition products, alkalinity, ammonium carbonates and other forms of ammonia-nitrogen, volatile acids, volume of substrate, rate of feeding and stirring, and the presence of toxis substances.

Knowledge of the limitations of some environmental factors is available from experience and controlled experiments.

Anaerobic colonies show a peak of activity in the mesophilic $(32^{\circ}C-42^{\circ}C)$ and thermophilic $(50^{\circ}C-55^{\circ}C)$ temperature ranges. The thermophilic colony exhibits the greatest activity, but the products from this digestion have not always justified the increased cost of operation.

The pH of satisfactory digestion is near the neutral point. There is some question whether the control of pH is an effective aid to fermentation; rather, it appears that suitable pH occurs when other conditions of digestion are satisfactory. Tests for alkalinity have been suggested as more informative for the control of digestion that pH. Satisfactory methane fermentation requires a minimum alkalinity of 2,000 p.p.m. in the substrate.

Nitrogen is required by living organisms for the building of their own structure. The methane-producing bacteria, and apparently many of the other organisms present, are capable of utilizing ammonia-nitrogen in their metabolism. Ammonia in combination with other ions has in some experimental work exhibited an inhibitory effect upon digestion. More research to determine the desirable concentration of ammonia-nitrogen is a definite need.

Volatile acids are the raw material from which the

methane is produced by the methane bacteria. Too high an acid concentration will cause digestion to stop. Control of volatile acids, by dilution, has been proposed as a method for maintaining digestion. The upper limit of volatile acid content for the substrate is between 2,000 and 3,000 parts per million.

Mixing is necessary to bring the digesting material . into contact with the biological colony and to keep it buffered against acids produced during decomposition. Mixing increases the rate of digestion and prevents localized pockets of inhibitory decomposition products or low temperature developing and upsetting the fermentation process. RELATION OF FEED TO SEED MATERIAL

Anaerobic action is the same whether practised for the treatment of sewage or organic industrial wastes. The strength and composition of industrial wastes have a greater range than sewage. Industrial wastes may be composed almost entirely of a single substance; they may be purely carbonaceous materials,-sugars and starches of simple structure; complex carbohydrates; lignin; fatty substances; or purely nitrogenous materials, such as packinghouse wastes.

No common basis for comparing all anaerobic processes could be discovered in the literature. An attempt was made to correlate some of the data obtained for this thesis, but it was necessary to abandon this attempt due to a lack of information. More could be accomplished in the study of treatment processes if reports in the literature contained more complete data.

There is a difference in emphasis for the operator handling separate sludge digestion and the operator treating the whole volume of waste. In the first case he is interested in the operation to destroy the concentration of organic matter; in the second he is interested in the removal of the pollutional material from the waste liquid. The difference in interest engenders a difference in reporting which makes correlation virtually impossible.

The percentage of **v**olatile matter supplied and the concentration of volatile acids in the tank appear to be good indices of sludge digester operation. Data regarding the volatile material usually are not supplied by the operator treating the whole waste, as he is concerned with the efficiency of removals based upon concentrations in the influent and is prone to make reports of B.O.D. and suspended solids. These are interesting, but are not readily converted to a common basis for comparisons among all sludges and wastes. Some information is available on relationships between waste components (94); but conversion is not sufficiently accurate to permit mathematical analysis.

Heukelekian points out, in discussing biological oxidation of industrial waste (54), that many factors limit the possibility of developing a universal oxidation rate even for domestic sewage. Among these are the chemical and

physical composition of the food substanes;-sugars are more readily available to the organisms than lignin, and substances in solution more available than those in suspension. Also to be considered are the concentration of the food substances and the relative number of organisms present.

It is not supposed that identical end products may be achieved regardless of the material entering the treatment device. The question is, can an index of loading be found that would indicate a similarity of effect by an anaerobic colony regardless of the waste being treated, and show an optimum ratio between seed and influent or a peak efficiency value for the fermentation process.

Rudolf notes (see page 49) that some of the data from various investigations show a universality of results in anaerobic treatment which indicates that the digestable portion of many wastes will be acted upon by the active biological colony at the same rate. Gehm (44) reports limiting values of B.O.D. loadings of 0.04 and 0.10 lb./cu. ft./ day in anaerobic treatment, depending upon the amount of stirring to which the digester contents are subjected. Rudolfs and Fontenelli (see page 53) found an optimum digester loading for sewage sludge of o.l pound of volatile matter per cubic foot per day of effective digester capacity. Refering to Table VII, page 102, a tendency for industrial waste volatile solids loadings to bunch near this same value may be observed.

Biochemical oxygen demand does not seem to be too satisfactory a parameter for comparisons between different

waste substances since it is only a qualitative index of the materials upon which the biological colony is acting. It is true that the other indices, such as volatile matter, do not completely indicate the availability of the material to the organisms, but they do give a quantitative picture of the amount of material to be reduced.

A possible measure of digester loading might be the pounds of volatile matter supplied per cubic foot per day, as indicated above. This would appear to be a rather relevant measure for comparison because it approximates the ratio of the amount of food supplied to the size of the colony being supplied. It is reasonable to suppose that the size of an active colony would be proportional to the food supply. Rankin (see page 49) found that the reduction in volatile matter, in established digesters, was a function of the volatile matter content and time of detention of the material supplied. It would seem that these figures could be reduced to volatile matter per cubic foot per day. Rudolfs and Trubnick working with yeast wastes found a constant reduction took place regardless of whether a strong waste was applied for a long period or a weak one for a shorter time.

These indications, together with the work of Schlenz and Buswell on the control of digestion by means of volatile acids content, would seem to show that attention should be directed to the volatile matter in anaerobic treatment. If

investigators will so direct their attention and such reports are made as routine in the literature, it is cautiously hoped that some interesting relationships might be discovered about anaerobic treatment.

THE UTILITY OF METHANE FERMENTATION

Organic matter may be stabilized by a process of anaerobic methane fermentation, and with proper care and control, most organic materials will yield to methane fermentation. On the basis of comparative investment the process is an economical one. The products of the process are a combustible mixture of methane and carbond dioxide gas and a humuslike sludge. These products have value, although not in all cases will the value be sufficient to warrant marketing them. The value of the sludge is sufficient to make its disposal possible without cost;- farmers and others will remove it from the plant. If the volume is sufficient, marketing as a trade product has been successful in some areas. Rawh (104) has shown that it may be disposed of by dilution.

The gas may be used as a fuel. The usual mixture may be combined with natural gas for distribution. The sale of digester gas is not usually practiced. Utilization of the gas within the plant itself is the ordinary procedure, the gas serving as fuel for heat, in gas engines (36), or for electric power generation (48).

CONCLUSIONS

Anaerobic treamtne may be successfully used to

stabilize the organic material in sewage and industrial wastes. The stabilization is not so complete as that obtainable by aerobic methods; however, the destruction may be more economical. Anaerobic treatment may be followed by aerobic treatment if additional stabilization is necessary.

Greatest success will be had when anaerobic fermentation is used as a process for the production of methane. This process achieves the greatest destruction of organic material and produces the largest quantity of a valuable by-product.

An anaerobic biological colony may be employed to effect some degree of treatment when the efficiency of methane fermentation is not desired or economical for the installation planned. Within limitations, sufficiently satisfactory results for many purposes may be obtained in this manner, but too great a demand should not be placed upon such limited treatment.

Complete knowledge about the process of anaerobic treatment is not presently available. Not even all the organisms involved have been cataloged. Research by the microbiologist is indicated.

Control of the environment, in which the biological colony work, is essential to the success of the process. Complete control can not be expected until more knowledge of the organisms is obtained and more factual data on the reaction of the colony to its environment are available. Particularly necessary is information on the ammonia-nitrogen requirements of the organisms, their tolerance to various ions and the effect of various products of decomposition.

Volatile matter content is indicated as a parameter for determining loading factors on anaerobic treatment devices. Volatile acids content appears as a method for control of digestion. Assembling data from different sources on the treatment of a variety of sewages and wastes might be facilitated if investigators included information on volatile matter in their reports.

In municipal sewage treatment the anaerobic devices are sometimes operated in a manner subordinate to the other devices in the plant. For efficient and satisfactory service they should be operated with the same care as any other biological treatment method.

In any treatment problem full consideration should be given to anaerobic methods of disposal. Economical solutions to many problems may often be obtained thereby. The by-products of the process can usually be utilized within the plant, or disposed of without cost. An important consideration in the production of other substances should be the cost of marketing those products.

Sufficient knowledge of the process and its control is available so that anaerobic treatment is feasible for most organic wastes.

117.

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ABBREVIATIONS

- <u>SWJ</u> Sewage Works Journal. Since January 1950 name changed to Sewage and Industrial Wastes.
- I & E Chem Journal of Industrial and Engineering Chemistry
- JACS Journal American Chemical Society