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ELECTRODE POTENTIALS AND THEIR CONTROL IN THE ANAEROBIC DIGESTION OF SEWAGE SLUDGE

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of the requirements for the degree of
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Professor Clarence J. Velz

DEDICATION

To Violet, Mark, Diane and Patricia
and to the memory of my father Setrak

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INTRODUCTION

During the past thirty years, the anaerobic digestion of sewage sludge has been accepted as the most economical way of disposing of the organic matter accumulated during the various stages of sewage treatment. Although it was recognized as early as 1860 that solids underwent reduction when kept in a closed tank, it was not until the decade 1925 to 1935 that the basic principles of the process were studied in detail. New and significant developments were made in these 10 years primarily in the United States, Germany and Holland. Many of the answers to better control of sludge digestion, however, are still forthcoming.

In recent years, an ever increasing demand has been exerted on sludge digesters due to increases in population, with its concomitant increase in the volume of sludge to be treated. For this reason, the development of improved monitoring and control procedures for the process is essential. Although much progress has been made in this direction, the gap between present operating procedures and the latest technological advances must be narrowed.

Sludge digestion is accomplished through various bacterial agencies, whereby organic matter is biologically degraded yielding a product which is not unpleasant in odor nor difficult to dewater. The microorganisms, in obtaining the energy required for growth and reproduction, oxidize the

organic matter in the sludge to simpler and more stable compounds. Inasmuch as oxygen is absent from the anaerobic environment, some of the organic compounds within the unit must act as hydrogen acceptors, thus becoming reduced as other compounds are oxidized. The process, in effect, consists of a multitude of biochemical oxidation-reduction reactions. This concept presents the fundamental theory of the process, and dictates the type of monitoring and control parameters which are essential to the successful operation of an anaerobic sludge digester.

Some of the most frequently used parameters during the practical operation of sludge digesters are: temperature, pH, alkalinity, volatile matter reduction, volatile acid concentration and gas production and composition. Temperature and pH are important, and must be sustained at near optimum levels to maintain the activity of bacterial enzyme systems. Alkalinity is useful from the point of view that it indicates the buffering capacity of the unit. The reduction of volatile matter is an important consideration since the aim of sludge digestion is the degradation of organic material; while volatile acid concentrations shows the completeness of the process, for volatile acids are intermediate products of degradation. The amount of gas produced is critical inasmuch as it is one of the primary products, while gas composition reflects the conditions under which gasification is taking place. The monitoring

of all of these parameters has increased the efficiency of the digestion process.

In recent years some consideration has been given to the use of the electrode potential as a monitoring parameter. The published data is meager, to say the least, ranging from a series of grab sample determinations to monitoring of batch digestion and short, nonuniform studies of various kinds. However, the results of these earlier studies show promise that electrode potentials can be used to monitor the continuous sludge digestion process. In order to demonstrate the applicability of electrode potential measurements as a monitoring device, studies must be carried out to simulate as near as possible the conditions normally encountered in plant operation. It was for this reason, and because present trends in high rate digestion require a more sensitive indicator of the progression of the biochemical process, that this thesis was initiated.

The primary objective of this thesis is to study electrode potentials in sludge digestion in such a way as to enhance its acceptance as a monitoring and control parameter. Furthermore, it is hoped that this improved method of control will lead to a more efficient process, thereby allowing a more efficient use of existing and proposed installations.

BIOCHEMICAL ASPECTS OF SEWAGE SOLIDS DEGRADATION

The biological degradation associated with a digester has been occurring for ages on the bottoms of lakes and ponds. There in an environment in which oxygen is absent, organic sediment is used as a food source by natural anaerobic bacteria and other organisms. In the process "marsh gas" or methane is formed, and rises to the surface of the water leaving on the bottoms mineralized residues of organic matter (1). This statement implies that if we are to gain a thorough understanding of sludge digestion, we must study the various phases of the problem such as food sources, methods of degradation of organic matter, intermediate products, and environmental conditions. In this way, it has been possible to improve the digestion process to the point where we are not only duplicating natural processes but accelerating them by controlling the various environmental factors at their respective optimum levels. A basic understanding of the biochemical aspects of the digestion process may lead to further improvements through the use of new monitoring and control parameters.

A number of investigations of digestion have been made where the food supply has been in the form of sewage sludge. Two such analyses are presented in Tables I and II.

Table I (2)

Approximate Organic Analysis of Sewage Solids

Constituent	Fresh Solids %of dry solids	Digested Solids %of dry solids
Protein (6.25 x N)	19.4	12.5
Grease (by petroleum ether)	25.2	6.9
Crude fiber	10.8	9.8
Humic Acid (pyridine soluble)	4.0	8.6
Total	59.4	37.8
Volatile matter by analysis	60.9	39.6

Table II (4)

Approximate Organic Analysis of Fresh Solids and Ripe Sludge

Constituent	Fresh Solids % of dry solids	Digested Solids % of dry solids
Ether-soluble	34.40	8.18
Soluble in cold or hot water	9.52	5.48
Alcohol-soluble	2.49	1.59
Hemicellulose	3.20	1.58
Cellulose	3.78	0.56
Lignin	5.78	8.37
Crude protein	27.12	19.68
Ash	24.13	56.00
Total	110.42	101.44

From Table II, the major constituent of raw solids appears to be the ether-soluble fraction which is subject to biological attack, as shown by the small amount remaining in digested sludge. This residual consists of mineral oils and other unsaponifiable material, although recent studies (3) show that there is definite destruction of unsaponifiables during high rate digestion.

The cold and hot water extract contains sugars, amino acids, organic acids, starches, tannins and pectins. Alcohol-soluble fractions contain such materials as waxes, resins, alkaloids and choline (4). Lignin is the only organic constituent that shows a higher percentage in the digested sludge than in the raw sludge.

More recently, additional information in regard to the organic constituents of fresh solids was obtained by Balmat as described by Heukelekian (4). He subjected the settleable solids and other particulate fractions of sewage to a complete analysis and obtained 19.13 percent total ether-soluble matter, 25.08 percent total nitrogenous matter and 23.56 percent carbohydrates on a dry weight basis. These three components totaled nearly 68 percent on a dry weight basis. The volatile solids in the settleable fraction were 78 percent. Heukelekian and Balmat (5) also showed the existence of fourteen amino acids in sewage sludge. Alanine, aspartic acid, glutamic acid, histidine, leucine, phenylalanine, serine, tyrosine, methionine and valine were present in relatively large amounts.

Further work on lipid components of fresh and digested sludge was carried out by Heukelekian and Mueller (3) and are shown in Table III.

Table III (3)

Lipid Components of Fresh and Digested Sludge

	Fresh Solids	Ripe Sludge
Components of total grease (% of total grease)		
Free fatty acids	40-6	1-20
Ester fatty acids	20-40	5-15
Unsaponifiable Matter	15-20	50-80
Components of free fatty acids (% of free fatty acids)		
Palmitic acid	25-45	20-35
Stearic acid	14-23	10-20
Monoenoic acid	25-30	30-50
Dienoic acid	2-6	2-20
Components of ester fatty acids (% of ester fatty acids)		
Palmitic acid	20-40	10-20
Stearic acid	10-20	5-10
Monoenoic acid	20-60	60-70
Dienoic acid	9-12	5-10

Fresh sewage solids may be said to consist essentially of various portions of fats, carbohydrates and proteins, each of which is broken down into simpler, more stable compounds during the course of sludge digestion. The raw solids contain 60 to 80 percent organic matter and 20-40 percent inorganic solids (8).

Of the organic matter about two thirds is destroyed during digestion.

The FSIWA Manual of Practice (7) indicates that the concentration of raw sludge solids may vary from 8 to 12% from dense primary sludge to 0.5% solids from dilute excess activated sludge.

It is apparent from the foregoing that sewage sludge is a relatively complete substrate for the growth of microorganisms. All sewage sludge contains within it the necessary constituents for good bacterial metabolism (8). Organic material is present as a source of carbon and energy, while the necessary nutrients and trace elements are also present along with the necessary seed organisms which act as consumers and transformers.

The biological process may be thought of as being carried out by two separate groups of organisms. It is a balanced process whereby the raw material is continuously being broken down to organic acids by one group of organisms (acid formers). These organic acids are then converted to methane and carbon dioxide by a second group of microorganisms, the methane bacteria (9). Chanin (10) describes the process as a never ending game, where team A's goal is to initiate digestion by converting the more complex organic matter in the sludge into simpler organic compounds. Team B's goal is to take these simpler organic compounds and convert them into gas, liquid and ash. As long as both teams are operating effectively and as long

as the weather (environment) is favorable the game proceeds. It is the proper understanding of the required environment which enables us to maintain the proper conditions in the digester which finally results in a stabilization of the organic matter therein.

Organisms obtain the energy required for maintaining their life processes and for reproduction through the oxidation of organic matter. The oxidation that takes place in biological systems is usually a dehydrogenation and consequently hydrogen acceptors must be present. In aerobic systems the ultimate hydrogen acceptor is molecular oxygen while in anaerobic systems organic compounds must act as hydrogen acceptors. Figure 1 shows the hydrogen transfer system in both aerobic and anaerobic systems. In both systems diphosphopyridine nucleotide (DPN) and triphosphopyridine nucleotide act most often as the initial hydrogen acceptor. Flavine Adenine dinucleotide (FAD) will then accept the hydrogen from DPN or TPN oxidizing these molecules back to their original state, in which condition they are free to carry on further oxidations. In the aerobic pathway reduced FAD will transfer hydrogen to the cytochrome system which then transfers the hydrogen to the ultimate acceptor, molecular oxygen. In anaerobic systems, such as sludge digestion, the hydrogen is accepted usually by an organic molecule, the net result being an oxidation-reduction reaction whereby one molecule is oxidized while another is reduced. Through this type of coupling of reactions, energy is gained by microorganisms through the

formation of high energy bonds which act as a storehouse of energy for further use.

Before solid organic matter can be metabolized by microorganisms it must be rendered soluble so that it can pass through the cell wall and so enter into the biochemical relations of metabolism (11). The process of liquefaction of organic matter is accomplished by the action of extracellular enzymes which break down the complex carbohydrates into simple sugars, proteins to peptides and further to amino acids, and fats to glycerol and fatty acids, thus preparing the organic matter for entrance into the cell. This stage of liquefaction is then followed by gasification through the action of methane forming organisms. Since organisms capable of producing gas cannot bring about liquefaction, they cannot carry out the sludge digestion process alone (4). As previously stated, the liquifying organisms and gasifying organisms must be operative under balanced conditions. If the rate of liquefaction exceeds greatly the rate of gasification, because of either a depression of the activities of gasifying organisms or an acceleration of the activities of liquifying organisms, the whole process of digestion is upset (12).

Degradation of Carbohydrates

Carbohydrates are carbon compounds belonging to the aldehyde and ketone groups, and are composed of carbon, hydrogen and oxygen. For every carbon compound formed in nature there exists some microbial agency for its eventual decomposition (13). According to Lackey and Hendrickson (14)

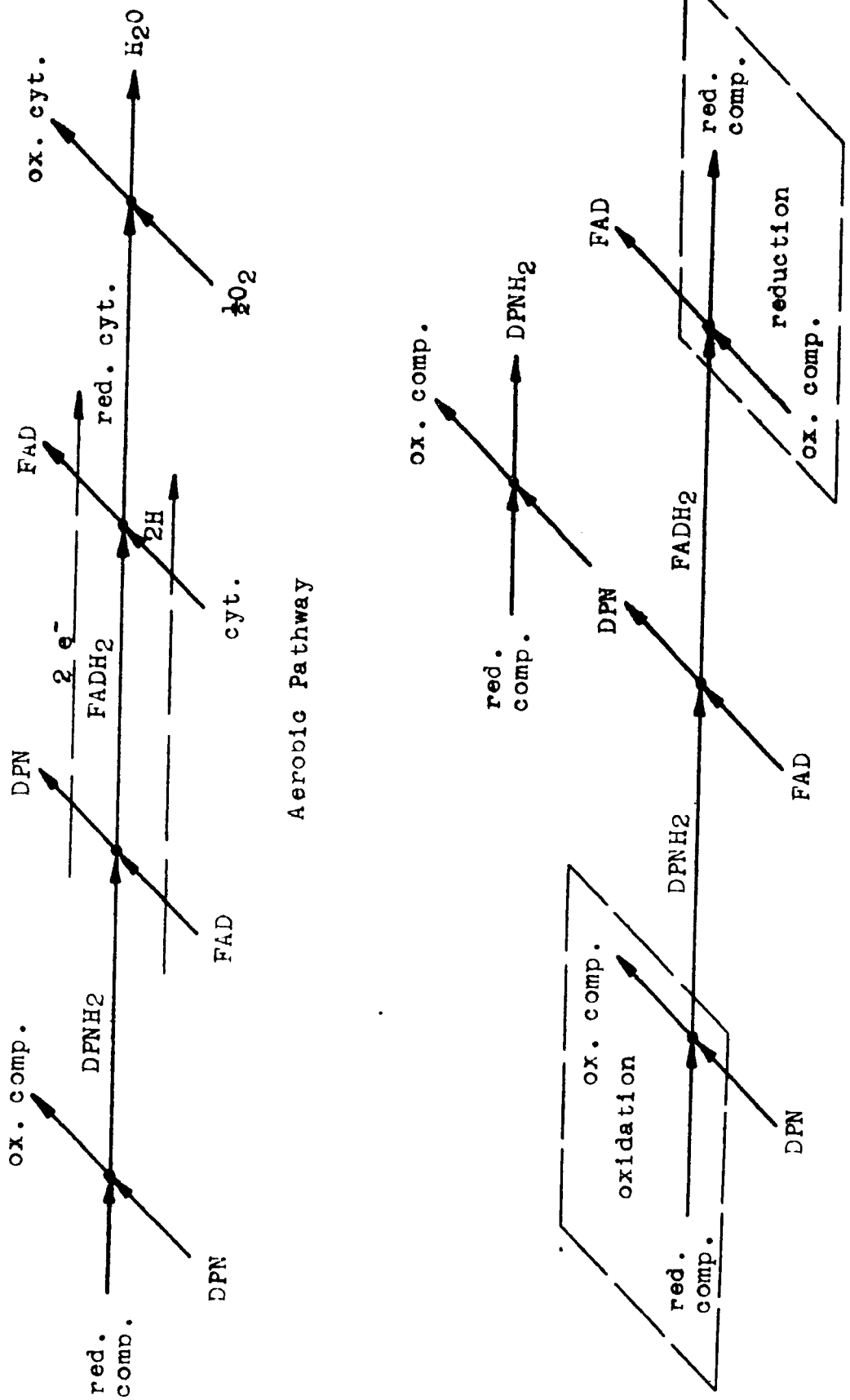


Fig. 1. Oxidative Pathways

carbohydrates must be simplified to the form of monosaccharides or disaccharides before they can penetrate the cell wall. The breakdown of starch to maltose residues is accomplished by the enzyme amylase which is produced by a variety of anaerobic or facultative organisms including: Clostridium perfringens, Bacillus macerans, Escherichia coli, Staphlococcus aureus and Clostridium acetobutylicum.

Cellulose is acted on by cellulase to produce cellobiose which is converted to glucose by the action of cellobiase. The preceding conversions are known to be carried out by Cl. dissolvens and Cl. omelianski both of which are found in human feces (14). Once carbohydrates are broken down into simple sugars so that they may penetrate the cell wall, a series of energy producing reactions takes place. Since the breakdown of glucose to various end products has been studied most thoroughly, it is probably desirable to explore this area, realizing that other simple sugars will be degradated by somewhat similar pathways.

The breakdown of glucose to various end products during intermediary metabolism results first in the formation of pyruvic acid which holds a central place in carbohydrate degradation. Pyruvate is then converted to a host of other end products depending on the type of organism for which it becomes a substrate. Figure 2 shows the degradation of glucose to pyruvate and further to the various end products. Figure 2 is a consolidation of the material presented by

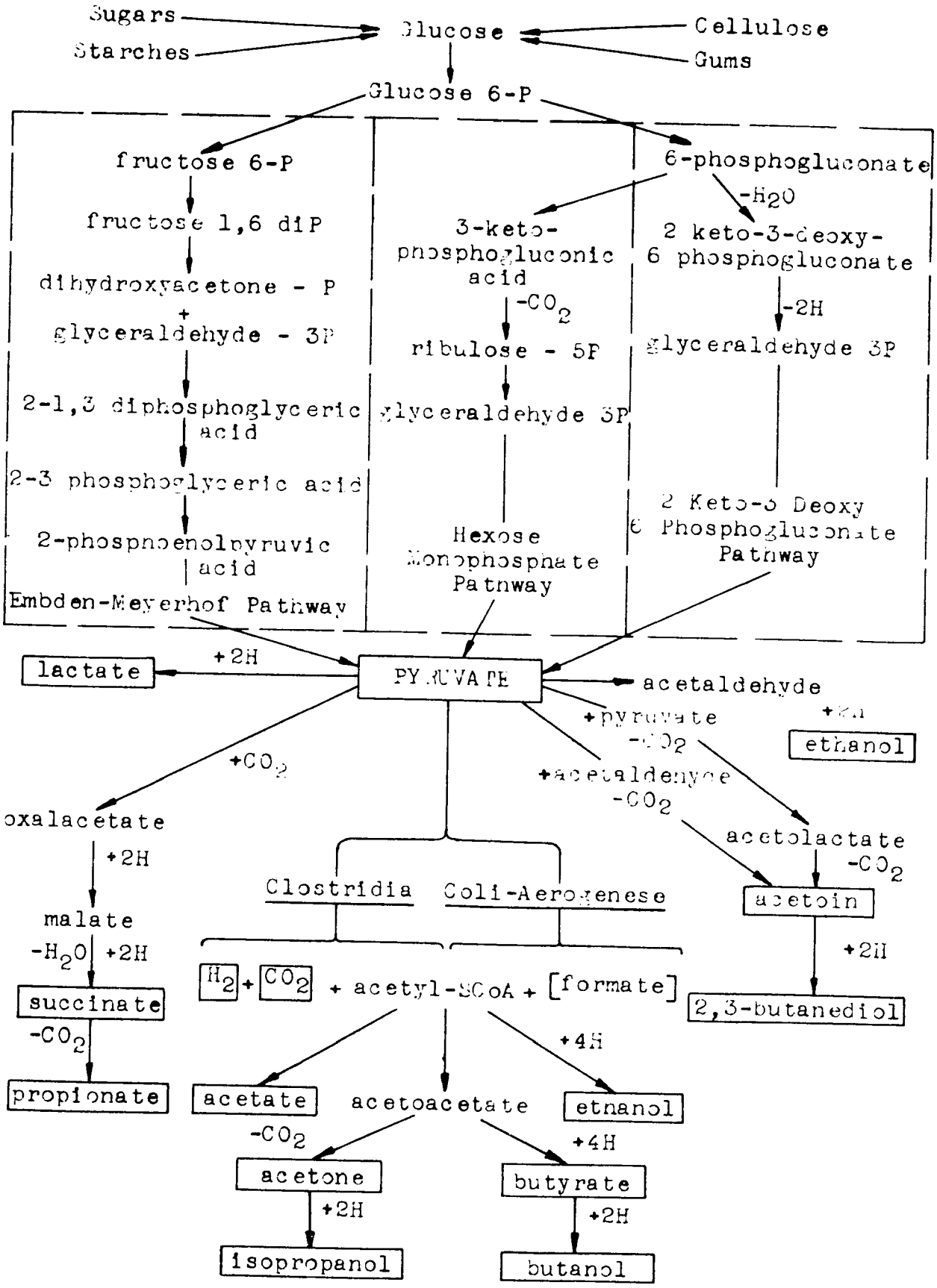


Fig. 2 Scheme for the Degradation of Carbohydrates

Oginsky and Umbreit (15) and Wood (16). As may be seen, the breakdown of glucose to pyruvic acid may follow one of three pathways. The first fermentation pathway visualized in detailed steps, and perhaps the most documented today, is the Embden-Meyerhof (Gylcolytic) scheme for the fermentation of glucose (16). The pathway results in the splitting of a hexose diphosphate to give, ultimately, 2 molecules of pyruvate. The second pathway is the hexose monophosphate pathway, commonly referred to as the monophosphate shunt. In this pathway, glucose-6-phosphate is oxidized to phosphogluconic acid, then decarboxylated to form ribulose-5-phosphate. Through a series of reactions, two molecules of glyceraldehyde-3-phosphate are formed and by means of the Glycolytic Pathway are converted into two molecules of pyruvate. The third and most recent pathway found, is the 2-keto, 3-deoxy, 6-phosphogluconic acid route (Entner-Doudoroff Pathway). This pathway is similar to the Hexose Monophosphate Shunt and also results in the formation of two molecules of pyruvic acid. The organisms involved in the above transformations and the pathways followed are varied and detailed, and a complete description is not warranted here. For further information the reader is referred to the work of Wood (16). More details of the three pathways mentioned above may be found in any recent biochemistry textbook.

The primary intermediate thus formed, pyruvic acid, is then fermented to the various end products as shown in Fig. 2.

The boxed compounds are the possible end products that may result from microbial agencies. It can be seen that almost all the products are simple alcohols and acids, the gases evolved consisting of hydrogen and carbon dioxide. These products, being ideal substrates for methane forming bacteria are then converted into gases as will be described later. Again it must be stated that the fermentations resulting from various organisms are too numerous to warrant further explanation here. One such fermentation, the mixed acid fermentation of Escherichia coli is worthy of mention from the point of view of the numbers of E. coli in sewage. This fermentation yields essentially volatile acids with negligible amounts of 2,3-butanediol. The products formed in order of quantity in a slightly alkaline fermentation are: formic acid, lactic acid, ethanol, acetic acid, succinic acid, carbon dioxide, hydrogen and a small amount of glycerol (16). Thus, carbohydrates are broken down to the acid stage by one group of organisms, the acid formers, the resulting acids becoming a substrate for methane producing bacteria.

Degradation of Fats

The general classification of "fats" includes all ether-soluble material such as oils, greases, soaps etc. (17). Basically the degradation of fat begins with the hydrolysis of the fat by hydrolytic enzymes into glycerol and the various fatty acids that make up the fat. Gylcerol may

then be converted to glyceraldehyde-3-phosphate and enter into the Glycolytic Pathway to give pyruvic acid. The manner of the degradation of the remaining fatty acids has received a considerable amount of study. Tarvin and Buswell (18) were under the impression that fatty acid degradation occurred by alpha-oxidation and gave reactions which supposedly verified this statement. However, it is generally agreed, presently, that fatty acid degradation follows Knoop's beta oxidation scheme (3)(14)(19). The beta oxidation cycle involves four steps resulting in the splitting off of an acetic acid fragment per cycle as is shown in Fig. 3. The four steps which occur during beta oxidation are shown in the reactions below:

1. Unsaturation reaction

$$CH_3CH_2CH_2CH_2COOH \xrightarrow{-2H} CH_2CH_2CH = CHCOOH$$

2. Hydration reaction

$$CH_3CH_2CH = CHCOOH \xrightarrow{HOH} CH_3CH_2CHOHCH_2COOH$$

3. Oxidation

$$CH_3CH_2CHOHCH_2COOH \xrightarrow{-2H} CH_3CH\overset{\overset{O}{\|}}{C}CH_2COOH$$

4. Splitting

$$CH_3CH_2\overset{\overset{O}{\|}}{C}CH_2COOH \xrightarrow{HOH} CH_3CH_2COOH + CH_3COOH$$

The cycle is repeated until the fatty acid is broken down into 1, 2 or 3 carbon fragments depending on whether the original fatty acid had an odd or even number of carbons.

With regard to digestion it can be said that lipids digest well (20). Rudolfs (21) found that the rate and

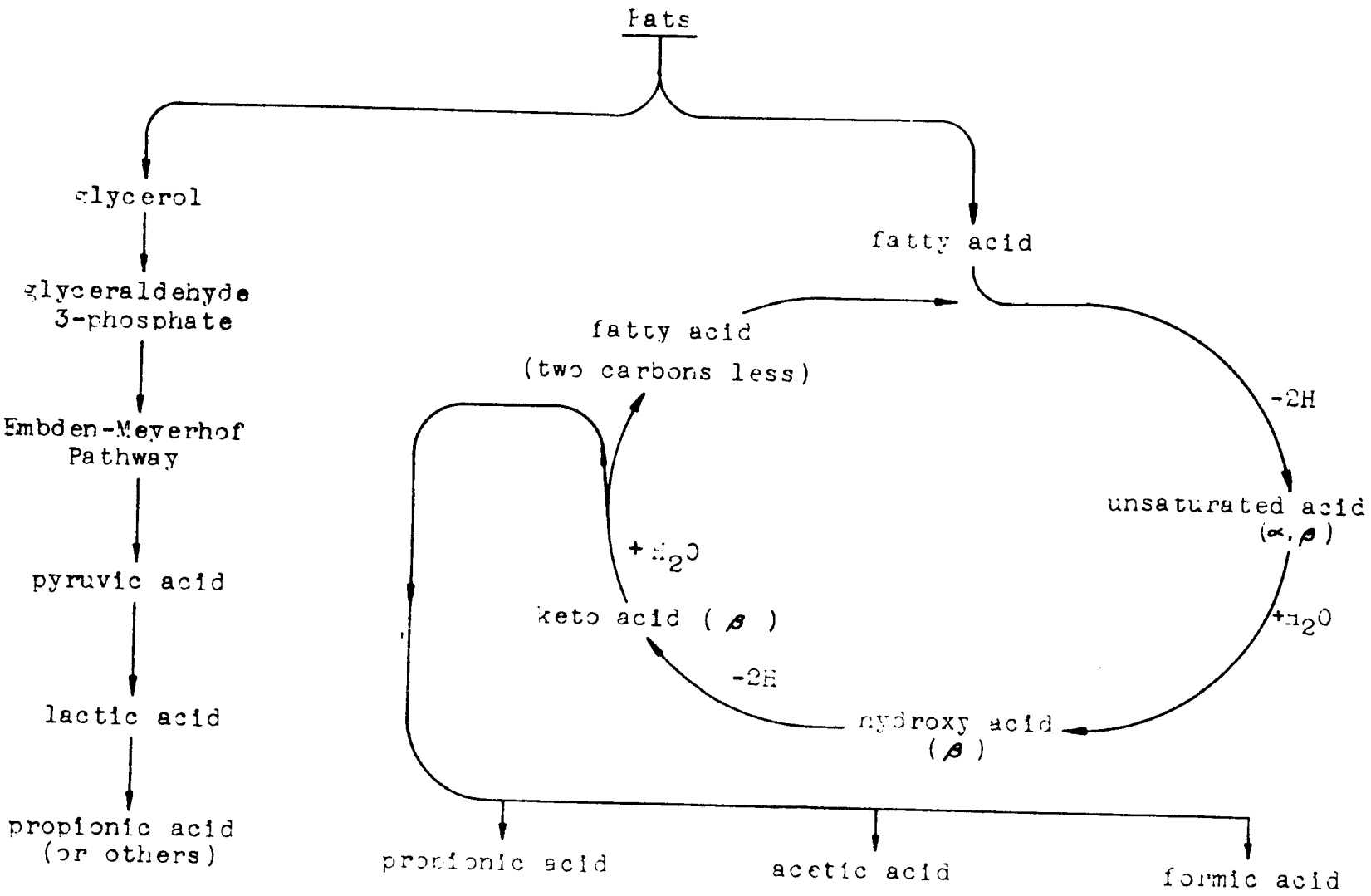


Fig. 3 Scheme for the Degradation of Fats

degree of grease decomposition are greater than the destruction of other volatile matters present in the sludges he investigated. As in the case of carbohydrate degradation the intermediates formed are ideal substrate for methane producing bacteria.

Degradation of Proteins

The proteins originate chiefly from animals. Proteins contain 16 percent nitrogen, 1 percent sulphur and a small amount of phosphorous (17). Since the protein molecule cannot enter the bacterial cell directly, it must first be broken down into simpler compounds. This is accomplished by hydrolysis of the peptide bonds eventually resulting in the production of amino acids.

Amino acid metabolism will result in a number of different compounds depending on the method of degradation and environmental conditions. At a neutral to alkaline pH most amino acids will be deaminated early in the reaction resulting in an abundant production of ammonia; whereas, in more acid media, decarboxylation will proceed rapidly with the production of amines (22). The following methods of protein decomposition, as given by Waksman (23), are:

1. Hydrolytic deamination - amino acid hydrolysis resulting in the formation of a hydroxy acid and ammonia, an alcohol, carbon dioxide and hydrogen; or an aldehyde, lower acid and ammonia as shown below:

$$RCHNH_2COOH + H_2O \longrightarrow RCHOHCOOH + NH_3$$

$$RCHNH_2COOH + H_2O \longrightarrow RCH_2OH + CO_2 + NH_3$$

$$RCHNH_2COOH + H_2O \longrightarrow RCHO + HCOOH + NH_3$$

2. Decarboxylation with amine and subsequent alcohol formation:

$$RCHNH_2COOH \longrightarrow RCH_2NH_2 + CO_2$$

$$RCH_2NH_2 + H_2O \longrightarrow RCH_2OH + NH_3$$

3. Reductive deamination with the production of saturated acids:

$$RCHNH_2COOH + 2H \longrightarrow RCH_2COOH + NH_3$$

4. Ammonia formation without reduction to form unsaturated fatty acids:

$$RCHNH_2COOH \longrightarrow RCH = CHCOOH + NH_3$$

E. coli is known to carry out such unsaturation reactions as that shown in 4 above. E. coli and Pseudomonas fluorescens are agents in the hydrolytic deamination of amino acids (22). It is apparent that reductive deamination will take place in an anaerobic environment. Delwiche (22) cites the work of Strickland who studied mutual oxidation-reduction reactions of amino acids. The organism used in this work was Clostridium sporogenese. With respect to this phenomenon, Lackey and Hendrickson (14) list the amino acids that act as hydrogen donors and those which act as hydrogen acceptors as shown below:

H - donors	H - acceptors
alanine	glycine
valine	proline
cysteine	hydroxyproline
histidine	arginine
leucine	tryptophane
glutamic acid	
phenylalanine	
serine	
aspartic acid	

Amino acid metabolism is a large and varied subject on which many volumes have been written. What has been presented here is but a word or two attempting to give only a general concept of protein degradation. The end products in protein degradation are saturated and unsaturated acids, alcohols and ammonia plus a series of malodorous intermediates, principally mercaptans and indols.

Methane Fermentation

The degradation of carbohydrates, fats and proteins by the so-called acid formers results in a number of organic acids and alcohols. These intermediates are further broken down to yield gases, principally carbon dioxide and methane. This stage of decomposition is usually referred to as gasification or methane fermentation, and is carried out by a group of methane producing bacteria.

Investigations on methane fermentation and methane producing bacteria are numerous (19)(24)(25)(26).

Heukelekian and Hinemann (27)(28)(29)(30) carried on a series of investigations with regard to methane producing bacteria in sewage sludge. The general characteristics of methane bacteria as expressed by Barker (26) are:

1. All the organisms are strict anaerobes.
2. All ferment specifically some of the simpler organic acids and alcohols provided the proper nutrients are present.
3. Nutrients required are the usual salts, CO_2, a reducing agent, a simple oxidizable compound, and ammonia as a source of nitrogen.
4. Optimum pH range is 6.4 to 7.2 although the limits are from pH 6 to 8.

The methane producing bacteria, eight known species in all, belonging to three genera, are listed in Table IV along with their preferred substrates.

The methane producing bacteria are an important link in the completion of sewage sludge stabilization. Mylroie and Hungate (31) concluded that the occurrence of Mb. formicicum in large numbers in sewage sludge indicates that it must be of importance in sewage fermentations. The rate of growth of these organisms is slow, causing Heukelekian and Hinemann (27) to say that this slow rate of development makes it almost necessary to seed the sludge tanks.

Table IV (26)

Classification of Methane Producing Organisms

I.	Methanobacterium---(rod-shaped cells)	
	1. *Mb. formicicium*	formate, CO, H_2
	2. *Mb. omelianski*	primary and sec. alcohols, H_2proprionate
	3. *Mb. propionicum*	proprionate
	4. *Mb. sohngenii*	acetate, butyrate
II.	Methanococcus--(spherical cells not in sarcina arrangement)	
	1. *Mc. mazei*	acetate, butyrate
	2. *Mc. vannielii*	formate, H_2
III.	Methanosarina---(spherical cells in sarcina arrangement)	
	1. *Ms. methanica*	acetate, butyrate (?)
	2. *Ms. barkerii*	methanol, acetate, H_2, CO

The mechanism of methane formation has received much attention. Buswell and Sollo (32) considered three possible mechanisms:

1. Preliminary decomposition of acetic acid to hydrogen and carbon dioxide with subsequent reduction of carbon dioxide to methane by hydrogen.
2. Carbon dioxide is directly reduced to methane and acetic acid thereby oxidized to CO_2.
3. Simple decarboxylation.

Buswell et al (33) in later experiments showed that carbon dioxide was definitely a precursor of methane. Kluyver

and Schnellen (34) believed that the fermentation of CO to CO_2 and CH_4 could be carried out by Ms. barkeri and Mb. propionicum according to the oxidation reduction reaction:

$$4CO + 4H_2O \longrightarrow 4CO_2 + 4H_2 \text{ oxid.}$$
$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O \text{ red.}$$
$$4CO + 2H_2O \longrightarrow 3CO_2 + CH_4 \text{ Net}$$

Recent work on methane fermentation shows agreement with the so called carbon dioxide reduction theory presented by van Neil in 1934. According to this theory, the organic compound is oxidized completely to carbon dioxide which is then reduced to methane by hydrogen. A representative oxidation-reduction reaction may be given as:

$$\text{oxid.} \quad 4CH_3CH_2COOH + 8H_2O \dashrightarrow 4CH_3COOH + 4CO_2 + 24H$$
$$\text{red.} \quad 3CO_2 + 24H \dashrightarrow 3CH_4 + 6H_2O$$
$$\text{Net} \quad 4CH_3CH_2COOH + 2H_2O \dashrightarrow 4CH_3COOH + 3CH_4 + CO_2$$

The carbon dioxide reduction theory has been shown to be true for most of the organic acids. However, there are exceptions to the rule as, for example, in the breakdown of acetic acid the methane was found to come from the methyl group while the carbon dioxide came from the carboxyl group. Studies by Stadtman and Barker (24) showed the following reaction to take place when the methyl group of acetic acid was radioactively labeled:

$$*CH_3COOH \longrightarrow *CH_4 + CO_2$$

It was also shown in the same manner that methanol

fermentation did not follow the carbon dioxide reduction theory.

In this chapter an attempt has been made to present, although briefly, the fundamental biochemical facts relating to the anaerobic digestion of sewage sludge. It has been shown that the large molecules are hydrolized by extracellular enzymes in order that they may enter the bacterial cell and participate in energy gaining reactions. It has been further indicated that the products of the first group of organisms, the acid formers, were various organic acids and alcohols along with hydrogen and carbon dioxide. These products serve as substrate for the methane producing bacteria and result in the formation of methane and carbon dioxide as the principal products.

PRACTICAL ASPECTS OF SEWAGE SLUDGE DIGESTION

Since sludge digestion is directly related to the life processes of bacteria, the practical application of these processes revolves around the creation of nutritional and environmental conditions, as ideal as possible for active growth. The creation of such conditions should be the primary aim in the design and operation of sludge digestion units. Only then will the most efficient process result. For this reason, it seems both desirable and necessary to enumerate the more important environmental factors, with particular reference to the actual problem of sludge digestion.

Temperature

All biological systems are dependent on temperature. The rate of growth is slow at low temperatures but increases as the temperature increases until the optimum temperature is reached, after which the rate falls off sharply. The optimum in most instances has been shown to be very close to the minimum temperature necessary for the inactivation of protein. Organisms have been characterized by their cardinal temperatures. One such classification is shown in Table V.

Table V (35)

Cardinal Temperatures of Bacteria

Class	Minimum °C	Optimum °C	Maximum °C
Psychrophillic	0	15	30
Mesophilic	5-25	18-45	30-50
Thermophilic	25-45	55	60-90

Fair and Moore (36) showed that the effect of temperature on batch digestion of sewage solids indicated three or possibly four distinct zones of activity, as follows:

1. Thermophilic Zone - above 42° C
2. Intermediate Zone - 28° - 42° C
3. Temperate Zone - 10° - 28° C
4. Cryophilic Zone - below 10° C

However, in practical, controlled sludge digestion only mesophilic and thermophilic temperatures are of importance. These authors in later studies (37) concluded that the optimum temperature for mesophilic digestion was 98° F, and that for thermophilic digestion was 128° F. The time required to obtain 90 percent of the apparent ultimate gas production was 22 days and 8 days respectively. Such data have shown that digestion time is reduced considerably under thermophilic conditions, but practical considerations have prevented wide adoption of digestion at thermophilic temperatures. Golueke (38) found that solids reduction increased from 41 percent at 30° C to 52 percent at 37° C

and then leveled off. A decrease began at 45° C showing about 48 percent reduction at 60° C; it then fell off rapidly to practically no reduction at 65°C. Sprague (39) recommends a digestion temperature of 80° to 95°F. This recommendation is in agreement with many other investigators (20)(40)(41)(42). The temperature most often adopted seems to be in the range of 32° - 35°C (90° - 95°F). Temperature levels are maintained either by heating coils within the digestion unit or through the use of external heat exchangers.

pH

Another component of the environment that exerts a decisive influence on the growth of bacterial cells is pH. The pH limits for the growth of any particular organism are a reflection of the pH limits for the enzyme system which is most critically effected and which is vital to that organisms metabolism.

The most critical range of pH in sludge digestion is defined by the limits for the methane producing bacteria, since they require a narrower pH range than the other microorganisms involved. It has already been stated that methane producing bacteria favor a pH range from 6.8 to 7.2, although growth is possible from pH 6 to 8. Cassell and Sawyer (43) recommend pH control within the range of 6.8 - 7.2, while Orford et al (44) say that the pH should be maintained between 7.0 and 7.2 for good digestion. According to Wooten (9) the pH should never be allowed

to drop below 6.4.

It has been stated (45) that pH is a poor monitoring parameter, for by the time a measurable change in pH can be detected the interference with digestion has already started. However, Cassell and Sawyer (43) are of the opinion that the maintenance of optimum pH conditions remains the factor of primary practical importance during the initiation of sludge digestion.

Volatile Acids

Volatile acids are defined by Standard Methods (46) as the first six lower molecular weight fatty acids classified as soluble fatty acids, and the only ones that can be distilled at atmospheric pressure. It was observed in the preceding chapter that the acid intermediates produced in the degradation of organic matter fall into this classification. It is thus apparent that if the methane producing bacteria are temporarily unable to carry out their function completely, an accumulation of volatile acids will occur. For this reason, the concentration of volatile acids within the digester has been ranked as probably the most accurate and rapid indication of any irregularities in the process. The volatile acids produced in anerobic digestion include valeric, butyric, propionic, acetic and formic acids (45).

Although Lohmeyer (1) states that normal digestion takes place at volatile acid concentrations between 500 and 700 mg/l, the literature indicates that digestion under conventional practice will usually produce less than 500 mg/l.

It is possible that during high rate digestion, the volatile acids concentration may be as much as 800 mg/l. The level of volatile acids during normal operation is not as critical as the change in this established level. A continued increase in the volatile acids concentration is a danger signal. Volatile acids in excess of 1500 mg/l. begin to become inhibiting to the methane producing bacteria. Buswell (47)(48) states that the volatile acids must not exceed 2000-3000 mg/l, while Backmeyer (49) sets the limit at 1800 mg/l. Morgan and Neuspill (50) found that an increase of 1000 mg/l in the volatile acids concentration was always accompanied by a decrease in gas volume.

Many investigations have been carried out to determine what action could be initiated to recover a digester that has become "stuck" because of a high level of volatile acids. To neutralize these acids lime was used. There are two opposing views on the use of lime for this purpose. One group of investigators believes that high acid concentrations are a result of too low an activity on the part of the methane producing organisms. They believe that volatile acids are toxic to these organisms through the reduction of pH, which can be relieved by adding lime. The other group of investigators feels that a volatile acids concentration above about 2000 mg/l causes a retardation of the methane producers regardless of the pH maintained. This infers that materials used to maintain the pH are ineffective (51).

Schlenz (52) states that lime in any form or amount has no place in a digester, and Buswell (48) is of the opinion that the only way to lower volatile acids is by reducing substrate concentration. On the other hand, much success has been achieved through the judicious application of lime to a sour digester. Sawyer et al (53) indicate that lime additions were found to have desirable effects in proportion to the amount added. According to Heukelekian (54) the addition of lime hastened the digestion by neutralizing the acids, which then decomposed much faster than if they had been allowed to take their natural course of decomposition and neutralization. Others (49)(55)(56) have successfully used lime to aid in the start up and control of digesters.

More recently McCarty and McKinney (57)(58) presented the idea of salt toxicity, stating that the decreased activity of methane bacteria, often observed following a rapid increase in volatile acid concentration and subsequent neutralization, is not due to "volatile acid" toxicity, but is associated in a more general way to "salt" toxicity. It was found that the least toxic salt contained calcium as the cation and concluded that volatile acids could be reduced using calcium and magnesium salts but not sodium, potassium or ammonium salts.

Alkalinity

Alkalinity is due to non-volatile salts which remain in solution over wide pH ranges (17). It comprises the

buffering action within the digester and consists essentially of ammonium bicarbonate along with other salts. The buffering capacity of fresh solids is due almost entirely to the alkalinity of the carriage water, and if low, it may not be able to supply the necessary buffering during the acid stage of digestion. Fortunately, normal digestion produces carbon dioxide and ammonia which then combine to produce alkalinity.

During normal digestion enough alkalinity is present to insure good buffering. Haseltine (17) found that thoroughly digested sludge has an alkalinity of 3000-3500 mg/l. He claims that alkalinity determinations are of more value than any measurable criteria and that from his experience the alkalinity should not be allowed to drop below 2000 mg/l. This is in agreement with some other investigators (41)(57) while Sawyer and Grumbling (59) found that high rate digestion gave higher values of alkalinity. On the other hand, Kozma (6) suggests that alkalinity should not be allowed to drop below 1000 mg/l.

Mueller et al (40) proposed the theory that it is not the actual value of alkalinity that produces critical conditions but rather the volatile acid-alkalinity equilibrium. They are of the opinion that variations in pH can occur only after the volatile acid-alkalinity equilibrium is upset.

Solids Reduction

One of the primary objectives in sludge digestion is the reduction of the volatile solids which comprise between 60 and 80% of the total solids. As such, the percent reduction of

volatile solids becomes an indicator of the digestion process. All carbon compounds cannot be broken down in the normal digestion time. As much as 50 percent of them may remain as humus (60).

Sawyer and Roy (61) in recent studies on high rate digestion showed that 52.2 percent of the volatile matter was destroyed in a digester operating at a six day detention time, while a twenty day detention time reduced the volatile matter by 58.2 percent. On the other hand, Torpey (62) found the volatile solids remaining after 30 days and 15 days were 62.5 percent and 67.5 percent respectively.

It is generally agreed that a 50 percent reduction in volatile matter (63) will give a well-digested sludge that is relatively easy to dewater and has no appreciable odor.

Gas Production and Composition

Since the primary end products of digestion are the gases carbon dioxide and methane, the quantity as well as the quality of the gas collected is an indication of the digestion process.

During normal digestion the quantity of gas collected varies but slightly and is usually expressed either in terms of cu. ft. per pound of volatile matter added or cu. ft. per pound of volatile matter destroyed, and more infrequently as cu. ft. per capita. According to Bloodgood (20), the usual amount of gas produced is 6 to 8 cu. ft. per pound of volatile matter added, while Rankin (64) cites 14.5 cu. ft. of gas per pound of volatile solids destroyed. Rudolfs (65) concludes that it is unlikely that gas production from settled sludge

will be greater than from 0.9 to 1.9 cu. ft. per capita even under conditions of prolonged digestion. Recent work in high rate digestion (50)(61)(62)(66) has produced somewhat similar results.

The gas produced from sludge digestion is principally carbon dioxide and methane. The sum of these two gases amounts to about 95 percent of the total with smaller amounts of hydrogen and hydrogen sulphide (67)(68). The ratio of carbon dioxide to methane varies depending on the type of substrate. The percentage of carbon dioxide in the gas during the destruction of carbohydrates is 50 percent, 25 to 38 percent during the degradation of fats and 25 to 35 percent for the destruction of protein (17). Bloodgood (69) states that sludge gases are composed of about 68 percent methane and 32 percent carbon dioxide, having a heating value of about 650 B.T.U. per cu. ft. He further indicates that hydrogen sulphide is present and may be detected at concentrations as low as 0.001 percent, while the presence of oxygen or nitrogen indicates a leak or poor testing procedures.

Malie (70), in describing sulphur in sewage, reveals that the average amount of hydrogen sulphide in sludge gases is about 300 ppm and that concentrations as low as 0.000001 ppm can be detected by smell; whereas, concentrations as high as 2.99 percent may cause death. He further indicates that the higher the digestion temperature, the higher the concentration of hydrogen sulphide. Aulenbach and Heukelekian (71) made further studies on the affect of

sulphides on the digestion process. The presence of hydrogen sulphide is a common biologic feature of all anaerobic treatment processes (72).

The percentage of carbon dioxide in sludge gases has been recognized as an indicator of the process. Miller and Barron (73) have proposed that the trend of rising carbon dioxide in digester sludge gas is the best early warning indication of impending digester trouble of any control measure now available, no matter what the cause. They further point out that the normal range of carbon dioxide is 31 to 35 percent, and when the percentage builds up to 36 or 37 percent trouble is impending.

Carbon dioxide is essential from a biological point of view for it is necessary in a medium to support cell growth; in fact, it is suggested that the lag in the growth of cells may be due largely, if not entirely, to the time it takes the culture to build up the carbon dioxide content of the medium (74).

Redox Potentials

Inasmuch as there are a very large number of oxidation-reduction reactions taking place in a digester, it would not seem incorrect to propose that oxidation-reduction potentials may be indicative of the digestion process. A limited amount of work has followed this direction, principally by Molof (75) and Grune and Chueh (76). Since electrode potentials will be the primary consideration throughout the

remainder of this paper, further discussion under this heading is unnecessary.

Loading and Detention Time

A close look at the biochemical reactions taking place in a sludge digester will reveal the importance of controlling the loading of digestion tanks. The first stage in the digestion of sewage sludge is that of intensive acid production, resulting in the formation of extremely large amounts of volatile acids as intermediates (77) along with a reduction in pH. Under these conditions the methane bacteria, which are important in the second stage of digestion (acid digestion), cannot grow and multiply. The third stage of digestion is that of the breakdown of the more resistant materials. While the digester is in the third stage, gasification is high, while intermediate acids are low and the pH is slightly above neutrality. The loading to the digester should be small enough so that the detrimental effects of the first stage are overcome by the beneficial effects of the second and third stages.

Digester loadings are usually stated in terms of pounds of volatile matter added per cu. ft. of digester capacity per day. Recommended loadings by various investigators vary considerably. Buswell (67) discloses that loadings of 0.14 lb. per cu. ft. per day of organic wastes have been found feasible in many pilot-plant studies. Mueller et all (40), on the other hand, observed that gas production began to fall off after the loading was increased

to 0.11 lb., and volatile acids increased to 2000 mg/l at a loading of 0.125 lb. When the loading was increased to 0.135 lb. a change in the pH occurred and the carbon dioxide content of the gas had increased to about 40 percent. As a result, this authority states that the critical loading level should be 0.100 lb. of v.m. per cu. ft. per day.

Kozma (6) states that 2 to 3 lbs of dry solids per cu. ft. of tank capacity per month should be the normal loading rate. When the percentage of volatile solids is considered, this loading is even less than the 0.1 lb. per cu. ft. recommended above.

According to the FSIWA Manual of Practice No. 8 (7) the required digester capacity varies from 2 to 6 cu. ft. per capita depending on the type of sludge to be digested. The normal unit-capacity requirements may be reduced provided the operations are controlled and carried out under the following conditions:

1. The tank contents are agitated so as to maintain an intimate mixture of raw and digesting solids.
2. The raw sludge is added more or less continuously to the digestion unit.
3. The raw sludge is concentrated or prethickened before being added to the digester.

The above conditions when followed usually result in high rate digestion, although the line of demarcation between conventional and high rate digestion is far from being well defined.

Sawyer (78) maintains that thermal homogeniety and food contact must be maintained through complete mixing of the digester contents. The concentration of inhibitory biological intermediates should also be kept at low levels if the digesting mass is mixed (59).

A study by Estrada (79) showed that agitation in sludge digesters increased to the extent of 130 installations in the United States as of 1960. He described the three principal types in use as:

1. Gas recirculation through more than one point of discharge into the digestion tank, with the bottom of the discharge pipe set about one third up from the bottom of the tank (Pearth Process).
2. Gas recirculation through a central point of discharge into the digestion tank with the bottom of the discharge pipe set just above the bottom of the tank (Catalytic Reduction Process).
3. Mechanical agitation through propeller blades and draft tube suspended in the digestion tank (Dorr-Oliver).

Studies by Morgan (66)(80) and Morgan and Neuspiel (50) led them to signify gas recirculation as giving better results than mechanical mixing. In laboratory studies they found that a volatile solids loading of 0.262 lb. per cu. ft. per day at a ten day detention time gives a suitably digested sludge. In studying the process during this time, it was found that the most important controls were gas production

and volatile acids concentration. In conclusion, they reveal that although a pilot plant was operated with monthly average loadings of 0.345 lb. per cu. ft., until more data is obtained the maximum loading should be taken as 0.200 lb. per cu. ft.

Fuhrman (81) found that the Pearth Process would not only prevent scum formation, but would also cause existing scum to disappear. A scum blanket of 9 1/2 ft. depth was reduced to 4 ft. in 13 days and once the scum was gone it never reformed. He found that the process also allowed increased solids loadings up to 0.15 lb. of volatile matter per cu. ft. per day. Langford (82) describes the creation of uniform conditions throughout the tank when the Pearth Process is used while Schreiber (83) explains that some plants using the process have successfully used suspended solids loadings of 530 lbs. per 1000 cu. ft. per day.

Blodgett (84) showed that a loading of 0.3 lb. per cu. ft. per day was feasible using the Catalytic Reduction Process.

Laboratory studies by Schulz (85) also showed the feasibility of increased solids loadings and Schlenz (86) has set forth a presentation of procedures which would provide "controlled digestion"

Although organic loading is the usual method of expressing solids charged to the digester another important factor must be considered, that of detention time. According to Sawyer and Grumbling (59)a combination of organic loading and detention time must be considered together

during high rate digestion. If increased amounts of low solids sludge is added to a digester, the detention time becomes so short that critical contact time is lost. Torpey (87) has shown that the digestion process fails rapidly at detention times of less than six days while Sawyer and Grumbling (59) would like to see seven days as a minimum detention time; and, in conjunction, report that six percent solids in the digester is the highest level that will permit proper mixing. Chemielowski et al (51) propose a minimum detention time of 8 to 10 days and Keefer (88) discloses that satisfactory digestion may be obtained in about 9 days. Torpey (62) thickened sludge to an average of about 11.2 percent over a period of a year and found that recirculation of the digester contents from bottom to top provided adequate mixing. In conclusion, he declared that the stability of the high rate digester, with high pH and alkalinity and low volatile acids, points toward the likelihood of significant increases in digester loading.

From the preceding two chapters, the relationship between the biochemical theory and the practical aspects of adequate control of the digestion process may be seen. The practical aspect of sludge digestion is concerned essentially with creating ideal conditions for biochemical activity and finding the proper parameters for following the process. In the following chapter emphasis will be placed on oxidation-reduction potentials so that the data presented in the remainder of this paper can be analyzed in its proper perspective.

OXIDATION REDUCTION POTENTIAL

Biological treatment of sewage and industrial wastes consists essentially of the biological oxidation of complex heterogeneous material into more simple, stable compounds. Microbial populations accomplish this oxidation while obtaining the energy necessary for reproduction and growth. Bacterial oxidation of organic matter is usually carried out by dehydrogenation. This involves a transfer of electrons, and is in agreement with the modern definition of oxidation which states that oxidation involves a loss of electrons and conversely, reduction is characterized by a gain of electrons. When a compound loses an electron it becomes positively charged. This charge is passed on to a hydrogen atom and the loss of both the atom and the electron results in the removal of a hydrogen ion. Stanier et al (89) state that this type of oxidation is referred to as a dehydrogenation. Similarly, a hydrogenation could be stated as a reduction. Most biological activities then involve oxidation-reduction reactions in which different compounds act as the final hydrogen acceptors. In aerobic systems, molecular oxygen is the ultimate hydrogen acceptor, while under anaerobic conditions various compounds act as hydrogen acceptors resulting in a multitude of oxidation-reduction reactions. The importance of oxidation-reduction potentials in biological systems thus becomes evident. This

importance was recognized rather early by Hewitt (90) who states, "oxidation-reduction systems are so essential that life might be defined as continuous oxidation-reduction reaction".

The derivation of the oxidation-reduction potential equation has been in the literature many years and may be found in any elementary physical chemistry textbook. For this reason, it is felt that such a review is not necessary here. A number of excellent texts on the subject are available (90)(91)(92), and there are several which stress oxidation-reduction potentials in biological systems (90) (91). Nevertheless, it is necessary that certain statements be made regarding oxidation-reduction potentials and their application to biological systems.

The general equation for the oxidation-reduction potential is given by:

$$E_h = E_o + \frac{RT}{NF} \log \frac{(\text{oxidants})}{(\text{reductants})}$$

where: R = gas constant

T = temperature ^oK

N = number of electrons

F = Faradays constant

( ) = Molar concentration of substances involved

E_o = the potential when (oxidants) = (reductants)

at 25^oC and N equal to unity the above equation becomes:

$$E_h = E_o + .0591 \log \frac{(\text{oxidants})}{(\text{reductants})}$$

For systems involving the coupling of electron transfer with hydrogen ion transfer as for the process:

$$Ox + 2e \rightleftharpoons R^{=}$$

The general equation becomes (93):

$$E_h = E_o + .03 \log \frac{(\text{oxidants})}{(\text{reductants})} - .03\ pH$$

Since biological metabolism involves the transfer of electrons and hydrogen ions, it is apparent that in biological systems, E_h is related to pH.

The above oxidation-reduction potential equations are derived on the assumption that thermodynamic equilibrium exists; that is, constant pressure, temperature and reversibility. It is well known that biological systems are not in thermodynamic equilibrium but are, in fact, steady state systems whereby a material is continuously being broken down into various products through bacterial enzyme systems.

Although biological systems cannot be expected to follow quantitatively the oxidation-reduction potential equations shown above, such equations may be used in a qualitative manner, inasmuch as electrons are being transferred in these systems. Since the result of a transfer of electrons from one compound to another creates a potential difference, we can measure this difference by use of a potentiometer. The direction in which a reaction proceeds is dependent on the free electrons in the system. If the number of electrons is increased, more of the reductant is produced and if the number of electrons is

decreased, more of the oxidant is produced (76). Rohlich (94) states "oxidation-reduction reactions maintain a dominant place in any consideration which is given to the biological process". However, since biological systems do not follow the thermodynamic equations the potential developed is referred to as the electrode potential instead of an oxidation-reduction potential. This terminology will be used when the work carried out during this dissertation is discussed.

Oxidation-reduction potentials have been measured in biological systems for many years, and a very complete listing of potential values of organic systems is given by Clark (91).

The potential developed in a biological system may be determined by substituting the glass electrode used in pH measurements by a noble metal usually gold or platinum. The results are read on a standard vacuum tube potentiometer calibrated to read directly in millivolts. Although platinum and gold electrodes are most often used, other electrodes used consisted of iridium, tungsten, graphite, mercury, rhodium and palladium (2). Electrodes of various sizes and shapes have also been reported. To complete the cell any standard half cell may be used as the reference electrode. Probably the half cell most often used is the calomel half cell, although Grune et al (95) have used a silver-silver chloride half cell along with a platinum flow-through cell.

The potential developed, using a standard reference electrode, is then converted to the standard hydrogen electrode. Potentials thus converted show the relationship of the potential to the normal hydrogen electrode which is taken as zero. The above correction may be made by using the following equation:

$$E_h = E_s + E_r$$

where E_h = potential with respect to the standard hydrogen electrode

E_s = potential of the system

E_r = potential of the reference electrode

For the calomel (KCl saturated, 25°C) reference electrode E_r = + .244 v. while for the silver-silver chloride (4M KCl, 25°C) reference electrode E_r = + .199 v. These values, however, vary with temperature and since the saturated calomel electrode is most often used, Tobin (96) has presented the following table:

Table VI

Potential of Calomel Electrode at Various Temperatures

Temperature °C	EMF
20	.250 v
25	.246 v
30	.242 v
38	.236 v
40	.234 v

Thus, it is possible to measure oxidation-reduction potentials

with a standard reference half cell, a noble metal electrode and a potentiometer that is graduated to read millivolts directly.

The measurement of oxidation-reduction potentials has been criticized from the point of view of the difficulties experienced in various investigations. A brief summary of a portion of the literature on this subject may prove advantageous.

Techniques in Potential Measurements

The noble metal electrodes most often used in making potential measurements are gold and platinum. Diverse opinions have been expressed on the desirability of using one rather than the other. Ward (97) would prefer the use of platinum electrodes over gold, since he found that there was no apparent sluggishness of platinum types as with gold forms during the study of oxidation-reduction potentials in bacteriological systems. It has been expressed that wires of 24K gold from any source are likely to be erratic in their behavior and that in systems where its presence does not cause difficulty, platinum is to be preferred (98). On the other hand, Longsworth and MacInnes (99) compared gold and platinum electrodes in a broth containing Lactobacillus acidophilus under anaerobic conditions and found that platinum was more sluggish than gold. Molof (75) states that the greater sensitivity of gold to quinhydrone, a well poised system yielding rapid potential equilibrium could be significant for the measurement of biological systems which are low capacity and often

behave in a sluggish manner. If platinum was less sensitive in quinhydrone perhaps, but not necessarily, it would be the same in biological solutions. Molof (75) presents a very complete discussion of the advantages and disadvantages of gold and platinum electrodes and has reviewed the literature on the subject thoroughly.

Electrodes used have been constructed mainly by each investigator for his own use although commercial electrodes have been used. Henry (100) found that thimble-type commercial electrodes gave trouble in that the metal broke away from the glass creating pockets of constant potential. The so called "home-made" electrodes are usually made of gold and platinum tips joined to copper leads either by fusing (101), silver soldering (102) or by means of mercury contact (103). Potter (102)thought there would be an electrical effect at the junction of the platinum and copper which was silver soldered. This fear, however, was not borne out by tests (this author has experienced similar results). The electrodes were then sealed in glass tubing. Molof (75) found that he could not get a glass-metal seal with gold electrodes until he used a special glass tubing having the same coefficient of expansion as gold.

Once the electrode has been constructed, periodically throughout its use, it should be standardized. Grune and Chueh (76) standardized electrodes using a pinch of quinhydrone in a 0.05M potassium acid pthalate solution

(pH = 4.008 at 25°C). The potential of this solution with respect to the calomel electrode is + 218 mv. and is generally accepted as a primary standard. Molof (75), however, found that in using platinum electrodes, the readings changed with the concentration of quinhydrone until the solution had become saturated. It has been suggested (104) that electrodes be calibrated in two "standard" solutions making sure that a non-drifting final measurement is attained. It should be mentioned, however, that standardization in such a well poised system will not guarantee a sensitive electrode in a poorly poised medium.

The measurement of electrode potentials in biological systems is not as rapid nor as stable as in the well poised systems familiar to the chemist. The length of time required for an electrode to come into equilibrium is considerably longer in a poorly poised medium. Bckenfelder and Hood (105) used 30 minutes as the usual testing period, indicating that the electrode after this period of time was essentially in equilibrium. It was found in some instances that stable readings were obtained in anywhere from 5 to 60 min. by Henry (100). Grune and Chueh (76) state that although 2 hours or more may be required before a stabilized reading is reached, preliminary observations showed that 90 to 95% of the final stabilized value potential was attained within 30 minutes after immersion of the electrode in the sludge. However, many of the [illegible] samples of mourning waters were [illegible]

Later studies by Molof (75) revealed that 30 to 40 hours were required to give stabilized readings in a sample of non-agitated sewage sludge. However, he further indicated that stabilized readings could be obtained in as little as four hours if the sample was continuously mixed. This would seem to stress the difficulty in obtaining stabilized readings in poorly poised media.

Erratic results often occur due to "poisoning" of the electrodes. In biological media it is found that a film will develop on the electrode that must be removed before it can be reused (94). Different cleaning techniques have been suggested by various investigators. Tobin (96) in working with a platinum button electrode revealed that the only method which gave him reproducible results was immersion in a hot potassium dichromate-sulphuric acid cleaning mixture, followed by repeated washings with distilled water. Another method suggested called for cleaning electrodes by immersing them alternately in hot dilute nitric acid and sodium bisulphite followed by washing in distilled water (72). Rohlich (106) cleaned electrodes by rubbing with levigated alumina, followed by soaking in hot nitric acid and washing in distilled water. He also recommended removing the surface film by polishing with clean filter paper or a mild abrasive such as Bon Ami or levigated alumina. Cleaning platinum electrodes by electrolysis, with a dilute paste of hydrochloric acid and alconox, or by heating the electrode to redness has also been investigated (100). Comparisons

of hot chromic acid, nitric acid and aqua regia as cleaning solutions showed that no one method was superior (97). On the other hand, rinsing and wiping also assured a clean surface (75)(104).

The fact that electrodes are covered with a film after being immersed in a medium for a period of time results in erratic readings. Since it is not possible to note an erratic electrode if it is in the medium alone, many investigators have expressed the desirability of using anywhere from two to four electrodes in the same sample.

For further details on the type, shape and construction of electrodes as well as methods of cleaning the reader is referred to the work of Molof (75) who has excellently presented the results of many investigators in this area.

In spite of the difficulties in making potential measurements, such measurements when properly applied aid considerably in the analysis of incompletely understood systems, as will be shown later. When the art of taking potential readings has been mastered, it is found that the results are not erratic and are reproducible. As an indication of what is considered reproducible, Henry (100) when using 4 electrodes in the same vessel termed the results excellent when they read within 5 mv., and an agreement within 20 mv. was considered good. Rohlich (106) asserts that electrodes should be cleaned when they fail to give results within 10 mv.

The fact that there is a pH change with a change in potential and that the potential is an intensity factor

only, are other considerations which must be realized. The "poising" capacity, which is similar to buffering capacity in pH work, is not measured by a noble metal electrode. The change in pH with potential will be discussed further.

Apart from the above considerations which deal mainly with the theory and art of potential measurement some consideration must be given to the investigations that have been carried out in the area of biological explorations.

Studies in Bacteriology and Biochemistry

Potter (102) was the first to notice in 1911 that certain electrical effects accompanied the decomposition of organic matter. He found that the electrode potential developed in an inoculated culture was more negative than that of a sterile medium. He showed the electrode potential of yeast fermentation to be in the range of -0.2 to -0.5 volts. Since that time a great many investigations have been made with regard to electrode potentials developed during bacterial growth.

Reed and Orr (107) concluded that a favorable O-R potential is essential for the proliferation of an organism. The optimum E_h for 15 species of the genus Clostridium is in the vicinity of -0.2 v. They further found that in a poorly poised medium, organisms will tend to produce a local area of reducing potential favorable to growth. It was further found that actively reducing substances such as sodium thioglycollate, cysteine, ascorbic acid, sodium formaldehyde, and sulfoxylate not only reduced the potential but

had effective poising characteristics.

Vennesland and Hanke (108) studied the ORP of mixed cultures of Bacteroides vulgatus and Alcaligenes fecalis in order to determine the upper limit at which growth would occur, but no upper limit of potential could be established. However, by controlling the potential with a mixed stream of oxygen and nitrogen it was found that the positive potential just limiting growth in a culture of Bacteroides vulgatus was + .150 volts at a pH of 6.6.

By electrolytically controlling the potential Hanke and Katz (109) were able to determine the limiting positive value of another organism, Clostridium sporogenese. This limiting value was found to be E_h = + .135 volts at pH = 7.0 and 6.2. They state that when the potential is kept sufficiently negative electrolytically, these anaerobes will grow in a continuous current of air. They explain that this method of control has an advantage in that there is no addition of foreign agents to the medium. This advantage plus the simplicity with which it controls the potential is what determined the use of this method of control in the laboratory experiments presented in this paper. A more complete discussion of this method of control follows in the next chapter.

Langlyke et al (110), in the study of the butyl alcohol fermentation, realized the value of obtaining reducing conditions early in the fermentation. Since butyl alcohol bacteria are strict anaerobes, these authors felt that it

was likely that many of the unsatisfactory results of the past occurred because toxic levels of oxygen had penetrated the medium before active fermentation had set in. The establishment and maintenance of low potentials decreased considerably the time required to ferment the sugar.

Squires and Hosler (111) carried on studies in a pilot plant fermenter with continuous electrode potential measurements. They found, as would be expected, that with increased aeration there was a rise in the electrode potential, but when the air supply was shut off the electrode potentials began to fall. These studies showed that the electrode potentials were proportional to the logarithm of the oxygen concentration.

Similar results were obtained by Tengerdy (112)(116) during the study of the 2-keto-L-gluconic acid fermentation. The data show that the redox curve qualitatively characterizes the existing oxygen demand of the culture. The highest oxygen demand coincided approximately with the redox minimum and the highest growth rate. He states that the linear logarithmic relationship between dissolved oxygen and redox potential offers a simple new method for dissolved oxygen measurement. The results obtained showed a significant correlation between redox potential and product formation, in fact the curves show product formation begins after the redox potential reaches its minimum level.

The importance of maintaining optimum potential levels for the active proliferation of organisms has been established.

Hall (114) presents an excellent compilation of the physical and chemical agents and their effect on establishing reducing potentials for the cultivation of anaerobes. However, he concludes by saying that no matter how great the reducing powers of any one of these chemical reducing agents may be, they are not able to make narmless the atmospheric oxygen which re-enters the medium when the latter is poured into petri dishes. Knight (115) discusses the possibility of maintaining a constant potential by the addition of dyes. A dye will control the potential until it is used up and more must be added. The potential can be held for a longer time by continuously adding more dye but there may be a chemical effect on the microorganism. He further found that very good control of the potential could be obtained by passing a mixture of oxygen and nitrogen through the medium. Knight concluded by stating that while this method of poising has at present only been used with bacteriological culture media, it could obviously be applied to any other system which exhibited a negative potential drift with time. More recently, Scheff et al (116) have described a method of controlling the potential by use of dropping mercury electrodes.

This discussion of some studies of electrode potentials in bacteriological systems has necessarily been brief. For a more detailed coverage of this area, two excellent texts are recommended, namely that by Clark (91) and Hewitt (121).

Studies in Waste Treatment

One of the earlier potential studies in waste treatment process was carried out by Hood (101). He plotted the electrode potential profile through a sewage treatment plant and found the potential of the influent to be + 278 mv., while in the aeration tank the value was found to be + 553 mv. After a small drop in potential during secondary clarification, the potential rose to + 698 mv. after chlorination. He further proposed that the potential in anaerobic units should be from -100 to -200 mv. At that time many areas of possible investigation were presented and some of these have been and are now receiving a great deal of attention. In contrast to the above values, Kehoe and Jones (104) found the value of incoming raw sewage to be anywhere from -300 to + 100 mv. They also suggested the possibility of using potential values for odor control, asserting that odors were apparent at potential values of less than -100 mv.

In studies conducted at the Miami Sewage Plant (117), it was found that raw sewage had potentials between E_c = -420 mv. and -170 mv. with an average value of -303 mv. Apparently, prechlorination did not increase the potential appreciably, and after grit removal the potential values had changed but slightly. However, the effluent from the aeration tank showed values of potential as high as E_c = + 160 mv. which is equivalent to about + 305 mv. with respect to the hydrogen electrode. These studies indicate that dissolved oxygen is present at a potential higher

than E_c = -160 mv.

Potential values found at the Hyperion Plant (118) were essentially the same as those at Miami. Truely aerobic conditions did not exist throughout the plant except in the aeration process and secondary effluent. Results of this study showed that aerobic processes operate at over + 200 mv. E_h while anaerobic processes operate below + 50 mv. E_h. It was further revealed that the potential of sewage was depressed greatly during travel in a sewer. An average decrease of 200 mv. was noted during a nine mile travel.

Rohlich (106) found the potential of sewage and activated sludge systems increased with aeration. Aerated sewage developed a potential of + .3 volts while the unaerated sewage had a potential of -.27 volts. Similarly, the potential of activated sludge increased from -.13 volts to + .37 volts after aeration. In contrast to investigations cited previously, Rohlich found that E_h values remained rather constant until the dissolved oxygen dropped to less than 1 ppm, then it decreased sharply.

Moore and Ruchhoft (119) state that the metabolic activities of various bacterial species in sewage does effect a lowering of the potential even in the presence of dissolved oxygen. Under anaerobic conditions the potential of sewage dropped to -.22 volts in 24 hours. It was further shown that the presence of other hydrogen acceptors such as nitrates and sulphates retarded the development of strongly

reducing conditions.

Nussberger (120) attempted to determine the condition of activated sludge by plotting potential values against time. He described three types of curves. In what is termed underaerated or overloaded activated sludge, the potential decreased sharply and quickly while for a normal activated sludge the potential decreased slowly. In an overaerated or underloaded sludge the potential held steady for a period of time and then decreased. In this study it was also found that the potential decreased 200 mv. from the influent to the effluent of the secondary settling basin. Goodman (121) in attempting to obtain similar results in activated sludge systems was unable to obtain a correlation. He pointed up the fact that industrial wastes may have a considerable effect on the potential. It is to be noted, however, that only one metallic electrode was used and this in itself may have caused erratic results.

Shapiro (122) in discussing electrode potentials in activated sludge states that at low potentials unfavorable anaerobes take over. At a very high potential the formation of hydrogen peroxide may be lethal to some organisms and the enzyme system of others will not function. This condition would represent a so called overoxidized, underloaded activated sludge and would be evidenced by a dissolution or breakdown of the sludge floc with turbidity formation.

Hoot (123) explains the use of electrode potentials

during the chlorination of sewage. An automatic control actuated by electrode potentials was used. When the reading went up, chlorine was shut off, when the reading went down, chlorine was increased. Although wide variations in potential were obtained the primary purpose of odor control was achieved. In somewhat similar studies, Keefer and Meisel (124) found that in chlorinating both raw sewage and humus tank effluent the E_h potential curves approached an asymptote with a value slightly less than 1400 mv.

Eckenfelder and Hood (105) studied electrode potentials in various wastes and studied the relationship between E_h and pH. In a sewage sludge it was found that there was a change of about 50 mv. for each pH unit. The addition of sulphate to a digesting mixture resulted in the depression of the reductive intensity level from a range of 0 to -100 mv. E_h to -125 to -170 mv. E_h. These low values of potential attained during anaerobic digestion were found to be desirable for the growth of Salmonella typhosa (125).

Grune and Lotze (126) state that ORP and pH measurements will offer a convenient and valuable means of improving the economical operation of sludge digestion. They conclude that trends in redox potentials are reproducible and that redox potentials can be correlated with the cumulative gas production. The redox potential during normal digestion as observed by them was about -250 mv. E_h. Grune and Peek (95) in advocating the use of electrode potentials during sludge digestion assert, that

previously it had not been possible to measure the precursors of gas production, acidification, and other digestion phenomena, and that the only data collected from a digester have been after the fact. They state that acidification and gas production may be expected after certain changes in redox potential are noted. Furthermore, redox potentials can spot strongly oxidizing or reducing forms of waste.

Molof (75) has done a considerable amount of work with electrode potentials during sludge digestion, including observations on the time required for stabilized readings, standardization of electrodes and observations on potential values developed under various conditions. It would be appropriate at this point to restate some of his conclusions. Oxidation-reduction potentials are of considerable value in detecting abnormal digestion conditions. He states further that under normal digestion conditions the potential will remain constant. A continued positive trend of the potential can be indicative of overloading. The optimum range for sludge digestion in his work was -460 to -530 mv. or an E_h of -220 to -290 mv. The most representative potential of a ripe sludge was -500 mv. or an E_h of -260 mv. With respect to gas production, his results indicated that the potential changes and gas rate changes were related for batch experiments. For continuous operation where conditions were relatively steady, there was no relationship exhibited. Molof (75) also stressed the necessity of using

a minimum of three electrodes for any sludge potential measurement, and observed that gold and platinum electrodes did not differ significantly in the readings obtained in his digestion studies.

It may be seen from the preceding discussion that electrode potentials when properly determined and interpreted can be of significant value in the study of biological systems. It is thought that with further study the use of electrode potentials in waste treatment can be an invaluable aid in the operation of waste treatment facilities.

EXPERIMENTAL APPARATUS

The design of the model digesters used in the experimental work was based on the expectation that continuous operation would be practiced. The units were especially adapted for making electrode potential measurements. Further considerations took into account the anticipated method of controlling the electrode potentials, and the method of collecting the gas produced. Accordingly, the description of the experimental apparatus will be covered in the following four sections:

1. The Digestion Unit and Its Appurtenances
2. Electrode Potential Measuring Apparatus
3. Electrode Potential Control Mechanism
4. Gas Measurement, Collection and Analysis Apparatus.

The Digestion Unit and Its Appurtenances:

The model digesters used for the experimental work were constructed from plexiglas. The cylindrical portion, or body, of each digester consisted of an 8 in. section of plexiglas tubing with an 8.25 in. inside diameter and 0.25 in. wall thickness. The bottom of each digester was made from one inch thick plexiglas and had a diameter of 9 inches. The bottom was sloped at an angle of approximately 10 degrees. The cylindrical body was glued into a slot

machined into the bottom plate. The top of each digester was also 9 in. in diameter and was made from .0312 in. thick plexiglas. It was so constructed that it could be fastened to 6 lugs equally spaced around the inside of the body of the digester. In order to insure air tightness, a soft rubber gasket 0.25 in. thick was placed between the walls and the top of the digester. The digester contained a drain in the bottom and a sampling tube located in the body about one and a half inches below the liquid level. A schematic drawing of the model digester is shown in Fig. 4.

An attempt was made to construct the digesters with a shape similar to normal plant units. Grune (127) found the average ratio of sidewall depth and diameter for separate sludge digesters in seven U. S. Cities to be 0.32. Due to practical aspects these digesters were made a little deeper and had a sidewall depth to diameter ratio of about 0.75. It was felt, however, that this difference in ratio would have little if any effect on the process.

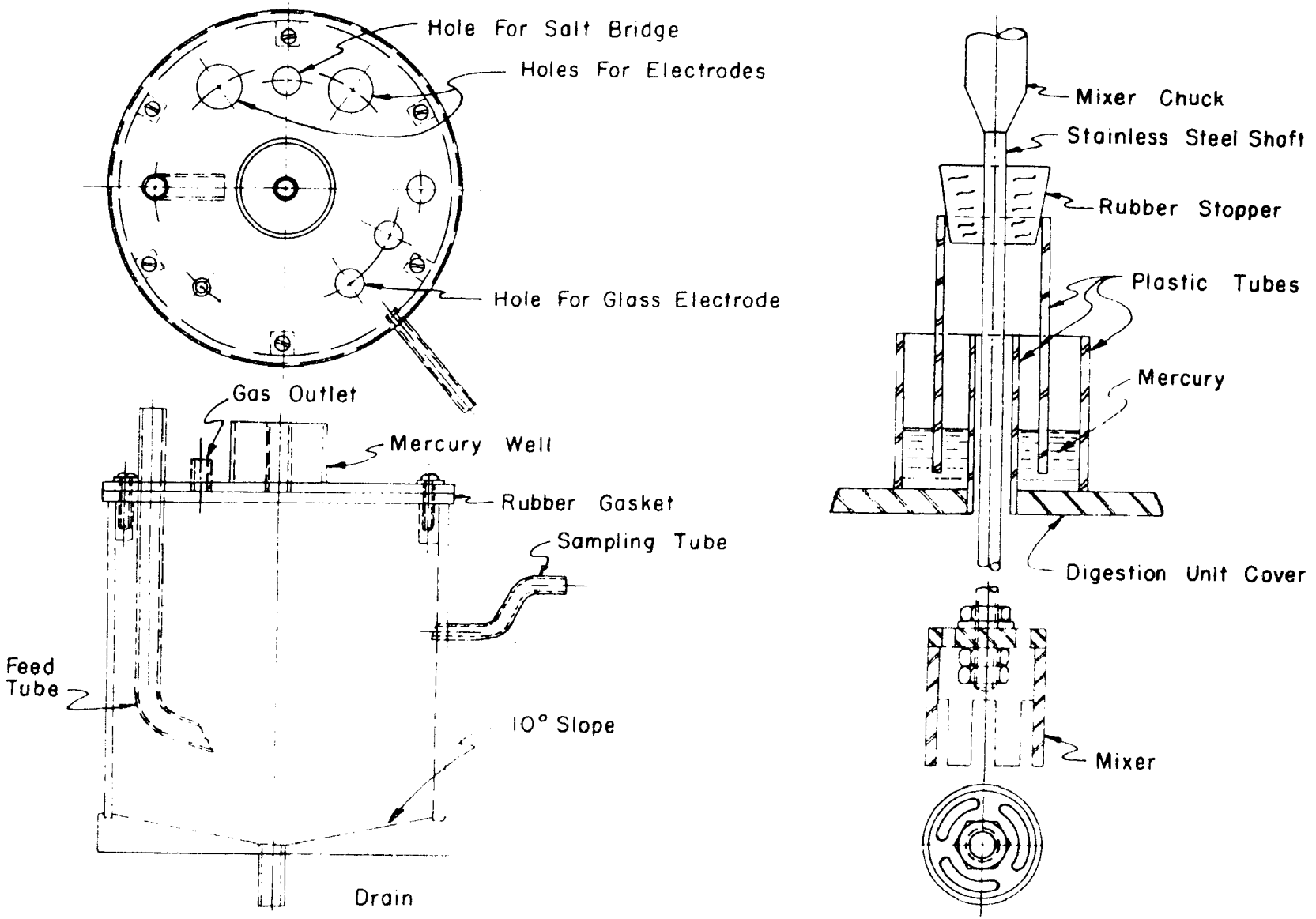
The liquid capacity of the digesters was 7 1/2 liters and the volume of sludge studied was maintained at 6 liters throughout the experimental work. Sizing of the digesters was based on the amount of sample required for daily chemical analyses.

Three digesters were placed in a constant temperature water bath heated by two 300 watt resistance heaters, the temperature being maintained within one half degree, plus or minus, by use of a thermoregulator. The digesters and

their placement in the water bath are shown in Fig. 5. A fourth digester which was used as a control throughout the experimental work was heated in a separate constant temperature water bath.

The mixing equipment consisted of a stainless steel shaft to which was attached a specially constructed impeller. Again, the material used for making these impellers was plexiglas. The design was essentially cylindrical with four vanes cut along the side to provide for circular mixing. In addition, slots were cut in the top of the mixer to give a certain amount of pumping action. In order to allow mixing while maintaining anaerobic conditions, a mercury well was utilized. The well consisted of a 2 1/2 in. diameter piece of plexiglas as the outer shell, a 1/2 in. diameter piece of plexiglas for the inner shell through which the mixer shaft passed. A piece of 1 1/2 in. plexiglas tubing was attached to the mixer shaft and rested in the mercury in the well to form the seal.

In some of the initial work, the mercury in the well was covered with about 1/4 in. of oil to suppress toxic vapors. However, it was soon discovered, that if the mixing speed was increased the oil and mercury seemed to form a paste which was not only a poor seal but kept spattering out of the well. As a result, all future experiments contained a layer of water over the mercury. This water served the same purpose as the oil but without its detrimental effect. A sketch of the mixer and mercury


Hole For Salt Bridge
Holes For Electrodes
Hole For Glass Electrode
Gas Outlet
Mercury Well
Rubber Gasket
Sampling Tube
Feed Tube
10° Slope
Drain
Mixer Chuck
Stainless Steel Shaft
Rubber Stopper
Plastic Tubes
Mercury
Digestion Unit Cover
Mixer

well can be seen in Fig. 4.

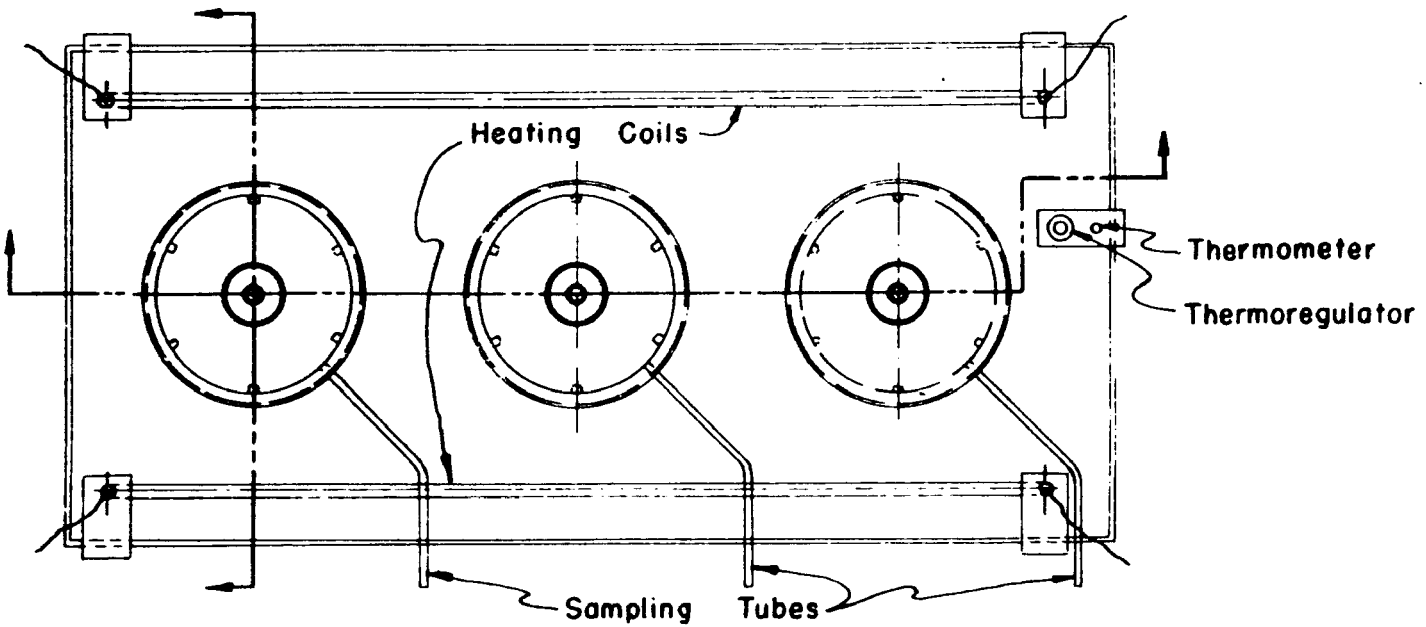
The three digesters set in a common water bath were mixed with spindle mixers which were driven by an air drill. The pressure to the drill was controlled by means of a pressure regulator. The fourth digester mixer was driven with a small induction motor the speed of which was regulated by a rheostat.

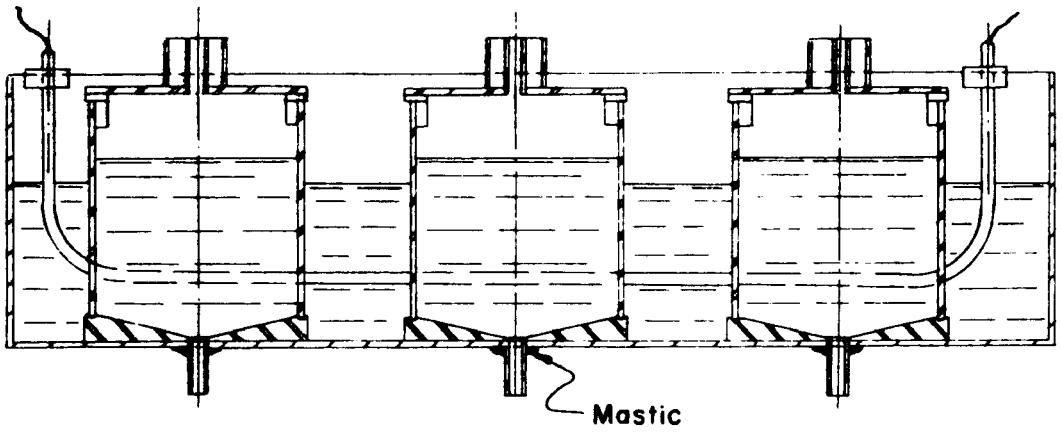
Electrode Potential Measuring Apparatus

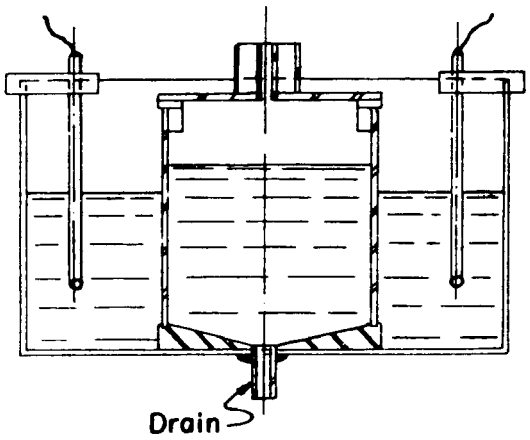
The electrode potential measurements were made by means of a Beckman Zeromatic pH meter, model 9600. Inasmuch as there were many electrodes in the set-up, a salt bridge interconnected between the digesters was used so that one reference electrode would suffice for all potential measurements.

The inert electrodes used in the experimental work were gold and platinum. Molof (75) found that the electrode potential was not significantly affected by the surface area of the electrode itself. The electrode tips were therefore constructed of 20 ga. noble metal with an exposed length of about 3/8 of an inch. The platinum and gold were then silver soldered to electrode leads of 16 gauge copper wire and sealed in glass. The gold electrodes were sealed in a specially made glass tubing having the same coefficient of expansion as gold. This specially manufactured glass tubing was the same as that used by Molof (75).

At first it was thought that the silver solder joint might have some effect on the electrode potentials obtained, but in a standard potassium acid pthalate solution the







Unit Assembl

electrodes gave very precise readings. This, however, is a well poised solution and to further verify that this was a proper construction technique, the electrodes were checked against two specially prepared electrodes. The two so-called standard electrodes were constructed with a mercury junction between the platinum metal and the copper lead. These electrodes were found to give similar results not only in a standard solution, but also in a digesting sludge.

Two gold and two platinum electrodes were placed in each digester. The necessity of using at least three electrodes for a potential measurement has been established by other investigators (75)(100). Quite often, one or the other of these electrodes appeared to acquire within seconds, a potential of more than 100 mv. less than the potential of the other electrodes. It has been found, in every case where this phenomenon was investigated, that a piece of stringy material had accumulated on the surface of the electrode. This along with the other inherent difficulties in taking potential readings makes it necessary to use, as a minimum, three electrodes and preferably more.

The electrodes, then, consisting of gold and platinum were placed in the digesters. The salt bridge was constructed in the following manner: A strand of asbestos fiber was sealed into a piece of glass tubing which was used as the salt bridge tip for each digester. This procedure was actually one of trial and error to get the right thickness of

asbestos fiber. The flow through the fiber was not measurable by ordinary means under a head of about six inches. The only indication that there would be contact came from the fact that there was a slight coating of salt on the outside of the tip. This indicated that the flow was so small that the water evaporated leaving only the salt. In actual installation, the head on the tip was not six inches but closer to two or three inches. The salt bridges were interconnected and the lead went into a small plexiglas unit containing a saturated solution of KCl and the calomel reference electrode. The lead from this reference electrode was connected to the pH meter. The complete bridge was so constructed that the tip leading to each digester could be clamped off. Furthermore, each section leading to a digester had a high point in the form of a tee which served to collect any bubbles that might accumulate in the bridge.

The inert electrodes, four in each digester, were brought into a sixteen point switch through shielded cable. A common lead from the switchbox then completed the circuit at the pH meter. In this manner it was possible to take potential readings simply by switching to the proper electrode. In order to prevent interfering stray currents the switchbox was shielded, as recommended by White (128).

Electrode Potential Control Mechanism

Inasmuch as potential control was to be practiced in the experimental work, it was necessary to determine how this control mechanism could be worked out. Reference has

been made previously to the techniques usually employed in control of electrode potentials.

It was thought that control, at least in the positive direction, could be accomplished through the use of hydrogen peroxide. Such a control was attempted on a digester operating under stable conditions. It was soon found that extremely small additions of peroxide resulted in quite radical changes in the potential. For example, only 25 ml. per day of peroxide was required to increase the potential 60 mv. In order to maintain this low flow a specially constructed tip similar to that used in the salt bridge construction was made. A 4 in. diameter plastic tubing was used as a constant head tank for feeding the peroxide at a constant rate. This method of increasing the potential was fairly satisfactory but the fluctuation in potentials was disappointing. After two days of operation the feeding mechanism broke down and the digester was fed an extremely heavy dose of peroxide, the net result being an increase in potential of about 200 mv., resulting in irrepairable damage to the digester. This unsuccessful effort pointed out the desirability of a new method for the control of potentials.

This new method of control, which was used throughout the remainder of the experimental work, was an electrolytic control similar to the one used by Hanke and Katz (109) to study anaerobiosis. In essence, the control mechanism consists of a source of D.C. voltage, a salt bridge and two large surface platinum electrodes. When the positive pole

of the supply is placed in the digester and the negative pole is connected to the digester by means of a salt bridge, the potential of the digester is increased. When the leads were reversed the potential decreased.

The adaptation of this method for use in this thesis was not without difficulties. It was first attempted using most of the materials that were being used for potential measurements. The two electrodes used were identical to those used in measuring the potential, which it will be recalled were of 20 gauge platinum with an exposed length of 3/8 inch. This, of course, proved too small a surface area and a much larger surface had to be provided. For economical reasons the large surface electrodes used were made of a 6 inch strip of 20 guage platinum. The electrodes were coiled so that space requirements would be small. However, it was soon discovered that the coiled electrode trapped sludge particles when placed in the digester. It wasn't very long before it was partially insulated by a sludge blanket, causing the resistance of the system to increase. As a result of this observation, the platinum electrode which was to be placed in the digester was unwound and allowed to string out within the unit.

Difficulties were also encountered with the salt bridge. At first a tip with a sealed-in asbestos fiber was used. This construction, however, resulted in an exceedingly large amount of resistance in the circuit and

current could not be passed through it. It was decided that a glass tube with the end well plugged with cotton would materially reduce this resistance. This type construction was attempted and found to be satisfactory.

With the electrode and salt bridge problems corrected current could now be passed through the circuit. In the preliminary work, dry cell batteries were used as the source of D.C. voltage.

For the experimental work, three D. C. supply units were constructed. These units were capable of delivering a variable voltage anywhere from 0 to 300 volts D. C. at a rating of about 200 milliamps. Each of these units was used to supply current to one of the digesters. It was found that with this type of construction the resistance in the total circuit was 1000 ohms. However, the resistance was not always constant, for at times portions of the cotton plug would become partially blocked by sludge, increasing the resistance.

A clarification of the above discussion can be obtained by noting the circuitry involved as shown in Fig. 6.

Gas Collection, Measurement and Analysis

The collection and measurement of the gas produced by the digestion process was of great importance during the experimental work. Basically, the gas collection was of the inverted can type with an acidified salt solution as the confining liquid.

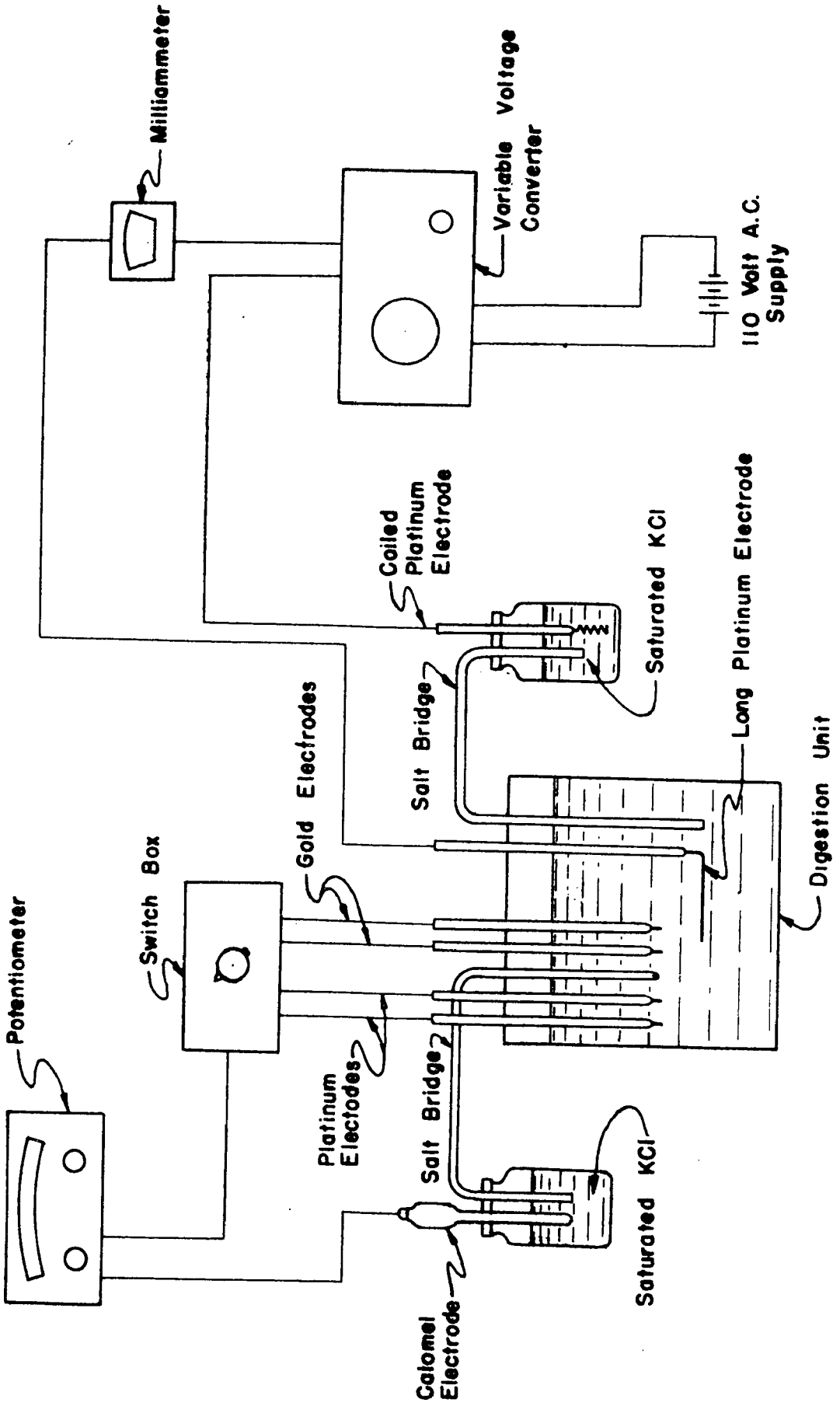
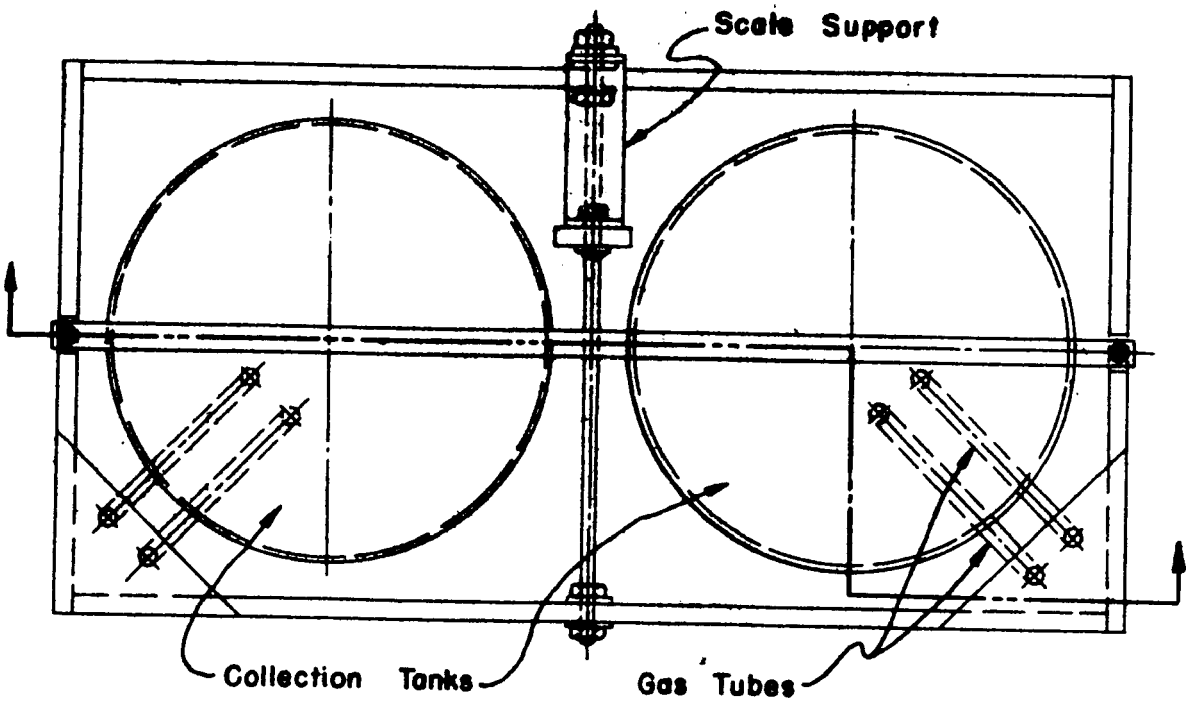


Fig. 6 Electrode Potential Measurement and Electrolytic Control Circuits

The biggest problem in the collection of gas is in the use of the confining liquid, which is extremely corrosive. At first, painted cans were used to collect the gas, but in no time at all the confining liquid had eaten holes in the cans. The next consideration was that of using polyethylene gallons for this purpose; but finding two containers sized so that one could be inverted into the other proved difficult. Therefore, a wooden box, large enough to hold two inverted polyethylene gallons, was constructed. This also proved unsuccessful. The final construction showed the inside of the box painted with three coats of a plastic paint. Two polyethylene gallons were inverted into the box, which was filled with the confining liquid. The inverted jugs were connected with a piece of wood and rode up and down on two drill rods placed at either end of the wooden box. A graduated scale was mounted on the box so that the amount of gas collected could be read off directly in liters and portions thereof. The collected gas was connected to a U tube manometer, one leg of which was open to the atmosphere to give the pressure at which the gas was collected. The weight of the inverted polyehtylene gallons was so small that the system was operating under a practically constant head of about one half inch of water.

It seemed desirable to have some means of taking instantaneous rates of gas flow. To accomplish this, another U tube manometer was placed in the gas line



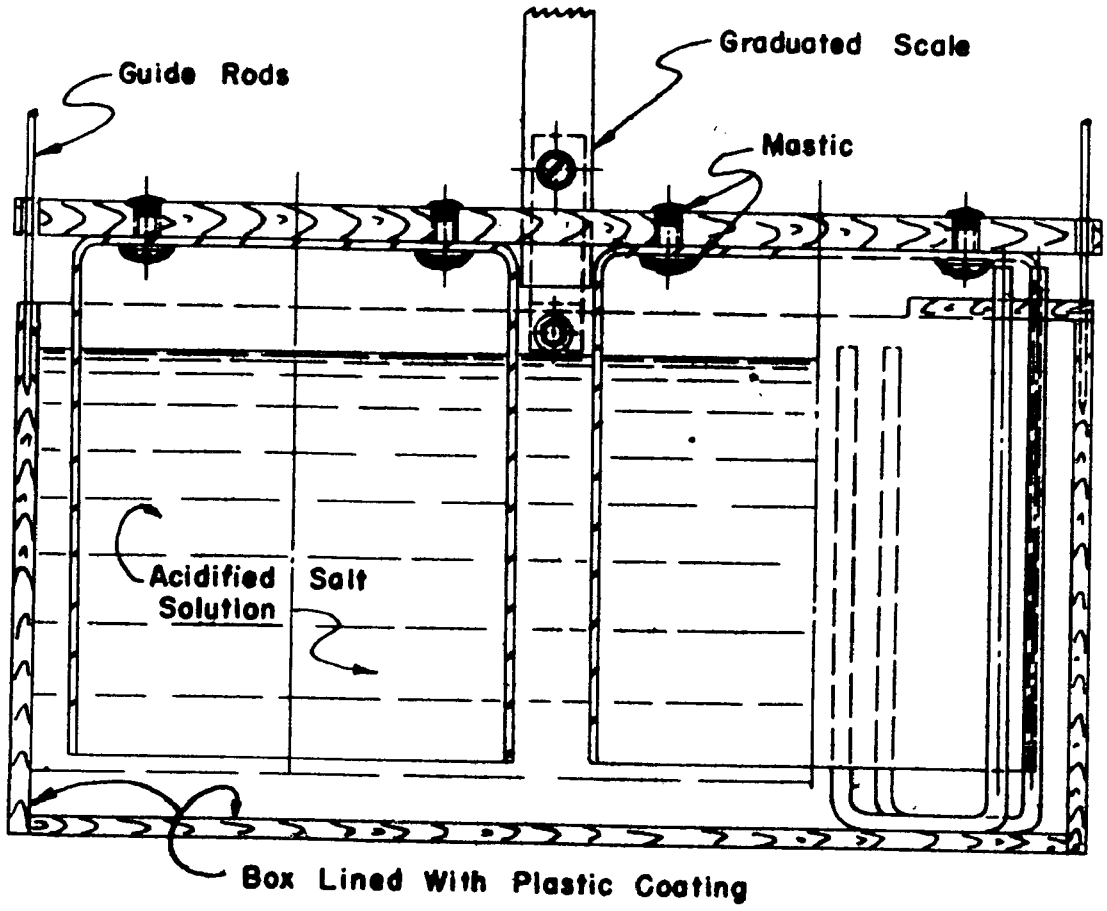


Fig. 7 Gas Collection Unit

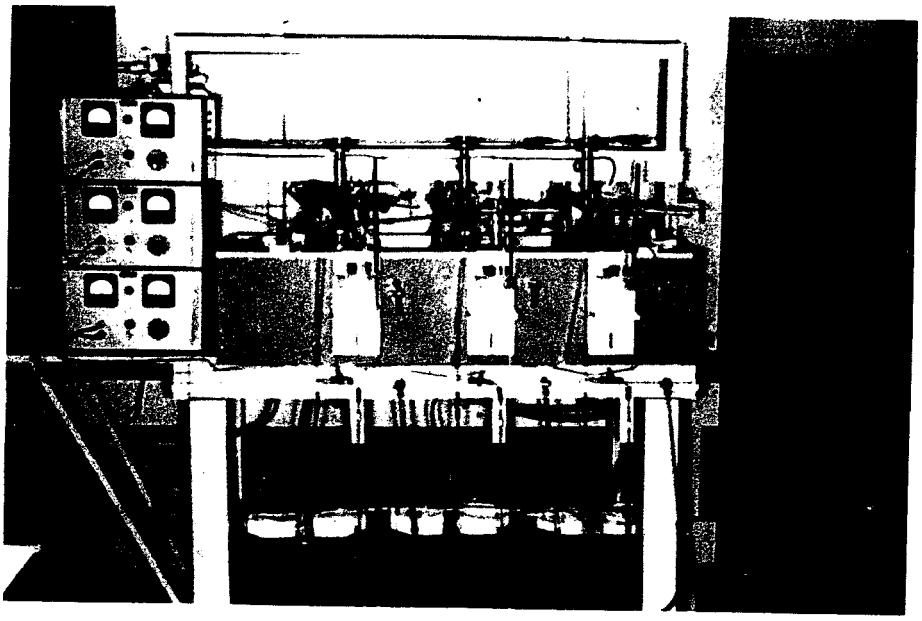


Fig. 8 View of Apparatus from Front

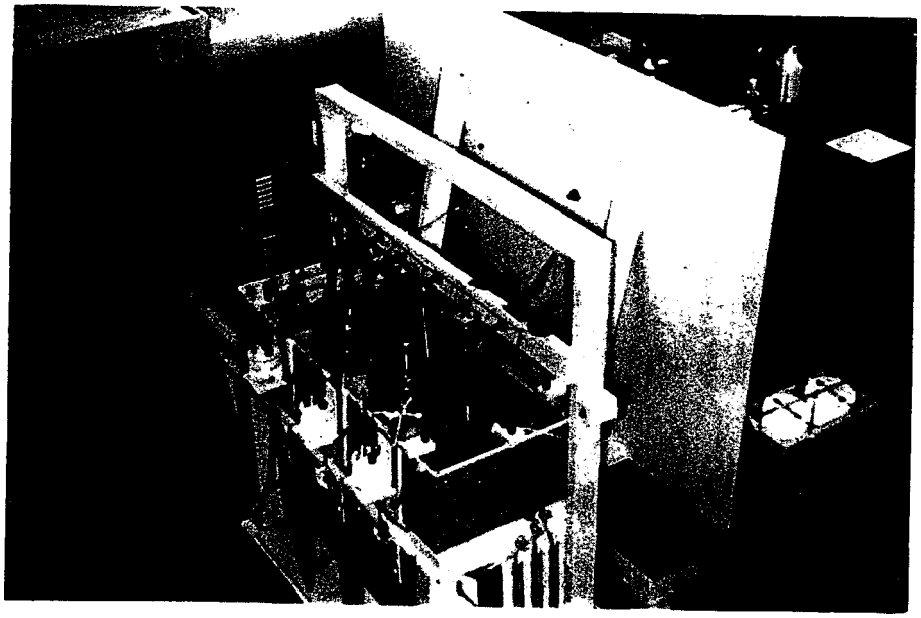


Fig. 9 View of Apparatus from Above

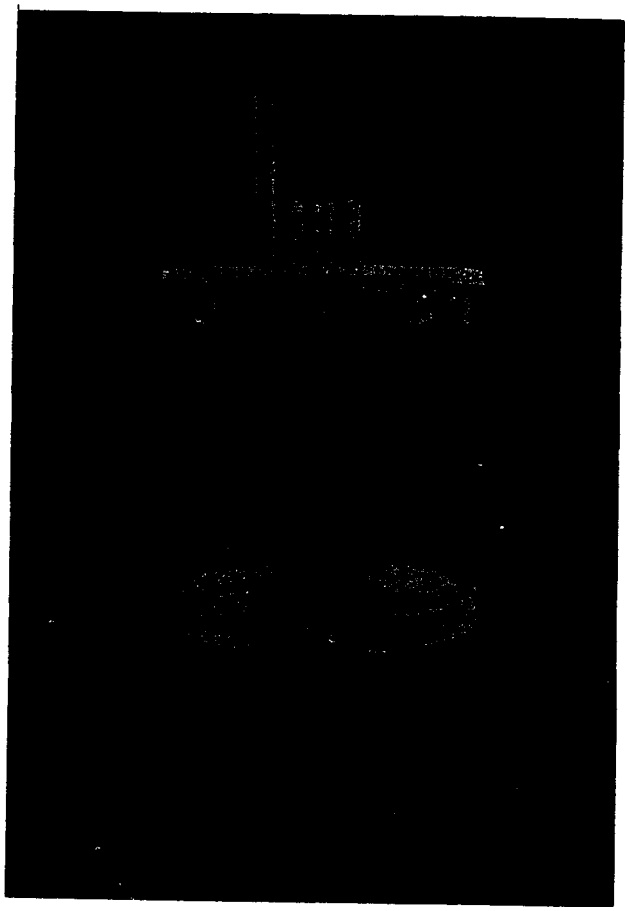


Fig. 10 Digestion Unit

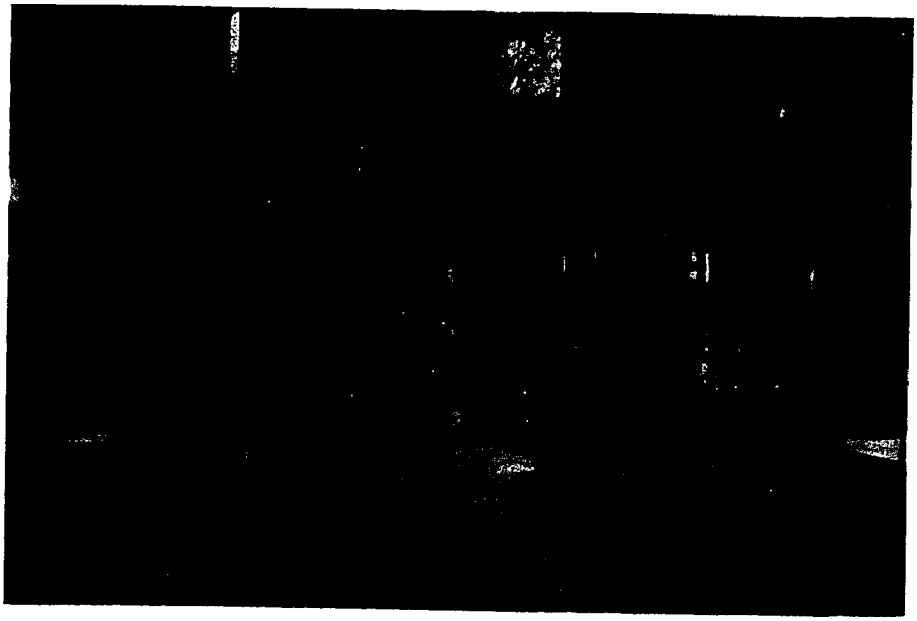


Fig. 11 View Showing Control Digester Potentiometer and Switchbox

between the digester and the gas collection unit in such a way that the gas flow could be diverted into the U tube manometer, one end of which was open to the atmosphere. By maintaining the liquid levels in both legs of the manometer at the same elevation, a measurable quantity of gas could be collected in a given time interval and at atmospheric pressure. Each digester was equipped with such a rate measuring device. Figure 7 shows the gas collection apparatus including the wooden box and inverted polyethylene containers.

Gas analyses throughout the experimental work were carried out using a Burrell Apparatus with mercury as the confining liquid. With the unit available, it was possible to test for oxygen, carbon dioxide, methane and hydrogen. The majority of the determinations consisted of a determination of the carbon dioxide content of the evolved gases.

Figure 8 shows a view of the assembled apparatus from the front, while Fig. 9 views the apparatus from above The D. C. supply units may be seen to the left of the constant temperature water bath, and the inverted can gas collection units are directly below the digesters. In front of the water bath may be seen the plexiglas units filled with saturated KCl for the electrolytic control circuit. The switchbox and potentiometer located at the back of the apparatus may be seen in Fig. 11, which also

shows the digester used as the control.

Figure 10 is a photograph of the digestion unit showing inlet and outlet line, bottom drain and the mercury well.

EXPERIMENTAL PROCEDURE

One of the primary considerations throughout this thesis was to attempt to maintain conditions similar to those normally experienced in plant operations. For this reason procedures used throughout were similar. A discussion of the general procedure will be given and any variations from this normal procedure will be cited.

At the end of each experiment and before the beginning of a new one, the digesters were completely emptied, washed and refilled with fresh digested sludge, obtained from the Ann Arbor Sewage Treatment Plant. In one study, however, different sludges were used in order to determine if all sludges digest at approximately the same potential

The digesters were fed twice daily on what might be considered a semi-continuous basis. The feedings were twelve hours apart, for the most part, although there were instances when the schedule could not be kept exactly. It was found that as long as the time between feedings was not less than ten hours the data was not affected. The only times that the digesters were not fed as described above occurred when the loading was suspended, according to a predetermined plan.

Before being charged to the digester, all sludges obtained from the treatment plant were passed through a 1/4 inch screen, in order to remove most of the larger

solids which might conceivably have plugged the inlet and sampling lines. After being screened the sludge was kept in a refrigerator at 4°C until it was used. Sludges which were refrigerated longer than twelve days were not used, since it was felt that after this time the sludge would have begun to deteriorate.

The sludge was introduced into the digester only after it had been warmed to approximately room temperature in a water bath. It had previously been discovered that if the sludge was fed to the digester directly after removal from the refrigerator, it caused a drop of about one degree in the digestion unit. On the other hand, if the sludge was raised to room temperature there was no effect on the digester.

In all results given, herein, gas rate has been expressed in terms of cc. per hour. This rate is based on the quantity of gas collected over a twelve hour period between feeds, or frequently on a twenty four hour period. The rate must then be considered as an average when consideration is given to variation in gas rate. It has been reported (80), and substantiated by these studies, that gas production increases after feed and reaches a maximum from about three to five hours later, then declining to the prefeed rate. However, in some instances, instantaneous gas rates were desired. At these times, the gas rate was found by using the manometer placed in the line for this purpose.

Chemical analyses throughout the experimental work consisted of pH, alkalinity, volatile acids, and total and volatile solids. These determinations were made daily from samples taken immediately before feeding the digesters. Volatile acids determinations were carried out using the direct titration method described by DiLallo and Albertson (129). This method gave consistent results and could be carried out in a much shorter time than either direct or steam distillation. The procedures used in all other chemical analyses were those presented in Standard Methods (46). The percentages of carbon dioxide in the sludge gases were determined once every other day using the Burrell Laboratory Apparatus. The percentages of methane and hydrogen were ascertained only occasionally.

Electrode potential measurements were made every two hours during the day, between the morning and evening feed. It was felt that changes in the potential during the day would be the same as those occurring during the period between the evening feed and the morning feed. The two hour schedule was not followed blindly but was altered to suit any given condition. When it became apparent that important changes were taking place readings were taken more often, and, similarly, when nothing could be gained by such frequent readings they were not taken as often. With this type of flexibility, many otherwise unnoticeable changes were recorded.

The values of electrode potentials plotted in the diagrams that follow are those which were recorded immediately before feeding, the time when samples were taken for the daily chemical analyses. The reason for this procedure is that electrode changes follow a pattern identical to gas rates and volatile acids; that is, the potential increases after feeding and then gradually returns to its prefeed level. Since four electrodes were installed in each digester, the plotted value is the arithmatic average. However, there were times when one electrode reading was considerably different from the others and the average of only three electrodes was determined. In rare instances, only two electrodes were in agreement and the average of these two was plotted, the others being disregarded. Some of the reasons for this erratic behavior will be discussed later.

It was initially decided that if the electrodes did not give results within 10 mv., they would be removed and cleaned. However, such conditions did not develop but, in order to be sure that the electrodes were not becoming "poisoned", they were removed and cleaned alternately so that each electrode was cleaned on an average of once every two weeks. Throughout the experimental work, electrodes were cleaned in the following manner: First the platinum or gold tip was scoured with levigated alumina and rinsed with distilled water. This was followed by soaking in a

ten percent solution of nitric acid, after which the electrodes were again rinsed and allowed to remain in distilled water until they were put back into use. If they were to be reused immediately the electrodes were kept in distilled water for 30 minutes before reuse.

The salt bridge tips also required a certain amount of care. It was soon discovered that the tips which connected the salt bridge to the various digesters would, in a matter of time, become clogged with sludge. When this occurred the electrode potentials showed a tendency to increase, probably due to the resistance to current flow. To remedy this condition the tip was removed and allowed to soak in a sulphuric acid solution. If this procedure was not able to affect a cure, the tip was discarded and a new one installed. Having experienced this difficulty, it was decided to install new tips at the beginning of each experiment so that errors would be reduced to a minimum. This procedure resolved the problem completely.

During the studies which involved electrode potential control, additional measures were taken. The salt bridge had to be checked periodically. Sludge accumulations around the tip had to be cleaned regularly. If the condition became too bad the tips were removed and new cotton plugs were inserted. Because of continued use, bubbles developed in the salt bridge and at times did become large enough to reduce or even prevent current flow. Both of these conditions

resulted in poor control of the potential and had to be rectified periodically.

The amount of current passing through each digester was not constant due to the above conditions and other inherent difficulties. For this reason exact values of current were not recorded. However, in later discussions some reference will be made to approximate currents maintained in the various phases of the experimental work.

The purpose of the above discussion is to provide an understanding of the general procedures carried out during the experimental work so that the experimental observations to be discussed may be interpreted in the proper light.

EXPERIMENTAL OBSERVATIONS

The laboratory studies conducted as a part of this study consisted of twelve experiments covering the various phases of electrode potentials accompanying the digestion of sewage sludge and their control.

For the purpose of discussing the experimental observations, the aforementioned experiments will be broken down into three categories. The first will include all experiments which deal with the monitoring of natural electrode potentials occurring during sludge digestion. The second category will deal with gross control of the potential to determine what range of values should be more exhaustively studied in furture experiments. In addition, a correlation was made between electrode potentials attained by electrolytic control and those attained by overloading the digesters with raw sewage sludge. The primary purpose for conducting the experiments in the third category was to attempt to define more closely the electrode potential ranges which would permit good, possible and poor sludge digestion.

It is felt that if the discussion is presented in the order outlined above, the importance of electrode potential values in sewage sludge digestion will be emphasized from at least two aspects. First, from the point of view of defining those normal potential levels which are developed during typical anaerobic digestion and second the results

that can be expected to occur in the digestion process if electrode potential levels are allowed to develop outside of desirable limits.

The experimental observations are discussed in the following three chapters.

POTENTIAL LEVELS DURING UNCONTROLLED DIGESTION

A series of seven experiments was conducted during this portion of the work. The first run dealt with electrode potential measurements during a slow start-up and a subsequent temperature change. The object of the second experiment was to operate three digesters in parallel and to determine what differences could be observed between digesters. This work also permitted the accumulation of further information on electrode potential values developed during normal digester operation. The third experiment in this category consisted of separate runs on each of five different sewage sludges obtained from distinctly different sewage treatment plants, in order to ascertain if different sewage sludges digest at approximately the same electrode potential levels.

Electrode Potential Levels Attained During Sludge Digestion

The first run was started by combining a mixture of about two liters of digested sludge, which had been dormant for about three years, and about one and a half liters of digested sludge, which had been used for some preliminary observations. To this was added 700 ml. of raw sludge. The material was placed in the digester and the entire unit held in a water bath at a temperature of 32°C.

In addition to this start-up material which gave a

ratio of raw to digested sludge of 1:6, the digester was loaded continuously at the rate of 0.1 lb. of v.m. per cu. ft. per day. The raw sludge used during this experiment averaged 3.13 percent solids, of which 72.8 percent were volatile. After start-up, the liquid capacity of the digester was maintained at 4 1/2 liters resulting in an average detention time of 14.2 days. In order to note the effect of temperature change, after seven days of operation the temperature was elevated to 35°C.

This experiment lasted 16 days and the results obtained are plotted in Fig. 12. Most of the parameters measured have been plotted on the same curve so that relationships between them may be viewed collectively.

The digesters were started in the evening and by morning the electrodes had come into equilibrium and a sample was withdrawn for a chemical analysis. This point in time is designated as zero days in Fig. 12.

It can be observed that definite trends began to take form immediately after start-up. Electrode potentials after one days operation had increased from E_c = -520 mv. to E_c = -511 mv. It should be noted at this time that whenever reference is made to electrode potentials, it will be with reference to the calomel electrode. Any exceptions to this will be clearly stated. The E_c value may be corrected to E_h in the manner previously explained.

The initial increase in the potential was accompanied

by an increase in both volatile acid concentration and gas rate, probably indicating that there was activity of the acid formers. The pH of the digesting mass began to fall off after the second day of operation, and by this time the electrode potential had increased to -499 mv. and the volatile acid concentration had risen to about 1200 mg/l.

This trend in monitoring parameters continued until the fourth day of operation when volatile acids and electrode potentials both reached a maximum value; the potential now being -487 mv. At this time the pH had also attained its lowest point of 6 7 while the alkalinity remained fairly constant and the gas rate continued to increase slowly. At this time the percent CO_2 in the sludge gas was found to be 34 percent.

After this period, volatile acid concentrations began to decrease as did electrode potentials. It can be noted that at this time, the pH began to increase and gas production rose to higher levels, reflecting the increased gasification of the volatile acids which had accumulated up to that time. These factors all indicated that the digester appeared headed toward normal digestion. It was at this time that the temperature was increased to 35°C to see if any change would result.

The result of the temperature change seemed to affect all measured parameters very slightly. The single exception was the potential, which took a quick dip followed by a

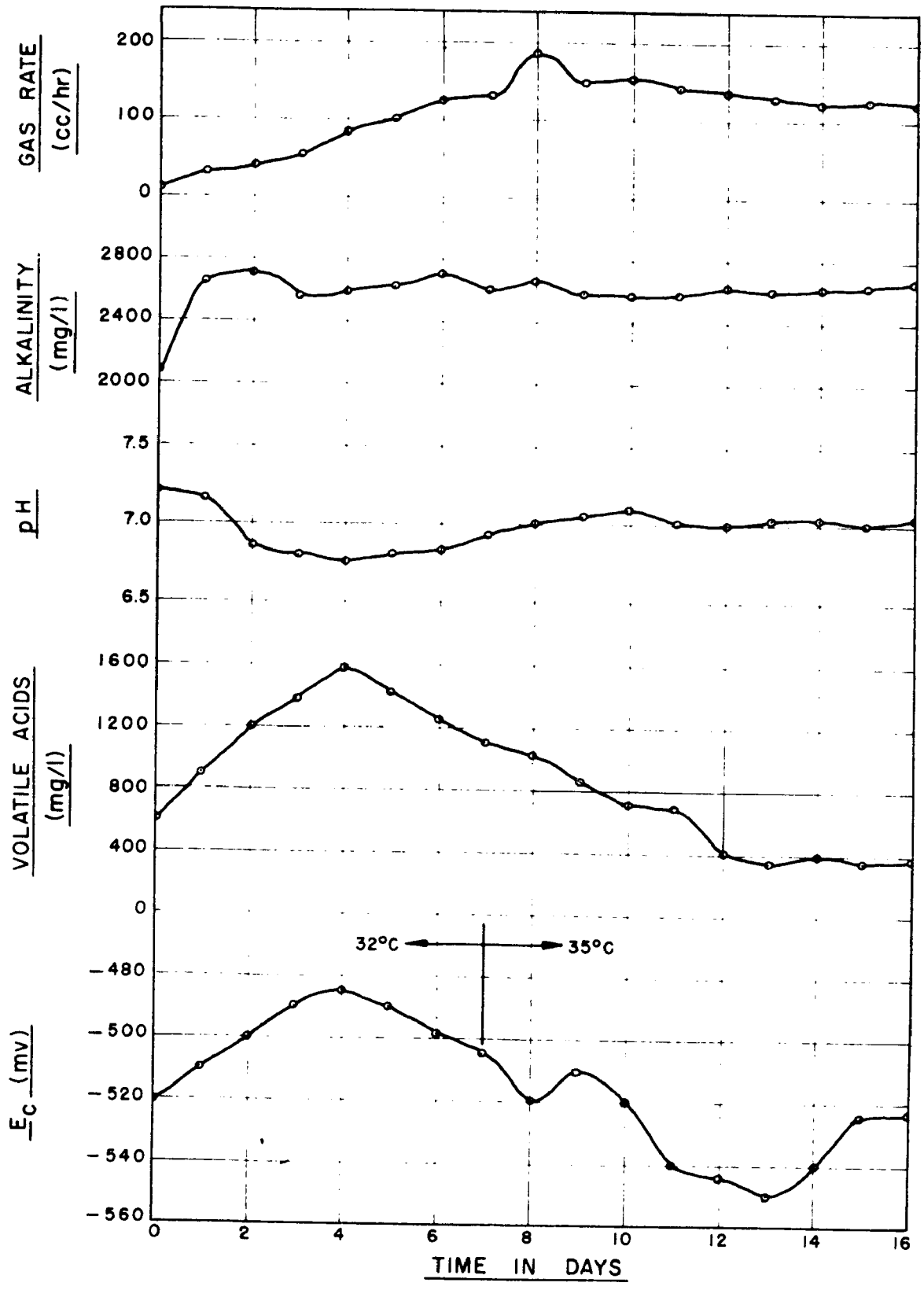


Fig. 12 Digestion Parameters During Slow Start-Up

slight recovery. After the initial variation, the potential decreased sharply, finally reaching a value of -550 mv. Following this decline the potential increased and finally leveled off near -525 mv. A short spurt in the gas production appeared immediately after the temperature change but it too leveled off rapidly. The changes in gas production seem to indicate an increase of metabolic activity which quickly returned to former levels soon after the flora adjusted to the new environment.

Solids reduction throughout this run averaged about 54 percent. The content of volatile solids in the digester increased up to the point where the volatile acid concentration was at its maximum. From this point on the percentage of volatile solids remained fairly constant indicating complete conversion to gas. The fact that the digester was continually mixed would allow such an equilibrium to take place.

It was stated previously that the electrode potential values plotted were those taken immediately preceding the morning feed. The reason for this consistency is that the potential value increases almost instantly after loading of the digester, reaches a maximum, and subsequently returns to its prefeed level. Morgan (80) has reported that gas production and volatile acids concentration follow a somewhat similar pattern. Figure 13 shows the similar trends exhibited by electrode potentials and gas rate. It should be mentioned that the data plotted in Fig. 13 result in a

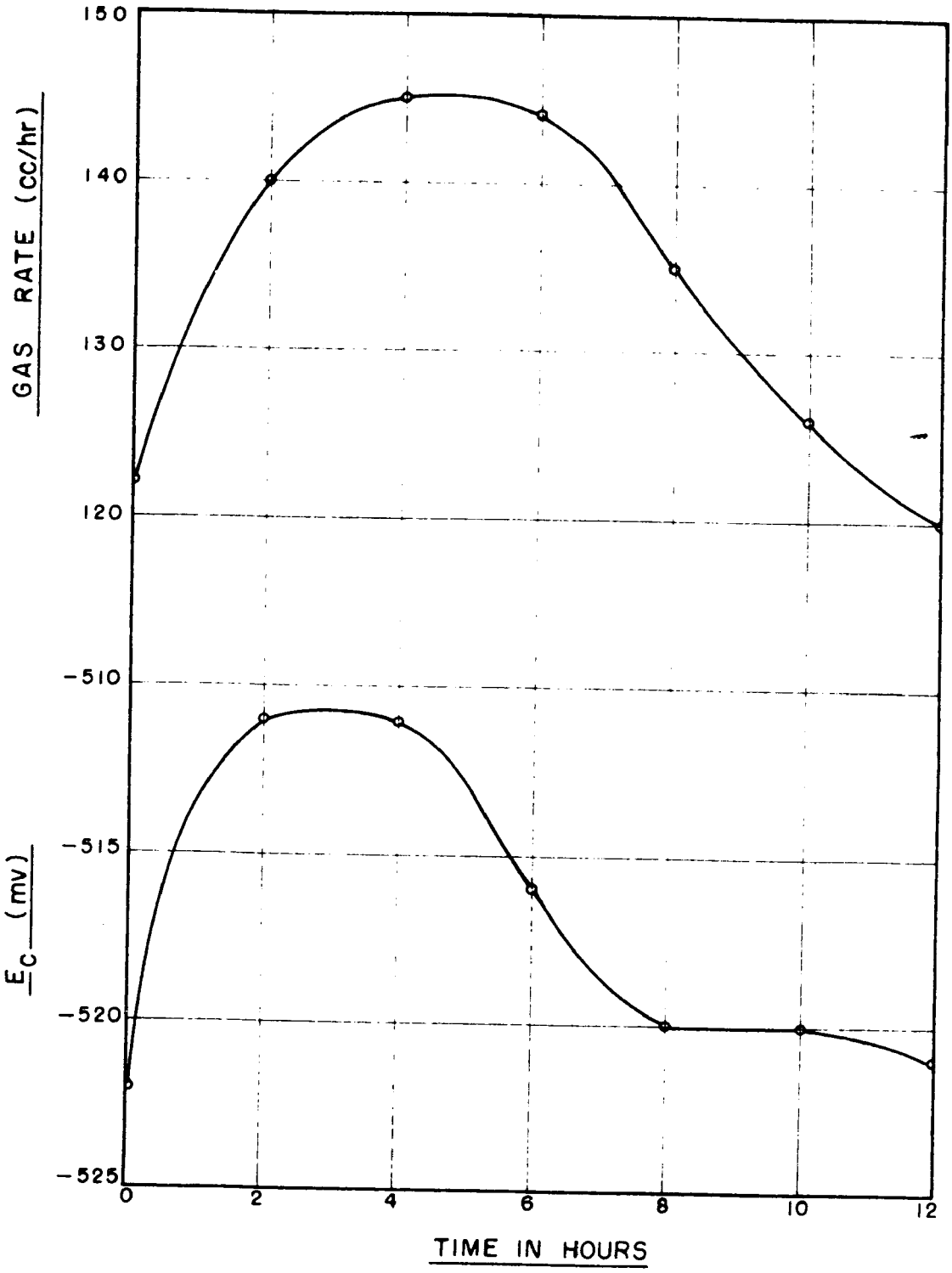


Fig. 13 Change in the Electrode Potential and Gas Rate Between Feedings

rather smooth curve. Most of the observations made would not allow such uniformity. However, the trend after every feed was similar to those shown.

The loading rate determines the magnitude of the changes in electrode potentials, gas rate, and presumably volatile acid concentrations. A loading rate of 0.1 lb. of v.m. per cu. ft. per day resulted in the data shown in Fig. 13. Lesser loading rates showed much smaller variations. Such fluctuations have been recorded repeatedly.

The aforementioned trends give a sound basis to the recommendation proposed by investigators of high rate digestion namely, that loadings should be as continuous as possible. Such a practice would tend to minimize environmental variations.

The observations made during this experiment showed a definite correlation between the concentration of volatile acids and corresponding electrode potential values. This in itself is a positive indication that electrode potential measurements can be of significant value in the monitoring of an anaerobic sludge digestion process.

Parallel Operation of Three Digesters

The second experiment had a twofold purpose. The primary objective was to determine if three identical digesters could be operated in parallel with relatively comparable results. It was felt that such an experiment was essential inasmuch as future runs would be carried out with each digester

operating under different conditions. If similar data could be obtained here, future results could be compared on the basis of imposed conditions.

As a second objective it was desired to obtain additional data regarding the electrode potential values developed during normal digestion. This information would amplify the conclusions drawn from the preceding experiment.

The procedure used in the start-up was similar to that used previously. Digested sludge over and above that necessary to complete the chemical analyses on the previous run was saved, and was used as the seeding material. In addition, one liter of fresh raw sludge was added to each digester before beginning the normal feeding schedule. The loading rate maintained throughout this run was 0.1 lb. of v.m. per cu. ft. per day. The raw sludge used averaged 3.28 percent solids of which 76.6 percent were volatile.

As in the previous experiment, data taking was begun on the morning following the day the digesters were put in operation.

Observations taken after the electrodes gave stable readings indicated that different potentials existed in each digester. The values for digesters A, B and C were, respectively, -485 mv., -464 mv. and -496 mv. Since the process had just begun the electrode potentials were changing rapidly. Further experiences have indicated that when rapid changes are taking place, agreement between electrodes is

not as good as under more stable conditions. Figure 14 shows that all three digesters were proceding toward more reduced conditions as indicated by decreasing potentials.

The decrease in potentials continued for 10 days after which time they began to level off in the range of about -525 mv. For example, on the fifteenth day the electrode potentials in digesters A, B and C were, respectively, -523, -528 and -520 mv., while on the twentieth day the potentials were -523, -527 and -530 mv. The data have shown that once "equilibrium" is attained, the electrode potentials of a digesting sludge are consistent and reproducible.

The concentrations of volatile acids in the digesters were rather high at the outset, as much as 1550 mg/l in digester B. Volatile acids remained at high levels for a considerable length of time until the methane producers became active and were able to reduce them to normal levels. It should be noted that the decrease in volatile acids occurred after the potential had become more or less stable, particularly in digesters A and B. After decreasing to normal concentrations, the volatile acids remained more or less constant throughout the remainder of the experiment, ranging between 200 and 400 mg/l.

The small increase in volatile acids at the start of the experiment was probably due to the fact that the acid forming organisms were active while the methane forming organisms had not yet developed in sufficient numbers to

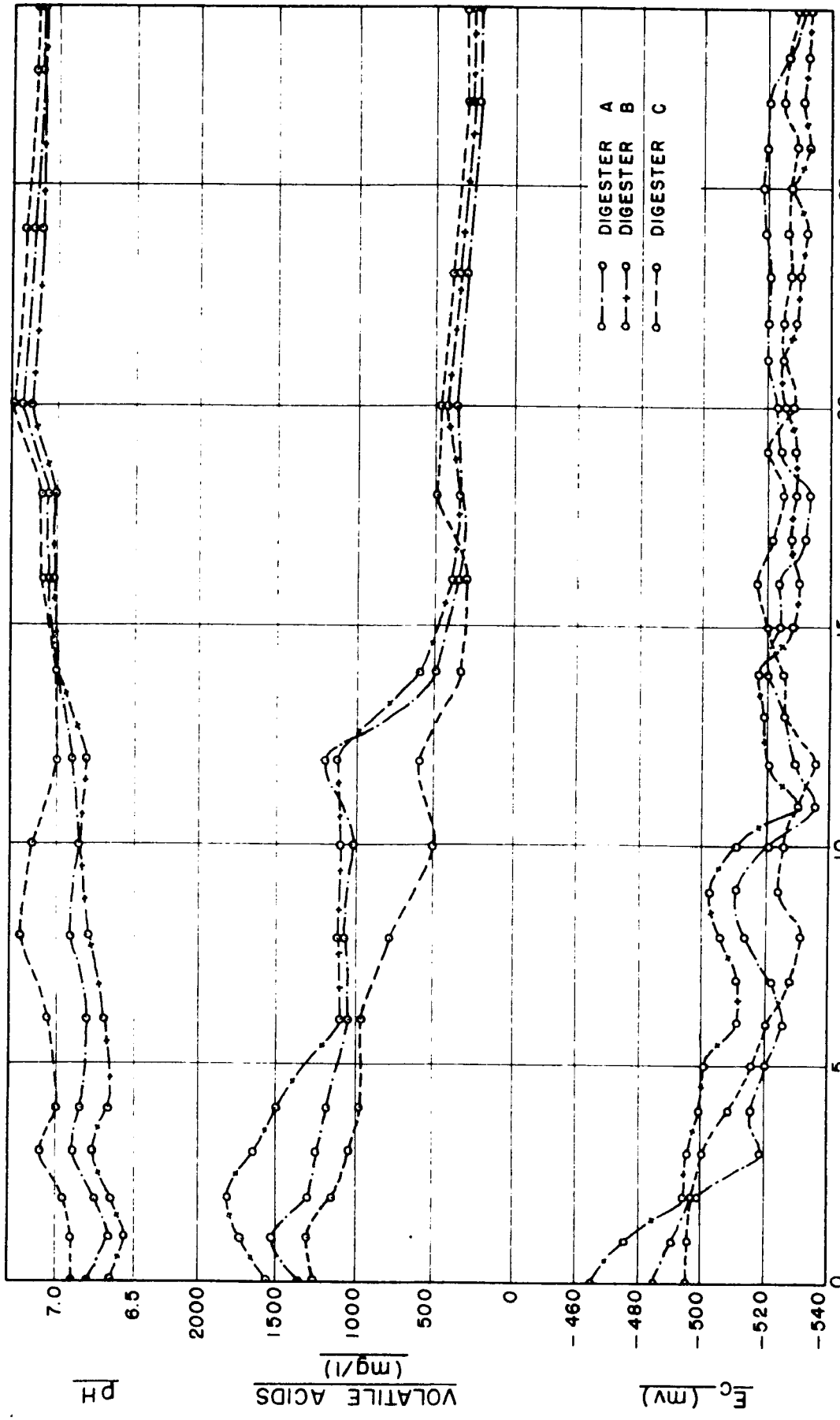


Fig. 11. Effect of Propionic, Valeric Acids and pH during Start-Up and Operation

break down the acids as they were formed. An active methane culture will actually convert to gas more acids than are formed under normal loading conditions. This fact is probably an essential consideration in high rate digestion.

The explanation of why digesters A and B required more time to come into equilibrium than did digester C can be traced to the type of seed material used. It will be recalled that the digested sludge which was used as the starting material was obtained through accumulation from the preceding experiment. It was found that the sludge used to start digesters A and B was from three to six weeks old while that used for digester C was only a few days out of the digester. This meant that the sludge used to start digesters A and B was older and less active, and required more time to develop a strong culture. This phenomenon is indicated in each of the monitoring parameters shown in Fig. 14 and Fig. 15.

Gas rates produced are shown in Fig. 15. Digester C during the first day of operation was producing gas at the rate of 160 cc. per hr., which was about three fourths of the average rate. By the fourth day, it was producing an average amount of gas which, for this loading amounted to about 210 cc. per hr. After this time, gas production in digester C exceeded the average rate for a few days and then decreased again to the average where it remained during the remainder of the experiment.

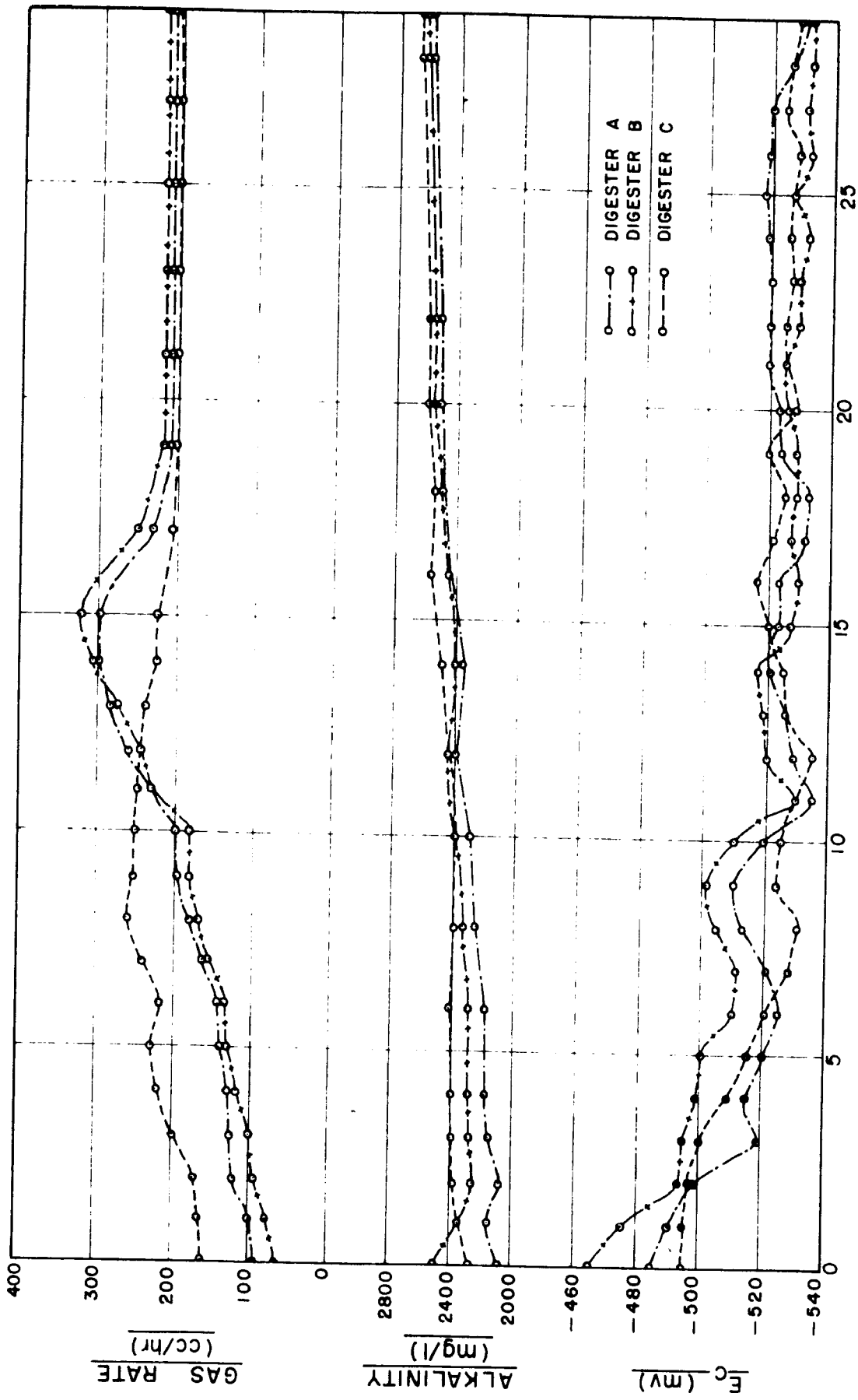


Fig. 15 Electrode Potentials, Alkalinity and Gas Rate during Start-Up and Operation

Digesters A and B, on the other hand, were slow to show an increased gas production and did not attain an average rate until after the tenth day. However, gas production in these two digesters continued to increase after this time with digester B producing as much as 327 cc. per hr. during the fifteenth day. The gas produced over and above that which was expected at this loading rate was produced at the expense of volatile acids, which decreased sharply at this time. After the excess volatile acids were gasified, the gas rate returned to the average rate. This had occurred by the nineteenth day, after which time digesters A, B and C all produced similar amounts of gas (about 210 cc. per hr.) throughout the remainder of the experiment.

Taking into consideration the loading rate of 0.1 lb. of v.m. per cu. ft. per day, the average gas production amounted to about 8.4 cu. ft. per pound of volatile matter added. On the basis that the average contribution of solids per capita per day is about 0.2 lb., the gas produced may also be expressed in terms of cu. ft. per capita. Assuming the average volatile matter throughout the run was 76.6 percent, the calculated value was 1.16 cu. ft. per capita. Both of these figures are quite similar to actual values of these parameters as reported in municipal practice.

The pH values followed a pattern which was expected. Initially the pH in digester C was 6.9 which is within the

usual normal digestion range. Shortly afterward, it increased to a point slightly above neutrality and thereafter remained on the alkaline side until the experiment had been completed. This result indicated that at no time was digester C ever in danger of becoming sour. Digesters A and B had a much lower pH at the outset, particularly digester B which exhibited a pH of 6.55 on the second day of operation. Had this low trend continued, the system would undoubtably have gone acid in a comparatively short time. However, after the second day both digesters A and B began an upward trend until they too were operating at a pH just above neutrality.

The immediate downward trend of electrode potentials could have been taken as support for the prediction that operation of the digesters would not deteriorate. On the other hand, such a prediction could not have been made on the basis of volatile acid concentrations, which in the case of digester B increased until the third day before beginning to decline.

Changes in alkalinity in this experiment were not of any great magnitude. The alkalinity of digesters A and B was lower than that of digester C during the early part of the run but all digesters contained approximately the same amount of buffering capacity after conditions became stabilized.

This experiment strengthened the belief that electrode potentials can definitely be correlated with the normal

parameters currently used as indicators of the process. Concurrent measurements have shown that definite trends in gas production, volatile acids and pH take place at the same time, or following changes in the potential.

Electrode potential values developed in all three digesters under average digestion conditions ranged between -520 and -530 mv. For this reason, when the term "normal potential" is used hereafter, it may be assumed that reference is being made to electrode potentials in this range.

Potentials of Different Sludges During Digestion

Observations up to this point had been made on Ann Arbor sludge only. It was felt that in order to make some statements about potentials developed during sludge digestion, a broader area should be investigated. All too often, limited investigations are made and broad generalized statements, which may or may not be true, have been made. It was with these thoughts in mind that the following experiment was designed.

The complete experiment consisted of the separate digestion of five different sludges. These sludges were especially selected so that electrode potentials could be observed during the digestion of sludge from sewage plants practicing different types of treatment. The sources were also selected in such a way that the effect of industrial wastes could be included. The study was carried out using sludge obtained from the treatment plants at Ann Arbor, Detroit, Saline, Ypsilanti and Chelsea. In the discussion to follow, statements made

regarding the type of treatment and sewage flows handled have been extracted from the 1957 Inventory of Municipal and Industrial Waste Facilities (130) published by the U. S. Public Health Service.

In order to maintain similarity all five runs were carried out using identical procedures. The loading rate during these studies was established at 0.075 lb. of volatile matter per cu. ft. per day. Detention times were different inasmuch as all the sludges did not have the same concentration of solids, and no attempt was made to control this factor. The digesting volume maintained throughout this test was 6 liters and the procedures followed were those explained previously.

Sludge from the Ann Arbor Sewage Treatment Plant was the first one of the five sludges to be studied. Since sludge from this plant was used consistently throughout the experimental work, it was felt that a portion of the data obtained elsewhere could be reproduced here to be used in comparison with data from the digestion of the other sludges. Figure 16 shows the electrode potentials along with the normal digestion parameters.

Ann Arbor Sludge

The Ann Arbor Plant utilizes secondary treatment in the form of activated sludge with diffused air aeration. Primary and secondary mixed sludge is digested in heated tanks with a floating cover. Processed sludge is either air dried on open beds or vacuum filtered. The dewatered sludge can be

dried or incinerated. As of 1957 the estimated population served was 80,000 and the average daily flow was 9 M.G.D. (130). Presently the flow handled is closer to 12 M.G.D.

The curves plotted in Fig. 16 are for a twelve day run. The concentration of solids in the raw sludge was 3.3 percent, 74.2 percent of which were volatile, giving an average detention time of about 24 days.

Electrode potentials averaged -524 mv. and were very consistent throughout this period. The other parameters were also relatively constant indicating that good digestion was taking place. Volatile acid concentrations were about 400 mg/l, pH remained slightly above neutrality at 7.1 and the alkalinity after building up to 2800 mg/l increased only slightly thereafter. Gas was produced at the rate of about 155 cc./hr. (8.25 cu. ft. per pound of v.m. added). The gas contained 32 percent carbon dioxide.

Saline Sludge

The second sludge to be studied was obtained from the Saline Sewage Treatment Plant. The Saline Plant served an estimated 1530 people with an average flow of 0.2 M.G.D. as of 1957. Secondary treatment is obtained using a trickling filter with a rotary distributor. Digestion of mixed sludges is carried out in a heated tank with a floating cover and sludge is dried on open beds.

The study made on Saline sludge would point up any difference which might exist in electrode potentials during

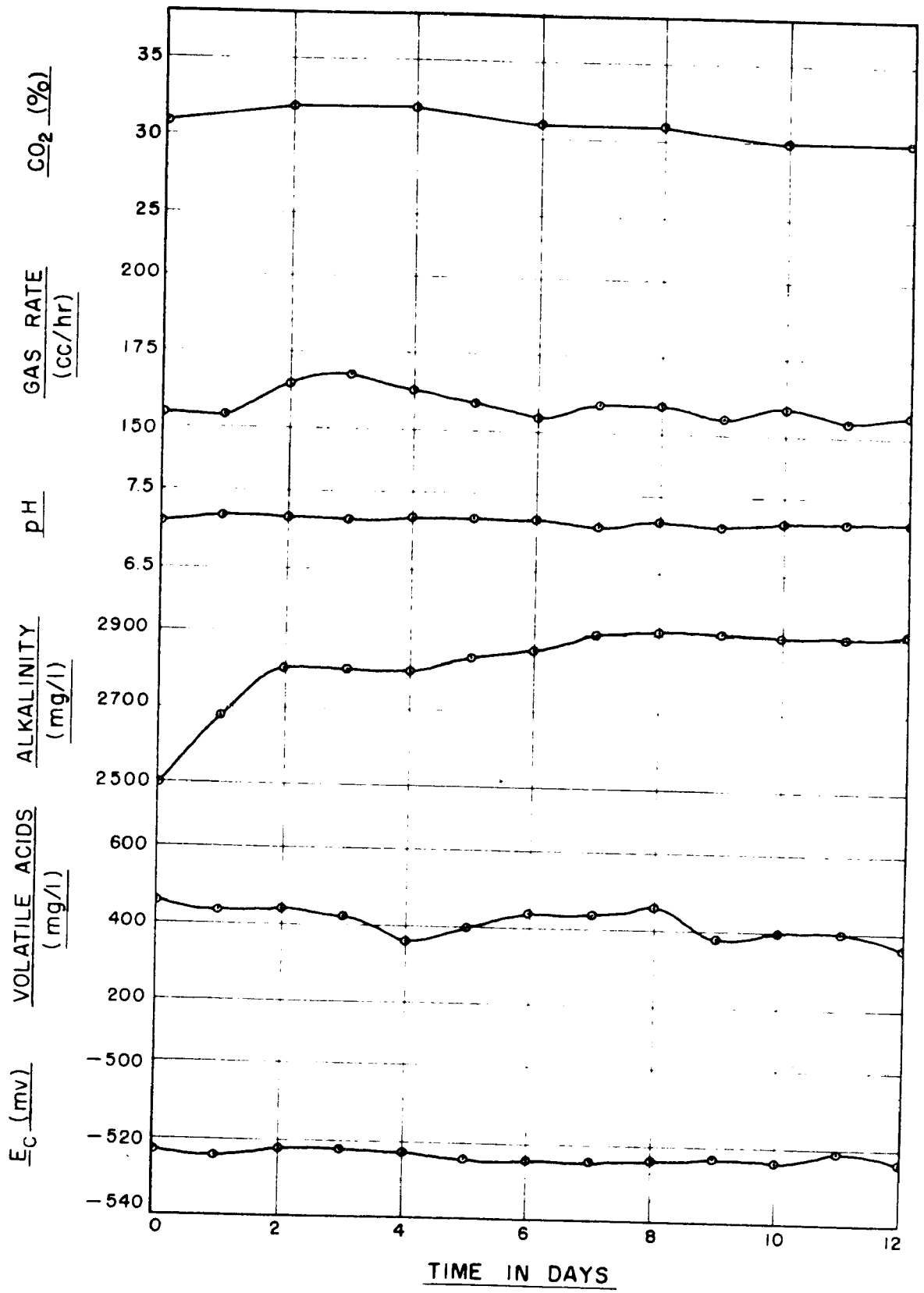


Fig. 1b Electrode Potentials and Normal Digestion Parameters for Anaerobic Studies

the digestion of sludge from a trickling filter plant and an activated sludge plant. There was a material difference in the concentration of solids as compared with the sludge from the Ann Arbor Plant. The solids in the Saline sludge averaged 6.1 percent, 77 percent of which were volatile. This solids concentration gave an average detention time of about 43 days in the experimental digestion unit.

The results of this run are shown in Fig. 17, and indicate a very good comparison of electrode potentials. The average potential during digestion was found to be -528 mv., as compared with -524 for Ann Arbor sludge. It should be noted that at the outset the potential was -510 mv., which reflects the fact that if a digesting mass is exposed to the atmosphere, if only during transfer, the electrode potential will increase indicating the sensitivity of the potential to oxygen. However, the electrode potentials decreased after the first days operation, probably due to the effectiveness of the flora in regaining reducing conditions.

Volatile acids in the digesting mass averaged about 350 mg/l, while the alkalinity followed its usual pattern of increasing slightly with time of operation. The amount of gas produced was about 10 cu. ft. per lb. of v.m. added at an average rate of about 187 cc. per hr. and having a carbon dioxide concentration of 36 percent. The average pH during digestion was found to be 7.0 and volatile solids were reduced by about 53 percent.

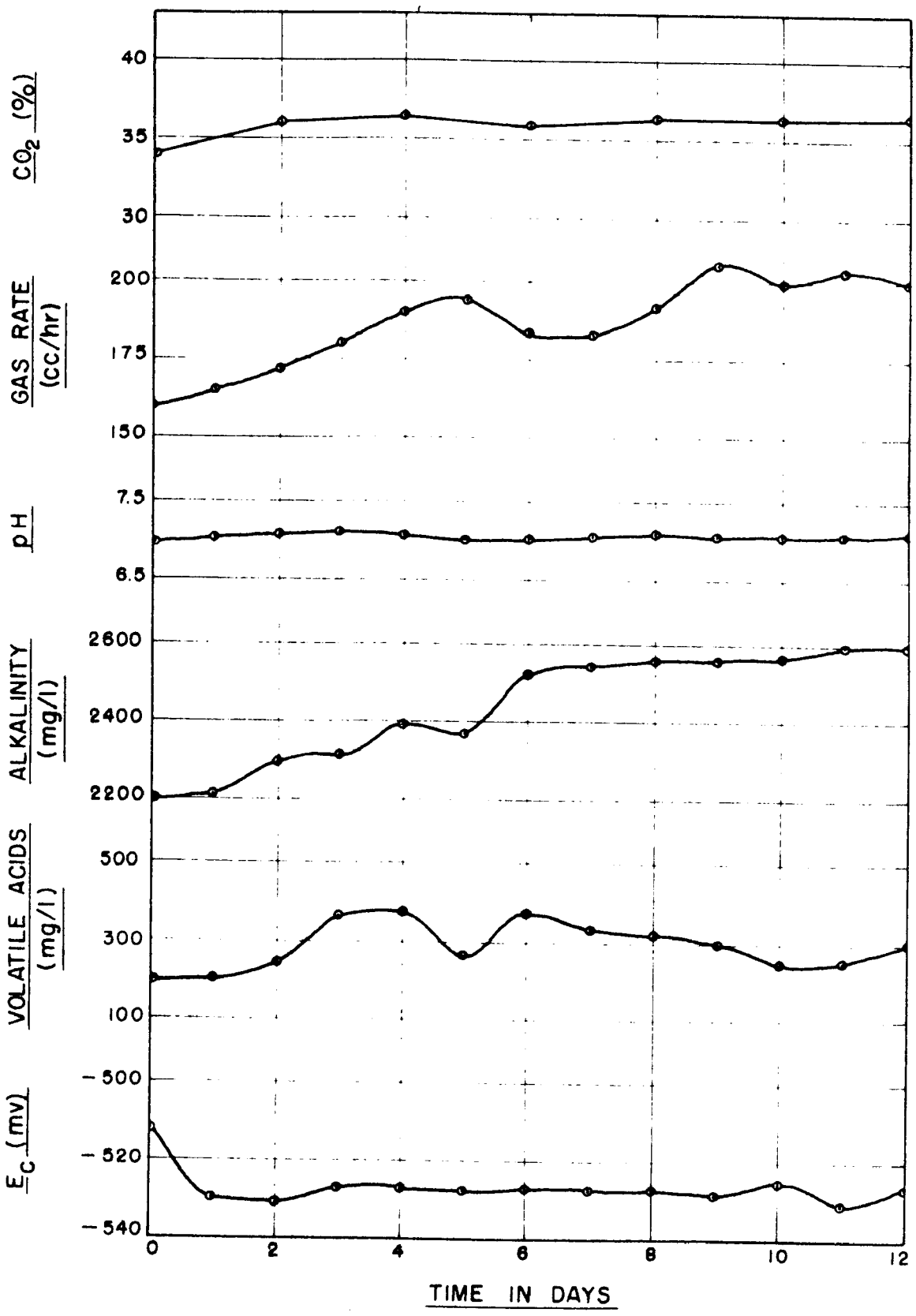


Fig. 17 Electrode Potentials and Normal Digestion Parameters for Saline Sludge

Detroit Sludge

The next contrasting sludge to be studied was that of the city of Detroit. In this case the sewage plant served a much larger city having an estimated population of 2,252,000 as of 1957, but the process consists only of primary treatment. In addition it may be said that Detroit sewage contains a considerable amount of industrial waste which might conceivably have some effect on the electrode potentials developed. Detroit practices incomplete digestion carrying the process only to the point where the gas produced satisfies the plant heating requirements.

Digesters are heated, with floating covers and the sludge is vacuum dried and incinerated.

The raw sludge fed to the digester contained 5.75 percent solids. The volatile matter was quite low being only 60 percent of the total. The sludge before feeding had a distinctive oily odor, probably due to the effect of industrial wastes.

The observations during this digestion are shown in Fig. 18. The same general trends in electrode potentials may be seen. The average potential value of -521 mv. was slightly less than in the sludges previously studied, but still within the average range of potentials discussed earlier. With regard to electrode potentials, it must be said that the daily variation in potentials in the Detroit sludge was larger than the two sludges previously studied.

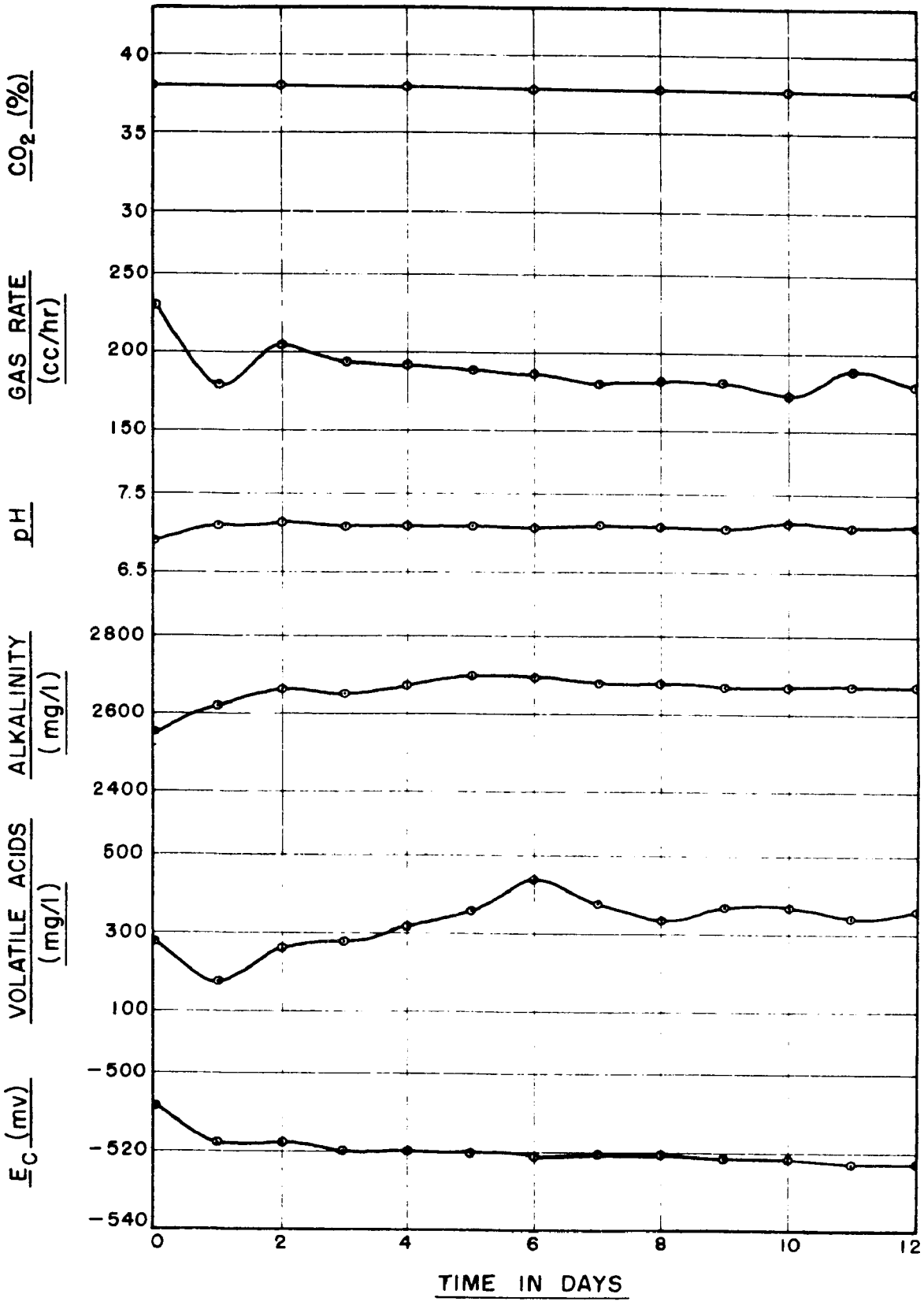


Fig. 18 Electrode Potentials and Normal Digestion Parameters for Detroit Sludge

This larger variation also occurred in the Ypsilanti sludge which was the next one to be studied. Since both the Detroit and Ypsilanti sludges contain a considerable amount of industrial waste, it may be logical to say that the larger variations observed may be due to the effects of industrial waste on electrode potential values.

The daily variation in volatile acids at the outset of the test was large but leveled off to about 340 mg/l, during the last five days of the run. It is interesting to note that the gas produced during the first day of operation was 230 cc. per hour. The production, however, dropped immediately and averaged 185 cc. per hr. for the remainder of the experiment. This high rate of gas production during the first day was attributed to the fact that Detroit practices incomplete digestion. The carbon dioxide concentration of the gas produced was 38 percent, which seems to conflict with the view of Miller and Barron (73) who state that trouble is impending when the carbon dioxide content of the gas builds up to 36 to 37 percent. It appears more consistent with the view that the amount of carbon dioxide in a sludge gas is a function of the type of substrate (17).

The pH of the digesting material averaged 7.05 while the alkalinity held relatively constant at slightly less than 2700 mg/l.

Ypsilanti Sludge

Ypsilanti serving a population of 18,300 with a sewage

flow of 1.5 M.G.D. has primary treatment only. Sludge is digested in a heated digester having a fixed roof and the digested sludge is dried on glass enclosed beds. Ypsilanti sludge was chosen for this study because it is similar in nature to Detroit sludge, that is, it is a sludge resulting from primary treatment and it does contain a considerable amount of industrial waste although serving a much smaller population.

The raw sludge charged to the digester had the same distinctive oily odor as did the Detroit sludge. The sludge was quite thick and had a solids content of 8.75 percent. The volatile solids portion comprised 60.5 percent of the total. Due to the heavy concentration of solids, the detention time of 42 days was quite long.

The data observed during the digestion of Ypsilanti sludge are shown in Fig. 19. At first glance, it may be concluded that the data are not indicative of good digestion, probably due to a slow start-up of the digester. Nevertheless, essential conclusions may be drawn from the curves.

As in all previous studies, the electrode potentials developed during normal digestion are within a limited range. The potential during the normal digestion of Ypsilanti sludge was found to be -521 mv. This slow rate of digestion is indicated by the gradual decline in the potential as contrasted with previous experiments.

The daily analysis for the concentration of volatile

acids also reflected the retarded start-up but after equilibrium began to be established, they had decreased to slightly over 400 mg/l. The pH also remained below neutrality until after the seventh day of operation after which time it averaged 7.02. Alkalinity was quite low and did not increase until the electrode potential and volatile acids dropped to average values.

Gas production was extremely low at the beginning and built up to produce an amount of gas that greatly exceeded what would normally be expected. This fact was probably due to the excess organic material which had accumulated in the digester. The gas rate subsequently decreased to 162 cc. per hr. which might be expected to be its normal rate. The carbon dioxide content of the gas decreased steadily from 38 to 36 percent.

Chelsea Sludge

The final run was made on Chelsea sludge. The Chelsea plant served a population of 2580 and had an average flow of 0.2 M.G.D. as of 1957 (130). It is a secondary treatment plant of the activated sludge type with diffused air aeration. Sludge is digested in a heated tank with a floating cover and the digested sludge is dried on open sand beds.

The raw sludge contained 3.40 percent solids, 70.5 percent of which were volatile, providing an average detention time 19.3 days.

Electrode potentials and normal digestion parameters

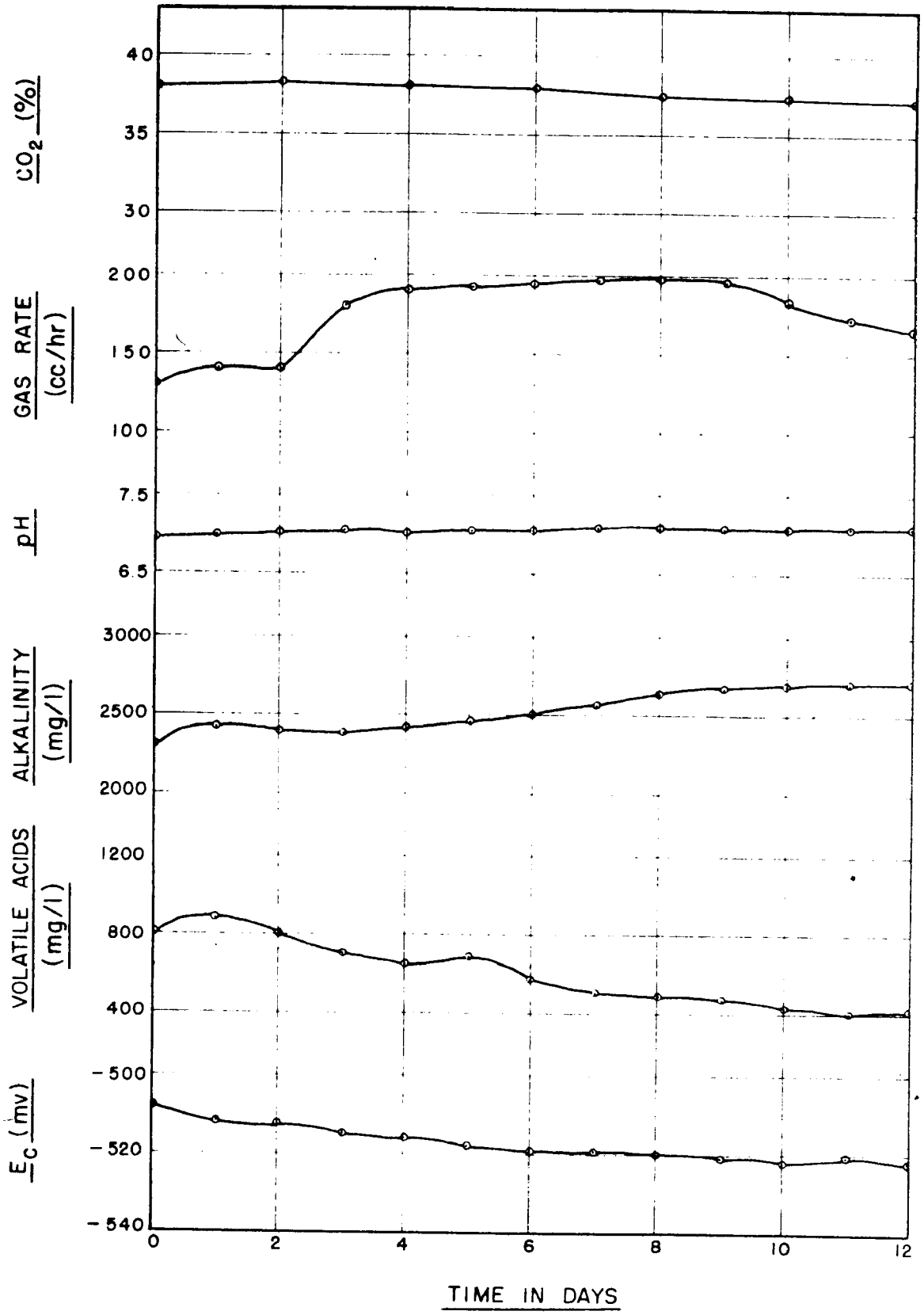


Fig. 19 Electrode Potentials and Normal Digestion Parameters for Ypsilanti Sludge

for the digestion of Chelsea sludge are shown in Fig. 20. The average electrode potential may be seen to be -522 mv. This result is in agreement with the sludges studied previously. The volatile acids concentrations averaged close to 500 mg/l and the pH held steady at about 7.05. Gas production during this run was somewhat lower, amounting to about 7.5 cu. ft. per lb. of v.m. added at a rate of about 140 cc. per hour. The carbon dioxide content of the gas produced was 35 percent.

The five sludges studied represented primary treatment only, activated sludge treatment and trickling filtration, and were obtained from various sized cities. Some of the sludges were essentially from domestic sewage while others contained considerable amounts of industrial wastes. It was felt that any differences in electrode potentials during sludge digestion would appear with this selected cross section of sludges.

The agreement between potentials during the digestion of these sludges was extremely good ranging from -521 to -528 mv. This fact would tend to support a statement that all sludges digest within a definite potential range of between -520 and -530 mv.

Table VII shows a compilation of the data obtained in the study of the aforementioned five sludges. It is felt that such a table will provide an adequate appraisal of the study.

The initial phase of this research was designed

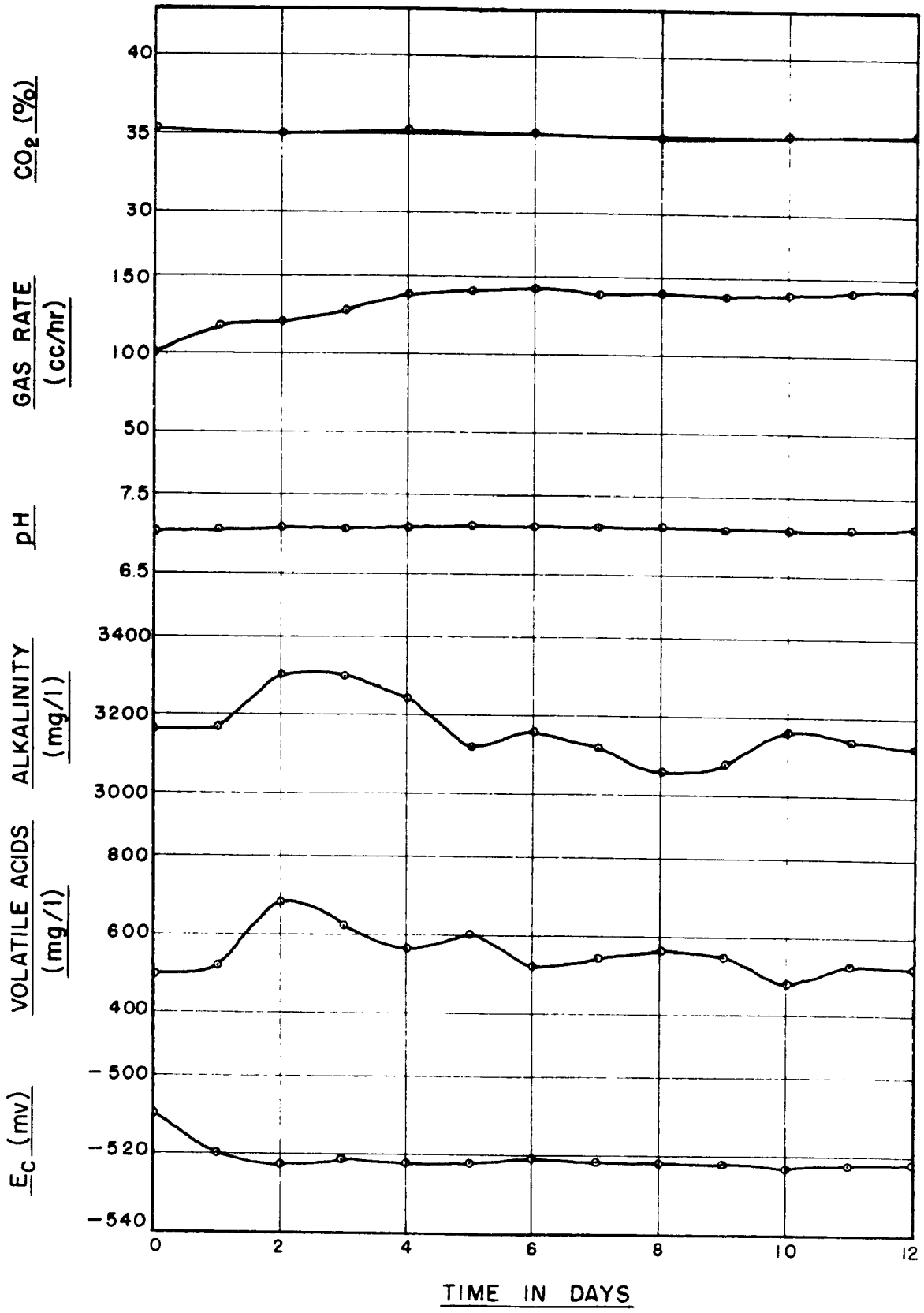


Fig. 30 Electrode Potentials and Normal Digestion Parameters for Chelsea Sludge

TABLE VII

Tabulation of Digestion Parameters
for Five Sludges

Sludge	Parameter*						
	Electrode Potential mv.	Volatile Acids mg/l	Gas Rate cc./hr.	Gas Production cu. ft./lb.	CO_2 o/o	pH	Alkalinity mg/l
Ann Arbor	-524	400	155	8.25	32	7.1	2800
Saline	-528	350	187	10.0	36	7.0	2690
Detroit	-521	340	185	9.87	38	7.05	2700
Ypsilanti	-521	440	162	8.64	36	7.02	2650
Chelsea	-522	525	140	7.5	35	7.05	3250

*Values are given as averages after normal digestion had commenced.

primarily to determine whether or not electrode potentials can adequately describe trends in the digestion process and thus be accepted as an additional monitoring parameter along with those presently used.

The observations showed that electrode potentials always fell in a restricted range, even though monitoring the digestion of sludges of different character. It was further observed that changes in the potential usually accompanied or preceded other changes in the process. When potentials decreased to the normal level optimum digestion was beginning to be established.

Electrode potentials were found to be more sensitive to changes in the process than many of the existing monitoring parameters. Any deviation from the normal digestion process is almost immediately reflected by a change in the electrode potential whereas many of the presently used monitoring parameters are slow in indicating changes in the process.

Future portions of this research will deal with the control of potentials during digestion and noting the effects on the operation of the process.

POTENTIAL CONTROL IN SLUDGE DIGESTION

The major portion of the second section of the research was aimed at observing the results obtained from electrolytically controlling the potential rather than permitting normal digestion to occur. To achieve this aim three separate experiments were carried out. In the first experiment the potential within the digester was increased, held constant and then decreased; primarily to note how accurate a control was maintained and what changes took place within the unit. The second run sought more specific information; therefore, the potentials in each of three digesters were increased to different levels and held constant while changes in the normal digestion parameters were observed. The third experiment was designed to rule out any possibility of irregularities that might appear during electrolytic control as opposed to normal deterioration of the process from overloading. It was felt that the results from this second portion of the research would give a fundamental basis for future, more precise studies on the effect of controlled potentials during sludge digestion.

Preliminary Potential Control Studies

Only one digester was used during the first experiment. Start-up was initiated by filling the digester with freshly digested sludge from the Ann Arbor Plant. The digester was fed twice daily commencing the following morning and

continuing throughout the run, at the rate of 0.075 lb. of v.m. per cu. ft. per day. The average detention time was about 24 days.

The digester was allowed to operate without control for five days until it appeared that equilibrium conditions had been established. This portion of the curves shown in Figs. 21 and 22 is labled normal operation. The electrolytic control was then turned on allowing a current passage of 40 ma. through the circuit. As mentioned previously, fluctuations in the resistance of the circuit required changes in the control mechanism so that no one current can be reported. Sometimes hourly changes in the applied voltage were necessary.

As may be seen from Figs. 21 and 22 the potential of the digester was increased to -460 mv. in two days. Inasmuch as the potential and pH are related, a drop in pH from 7.1 to 6.6 occurred during this period. The rapid increase in potential had obviously affected the methane producers for the volatile acids concentration increased rapidly, accompanied by a sharp decrease in the rate at which gas was produced. On the other hand, it appeared that the alkalinity was not affected.

Since the rapid increase in potential had created drastic changes, it was thought that maintaining the potential at this increased level might provide additional valuable information. What followed in the next five days

showed, without doubt, that the potential could be accurately controlled by the electrolytic method described in detail during the discussion of the experimental apparatus. Throughout this time the potential averaged -458 mv., attaining a high of -454 and a low of -462 mv.

During the time the potential was held constant at this increased level, volatile acid concentration and gas rate appeared to remain constant while slight decreases were observed in the pH and alkalinity. At first glance it might appear as though a second equilibrium might have been established at this increased level of potential. However, later studies have pointed up the fact that deterioration is a function of time.

After determining that the electrolytic control mechanism was capable of holding the potential at a given level, the potential was further increased at a slower rate until the electrodes showed that the digester was operating at a potential of -240 mv. which is equivalent to E_h = + 5 mv. Throughout this period of time, which amounted to 13 days, the normal monitoring parameters showed a progressively deteriorating process. The deterioration continued until on the twenty fifth day of operation gas production ceased entirely. Just before gas production stopped gas analysis indicated a carbon dioxide content of 58.5 percent. Volatile acids had accumulated to 2400 mg/l and the alkalinity dropped sharply to 800 mg/l. The fact that the digester had gone

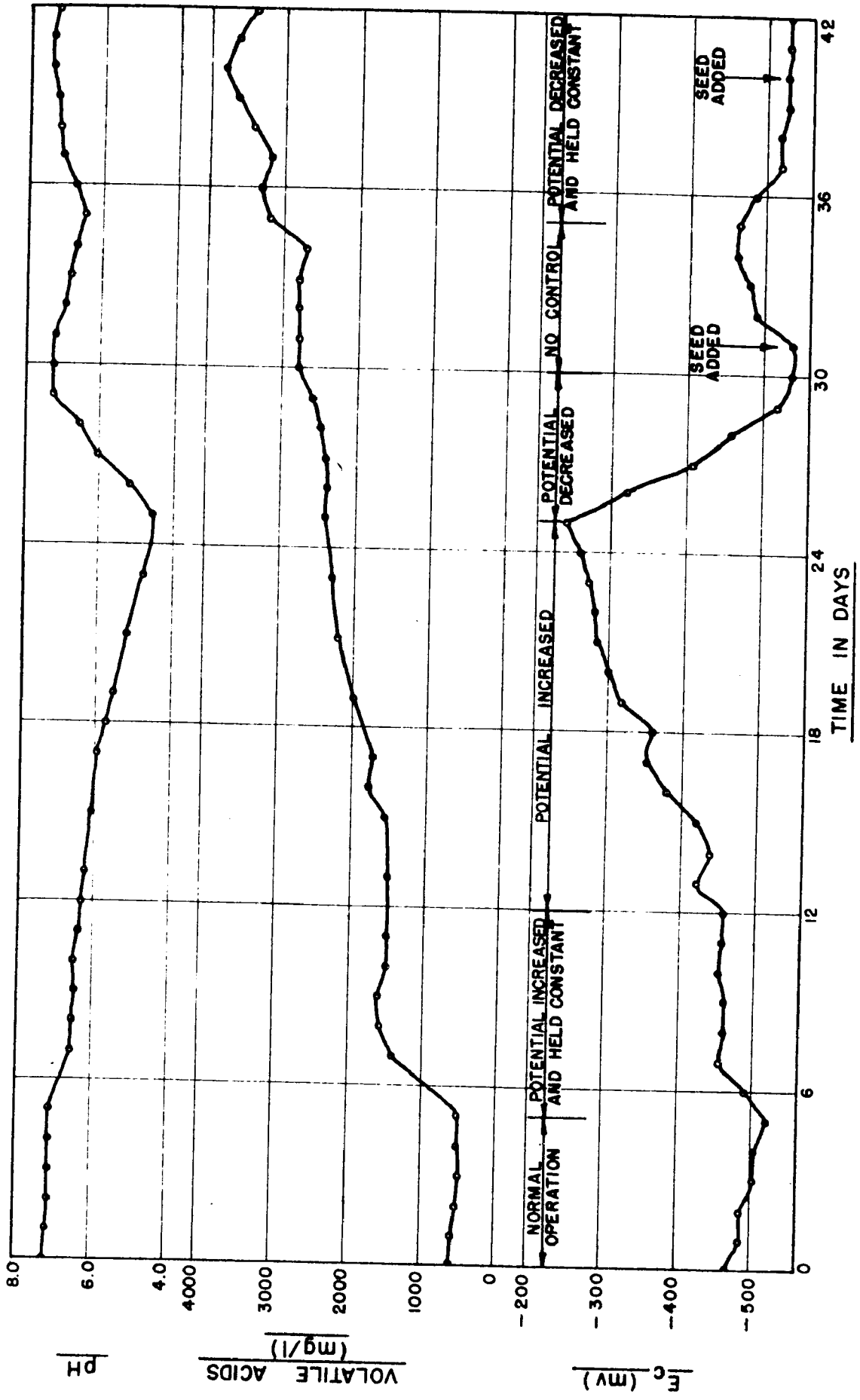


Fig. 21 Electrode Potentials, Volatile Acids and pH during Electrolytic Control Changes

acid was clearly indicated by a pH of 4.6. A 50 percent increase in the volatile matter content of the digester occurred during this thirteen day period. It may be said that the digester at this time was dead.

In order to gain further information, the direction of the current in the control mechanism was reversed and the potential was decreased. Within four days the potential had been reduced to -520 mv. and accompanying this decline was a sharp increase both in pH and alkalinity, these parameters reaching values of 7.2 and 2800 mg/l respectively. No gas was being produced and the concentration of volatile acids held constant at 2400 mg/l, indicating that possibly even the acid formers were inactive.

At this point the electrolytic control was shut off. A favorable environment had been reestablished except that the volatile acid concentration was high. Immediately after the control was shut off the volatile acids increased, possibly indicating that the acid formers were becoming active. However, if the acid formers were active a certain amount of gas should have been produced. One explanation might be that since the gas produced would have been carbon dioxide it might have gone into the production of alkalinity which had also increased.

A small amount of seed material, amounting to about two percent of the digester capacity, was introduced on the thirty first day of operation in the hope that some activity would be created. The day after this seed was added a

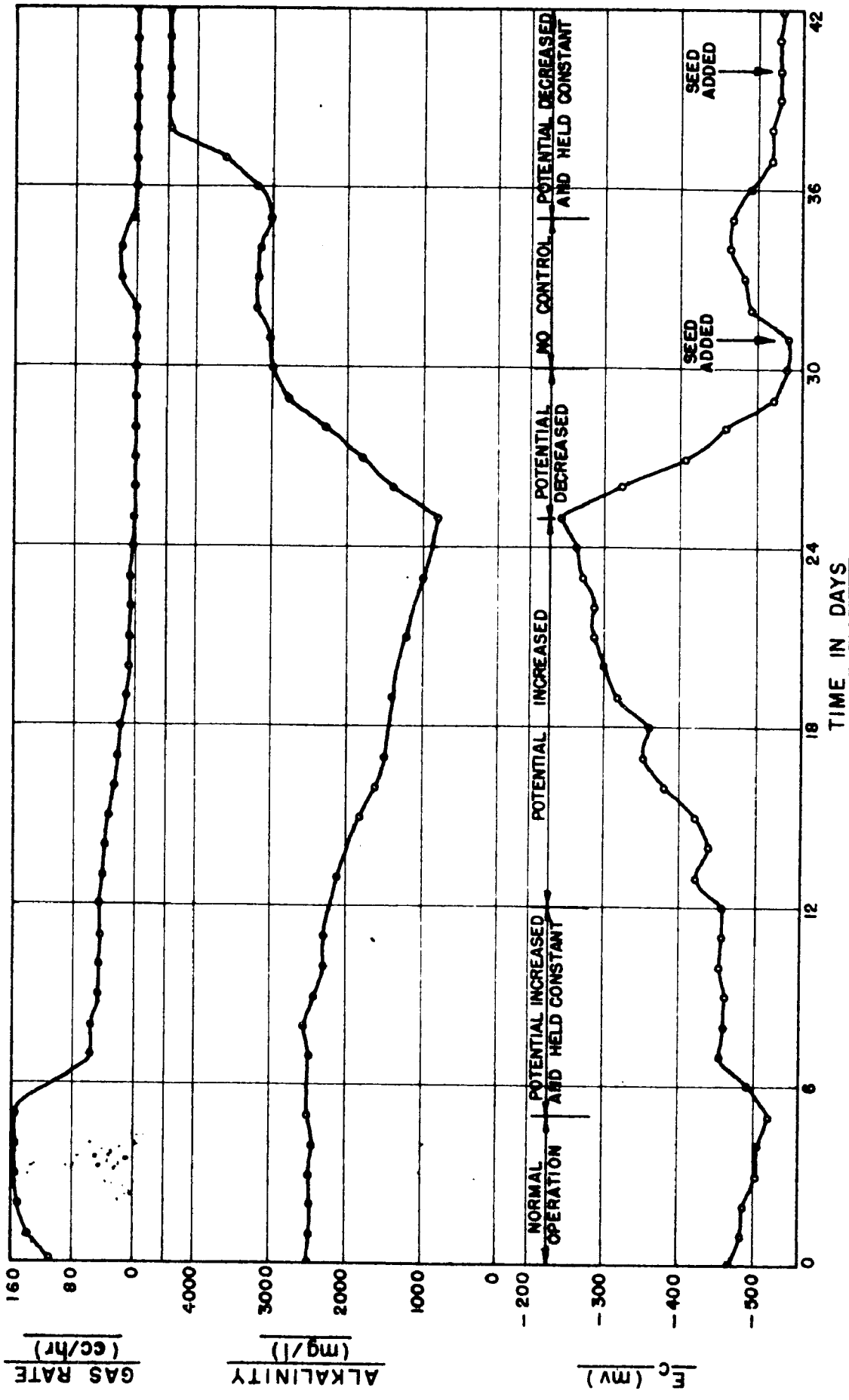


Fig. 22 Electrode Potentials, Alkalinity and Gas Rate during Electrolytic Control Changes

two-day spurt of gas production was noticed. It may be deduced that this short spurt of gas production was due to the methane formers which entered the digester with the seed, but were inhibited soon after by the high concentration of volatile acids. The high acid concentration could also have been considered instrumental in driving the electrode potential up and the pH down during this period when control was not practiced. The electrode potential increased to -466 mv. while the pH dropped to 6.3.

The potential control was again actuated for the purpose of reducing the potential to the normal range and keeping it there. Two days were required for the decrease and the potential level was maintained for a period of eight days. As usual with the decrease in potential the pH rose to 7.5 and the alkalinity built up to about 4400 mg/l. However, it again appeared that conditions were ideal for the acid forming bacteria as reflected by the further increase in volatile acids up to 3200 mg/l and subsequently as high as 4000 mg/l, while gas production was still zero. It appears that one consequence of attempting to recover a "stuck" digester is that the acid forming bacteria recover and reproduce much faster than the methane producing bacteria. The result being that the first step in recovery is a buildup of volatile acids which then exerts an inhibiting effect on the methane producers.

On the fortieth day of operation a second seed was introduced into the digester. This resulted in a temporary

decrease in volatile acids and the production of a small amount of gas. The effect was short lived again and, inasmuch as the primary aim of the experiment had been achieved, observations were discontinued.

The results obtained from this experiment showed that the potential of an anaerobic digester may not only be increased and decreased at a desired rate, but may also be maintained for short periods of time. Nothing was observed that might indicate that the potential could not be held constant for much longer periods of time. The results also indicated that when the electrode potential within the digester does not fall within a certain limited range, deterioration of the digestion process as we know it can be expected to follow.

The information gained in the preceding run enabled the design of the following, more specific experiment on the control of potentials in a digester.

Studies of the Effect of Poised Potentials on Sludge Digestion

In this experiment the plan was to use four digesters represented as A, B, C and D. Digester D was to be used as the control while the potentials in digesters A, B and C were to be poised at predetermined levels for a period of ten days, after which the potentials were to be reduced back to normal. From the information gained in the preceding experiment it was felt that poising the potential would cause one or more of the digesters to deteriorate. By

reducing the potentials back to their normal value possibly the digesters could be made to recover. The potentials in digesters A, B and C were to be poised at -430, -460 and -490 mv. respectively.

All digesters were loaded at the rate of 0.075 lb. of v.m. per cu. ft. per day. The average solids concentration of the sludge was 3.26 percent, 74.3 percent being volatile. This gave an average detention time of 20.1 days. The digesters were permitted to operate uncontrolled for five days before any data were plotted. Two days later potential control was begun. The results obtained from this experiment are depicted graphically in Figs. 23 and 24.

From the curves, it may be seen that five days were required to raise the potentials to their predetermined operating levels. During this time of potential adjustment changes were taking place in the other parameters of digestion. The rapid increase of 60 mv. in the potential of digester A had a severe effect on all parameters. An immediate decrease in the rate of gas production and increase in the volatile acids is noticeable. Only slight changes occurred in digesters B and C.

After the seventh day of operation when the potentials had been poised at their predetermined levels, both digesters A and B seemed to be in trouble, while digester C which was only raised to -490 mv. appeared to be operating only slightly off normal, as defined by the various other

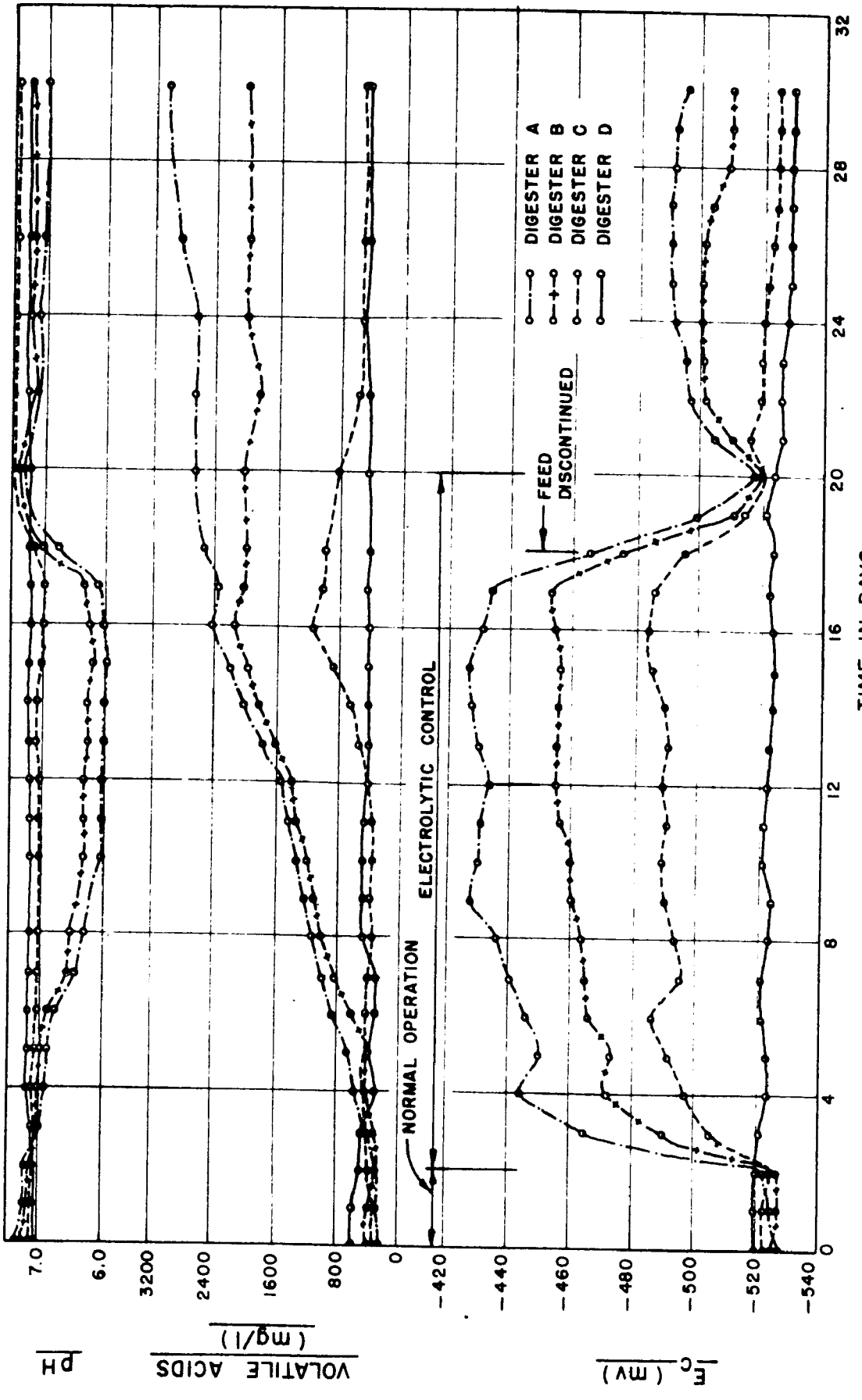


Fig. 23 Electrode Potentials, Volatile Acids and pH during Electrolytic Poising of the Potential

parameters recorded. Digesters A and B were operating with volatile acids in excess of 800 mg/l and at a gas production of about half the normal amount. Sludge gas snalyses showed the carbon dioxide content of digesters A and B to be 59 percent and 53 percent, respectively, while that of digester C was only 36 percent. The control digester at this time showed a carbon dioxide content of 31 percent. Changes in pH and alkalinity followed the expected pattern.

The potentials were successfully poised throughout the ten day period as may be seen in Figs. 23 and 24. The average potentials for digesters A, B and C were found to be -431, -458 and -490 mv., respectively, while the control developed an average potential of -523 mv.

The deterioration of digesters A and B continued throughout the 10 day poising period until at the end of the control period digester A had accumulated volatile acids to the extent of 2300 mg/l while digester B showed 2000 mg/l. It is interesting to note that digester C began to deteriorate on the twelfth day of operation, if we consider that a continuous increase in the volatile acids concentration indicates the onset of deterioration. On the seventeenth day, which was the end of the control period, chemical analyses showed that the concentration of volatile acids in digester C had increased to 1000 mg/l, while that of digester D, the control, remained at approximately 400 mg/l.

The definite relationship between gas production and

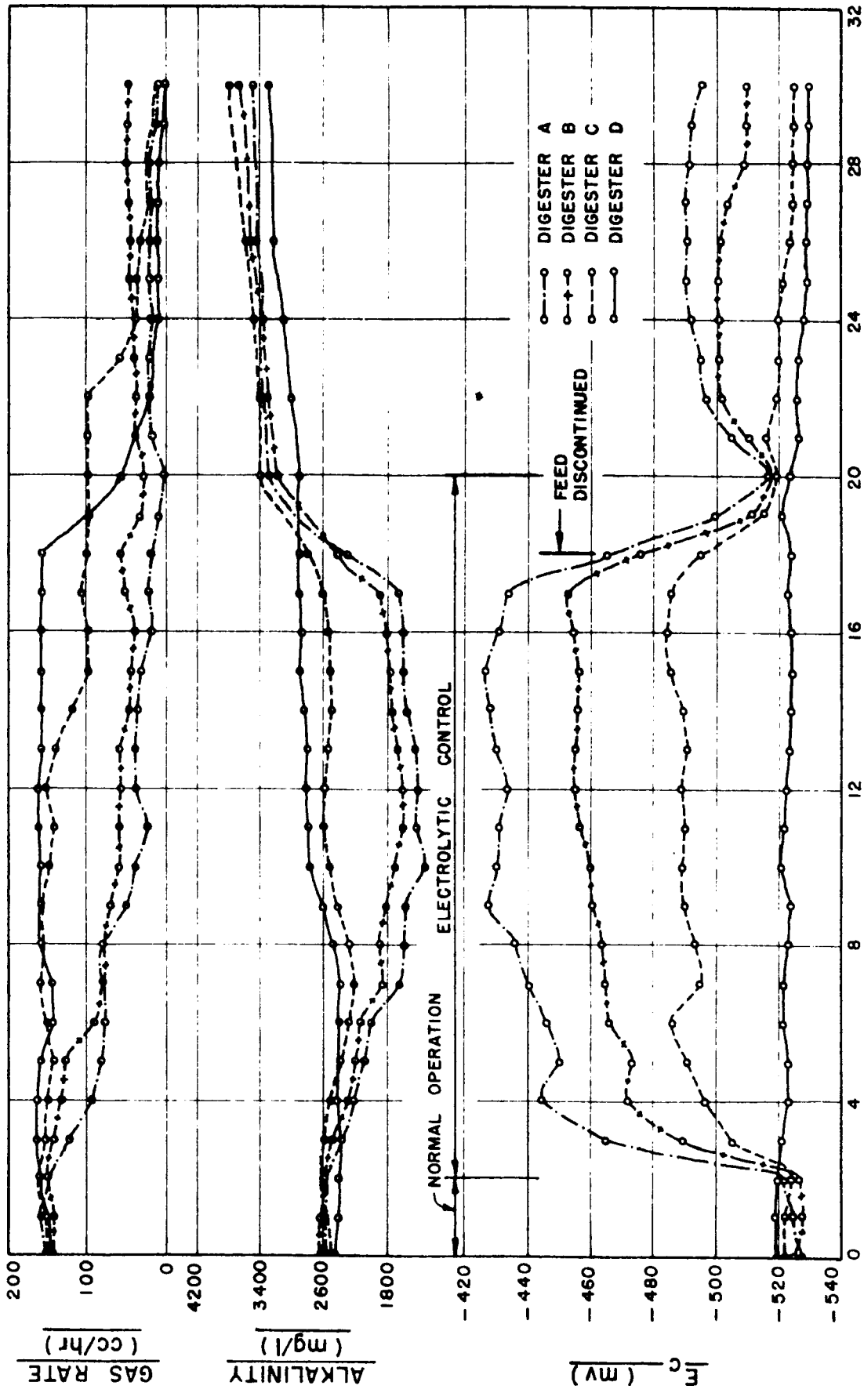


Fig. 24 Electrode Potentials, Alkalinity and Gas Rate during Electrolytic Poising of the Potential

volatile acids concentration is clearly indicated by the drop in the gas rate on exactly the same day that volatile acids increased. The gas production also continued on a downward trend, diminishing to about 1/5 the normal rate for digester A and about 1/4 that amount for B. The carbon dioxide content also showed further increases, the gas analyses taken on the sixteenth day showing percentages in digesters A, B, C and D of 70, 50, 40 and 31 percent respectively.

The pH in all of the digesters except the control also declined during the period of poised potentials, digester A recording a low of 5.9 and digester B dropping to 6.15. It may also be observed that digester C after having maintained a constant pH for about ten days dropped sharply on the fourteenth day, about two days after the volatile acids started to increase. Digester D maintained a pH of about 7.15 throughout.

According to the predetermined plan the potentials in all digesters were returned to the normal level. At the same time feeding was also discontinued.

The only change appearing in digester D was the typical reduction in gas rate which takes place whenever feeding is discontinued. This phenomenon is shown in Fig. 24.

Inasmuch as digester C had not reached a critical level, it recovered fairly rapidly. Volatile acids decreased to a normal operating level in just six days. Alkalinity and pH returned to slightly higher levels than would

normally be expected during optimum, uncontrolled digestion. The higher pH (7.5) may have shifted the carbon dioxide equilibrium enough to drop the percentage of carbon dioxide in the sludge gas to 19 percent. Gas production continued at a moderate rate, even though feeding was discontinued, indicating that the loss in volatile acids could be attributed to its conversion to gas. This becomes more apparent when it is noticed that the production of gas decreased sharply as the volatile acids concentration was approaching its normal level.

Digesters A and B did not recover under the conditions imposed. After the control was shut off the large amount of volatile acids was sufficient to drive the potentials to higher levels and to cause decreases in pH in both digesters.

The results from the preceding experiment indicate that favorable electrode potentials are necessary for the proliferation of the microorganisms responsible for the stabilization of sewage sludge, and that the extent of deviation from the desirable potential is a measure of the rapidity at which deterioration will take place. With these facts established future experiments were designed.

In order to determine whether or not the electrolytic potential control method was giving results similar to those that might be obtained during the practice of sludge digestion, the following experiment was designed and executed.

Potential Changes Induced by Overloading a Digester

Before continuing further work on the study of the control of electrode potentials during digestion, it was felt necessary to compare the results of digestion during electrolytic control and during overloading. Such a comparison would eliminate any thoughts that conditions induced through electrolytic control are quite different than those produced by overloading a digester with large quantities of organic matter. Thus the following experiment was designed to produce adverse digestion by overloading.

Higher rates of organic loading were used in digesters A, B and C, while digester D was again used as the control. To make conditions more extreme, the sludge used for feeding was not concentrated, resulting in overloading at decreased detention times. Digesters A, B, C and D were loaded at rates of 0.300, 0.225, 0.150 and 0.075 lb. of v.m. per cu. ft. per day, with a sludge that averaged 3.27 percent solids of which 79.4 percent were volatile. This loading resulted in detention times of 5.7, 8.6, 11.4 and 22 days for A, B, C and D respectively. Since previous investigators recommended an eight day minimum for detention time it was felt that digester A surely would deteriorate rapidly. In addition, the results from digesters B and C might supply additional information of digestion at increased solids loading. The increased loading rates were begun on the second day of operation after the digesters had come into

equilibrium. The results of this experiment are shown in Figs. 25 and 26. Electrode potentials recorded throughout the run are plotted with pH and volatile acids in Fig. 25 and with gas rate and alkalinity in Fig. 26.

The control digester continued to operate at normal conditions throughout the run and needs no further discussion. The data obtained from the control are plotted in Figs. 25 and 26 and may be used for comparison.

Digester C, loaded at twice the rate of the control showed no tendency to deteriorate whatsoever. The electrode potentials remained relatively constant with a high of only -520 mv. and a low of -525 mv. During the 29 days of operation under increased loadings, the electrode potentials in digester C were on the average about 4 mv. higher than the average potentials in the control. The other parameters also showed similar trends. The pH was only one half unit less than the control and the alkalinity was constant at a slightly lower level. Volatile acids in digester C were lower than those recorded in the control although this difference was not large enough to be considered significant. Gas production throughout the period of increased loading showed a rate of about 285 cc. per hr. as compared with the control which averaged about 150 cc. per hr. Thus, with a loading rate of twice that of the control, digester C was producing about 190 percent as much gas as digester D, indicating a very efficient process

at this increased loading rate. It is to be noticed that when loading was reduced to equal that of the control, gas production immediately fell off, and shortly thereafter the gas rate was similar to that established in the control. The carbon dioxide content of digester C increased only 2 percent throughout this period.

Conditions in digester B, loaded at a rate three times that of the control, were not as ideal. The average potential during the period of increased loadings was about -512 mv. The pH of the digester was about 7.0 while the alkalinity averaged about 2700 mg/l or 500 mg/l below that of the control. The concentration of volatile acids averaged about 150 mg/l higher than that of the control, but at no time did they exceed 700 mg/l which is far from being critical. The shorter detention time is reflected in the reduced gas rate. The gas produced amounted to about 214 percent of that from the control digester. Although the loading rate was three times the load applied to the control, digester B could not be expected to produce three times as much gas, primarily because of the lost contact time. Gas composition changed but slightly, showing a carbon dioxide content of 35 percent.

The result of loading digester A with four times that of the control was immediately apparent. The electrode potential increased rapidly and leveled off at about -496 mv. The potential remained at this level until the eighteenth

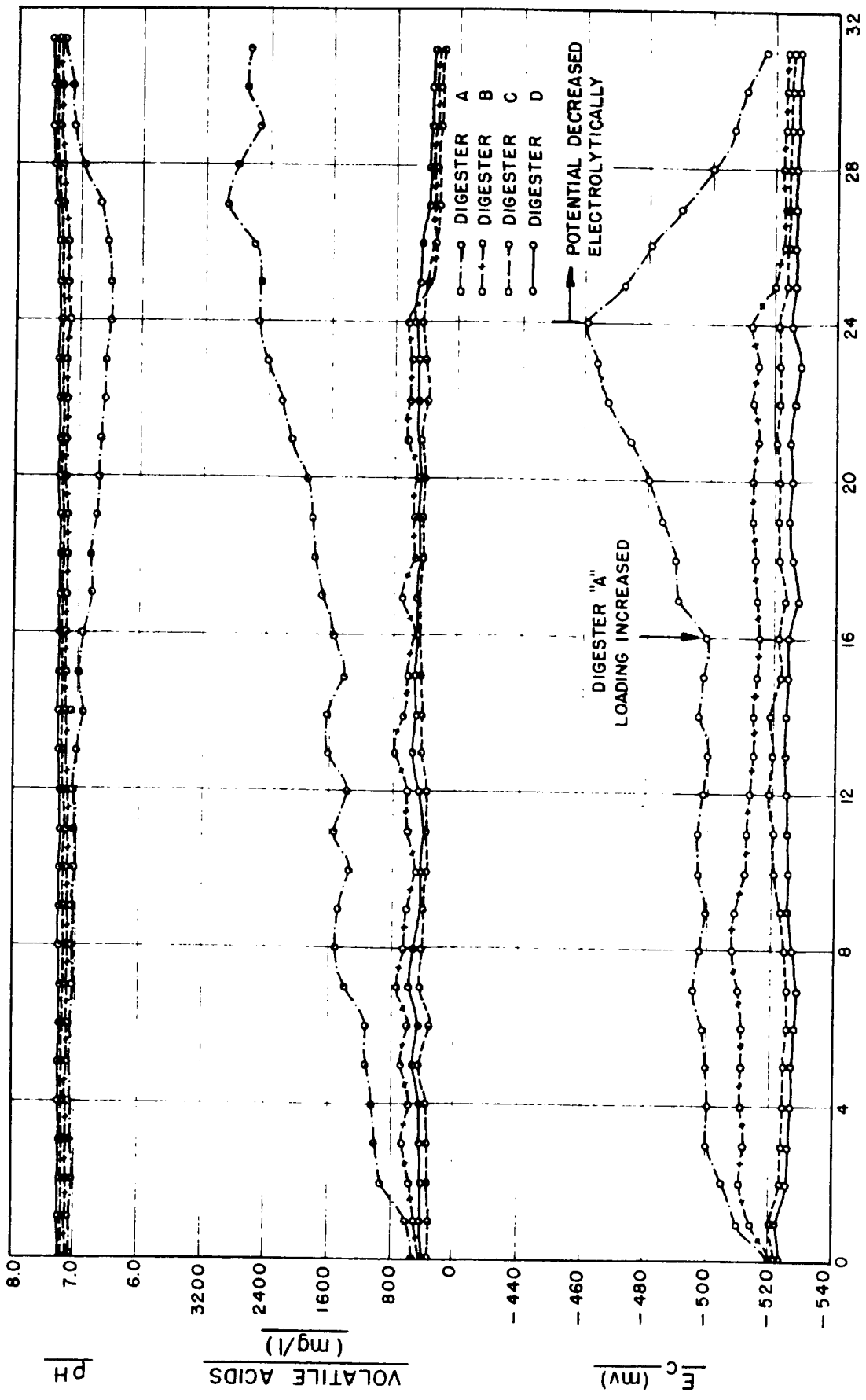


Fig. [illegible] Digester Potentials, Volatile Acids and pH Variations during Cycling Operation

day of operation when the loading was further increased to 0.375 lb. of v.m. per cu. ft. per day. The detention time was now 4.1 days. After this further increase in loading the potential increased and continued to increase at a fairly constant rate reaching a value of -460 mv. on the twenty fifth day of operation, at which time the potential was reduced electrolytically.

Changes in volatile acids followed a similar pattern. Immediately after the loading was increased, the volatile acids concentration rose first to about 800 mg/l and further to 1400 mg/l where it remained until the loading was again increased. The acids concentration continually increased up to 2400 mg/l before electrolytic control was initiated. The similar trends exhibited by electrode potentials and volatile acids is clearly shown in Fig. 25. After the potential was electrolytically reduced, the volatile acids increased further reaching about 2800 mg/l. The potential was reduced to see if recovery would take place but inasmuch as this was not an aim of the experiment the run was discontinued shortly thereafter.

Gas production in digester A averaged about 335 cc. per hr. or about 230 percent of digester D, the control. If the organic matter was converted at the same rate in each digester, A should have produced about 4 times as much gas as the control. However, it should be remembered that the detention time in digester A was less than one fourth

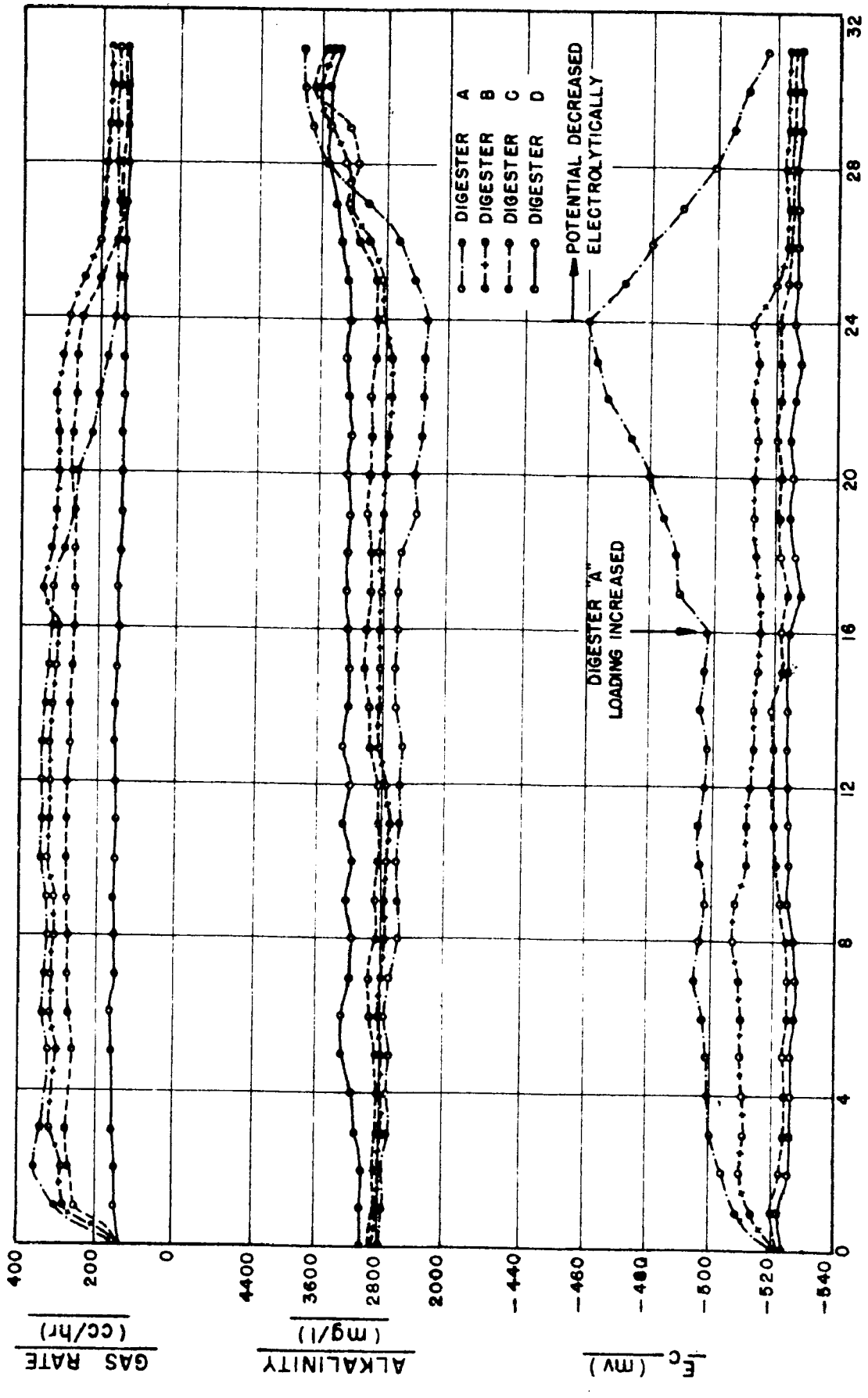


Fig. 26 Electrode Potentials, Alkalinity and Gas Rate Developed during Overloading

that of the control digester. The carbon dioxide content of the gas produced increased steadily until the twenty fourth day when it was 46 percent of the total.

It should be mentioned that on the twenty fifth day of operation, the feed in digesters B and C was returned to normal but that of digester A was maintained at the increased rate. This differentiates between the gas rate curves, all of which were falling. The drop in gas production in digesters B and C was due to the return to normal feeding, whereas the drop in gas production in digester A was due to a deterioration of the process and was actually definitely on the decline before this time.

An increase of more than 200 percent in the volatile matter in digester A indicated a further regression of biological activity. The volatile matter in digesters B and C remained relatively constant after a slight initial build up.

The effect of increased loading on the pH and alkalinity of digester A may be seen in Figs. 25 and 26. During the experiment the pH dropped as low as 6.4 and the alkalinity reached a low of 2250 mg/l.

The above facts indicate that the overloading of a digester produces results quite similar to those obtained by electrolytic control of the potential. This factor having been established, additional studies on sludge digestion through electrolytic control of the potential were possible.

POTENTIAL RANGE REQUIRED FOR DIGESTION

The purpose of this category of experimental work was aimed at determining a range of potentials within which good digestion would normally take place. Such a range is essential if electrode potentials are to be used for monitoring sludge digestion. A region of millivolt values on either side of the most optimum potential level would be of great value in this respect.

Two separate experiments were carried out to define this range. The first experiment explored the area of potential levels above normal and the second investigated potential levels below normal.

Digestion at Increased Electrode Potentials

This experiment was carried out using four digesters, three at increased potential levels and the fourth as a control. The potentials of digesters A, B and C were raised to -475, -495 and -510 respectively. The potential levels were to be poised until one of the digesters built up a volatile acids concentration of 1500 mg/l. Then the potentials were to be returned to normal levels with recovery noted if it occurred.

Throughout the run the digesters were loaded at a rate of 0.075 lb. of v.m. per cu. ft. per day, with a sludge solid content averaging 3.79 percent. The volatile solids averaged 76.8 percent of the total. The average detention

time was 24.2 days.

To begin the run, currents of 40, 20 and 10 ma. were passed through digesters A, B and C respectively. Within three days the potentials were poised at the desired level. The average potential maintained over the 16 day control period was -476 mv. for digester A, -496 mv. for B and -510 mv. for C. The potentials in all digesters were then decreased to the normal level and the controls shut off, although they were held in readiness if additional control was thought necessary.

The results of the experiment are shown in Figs. 27 and 28. To present the observed results with clarity, each digester will be considered separately, except digester D which was operating under normal conditions and produced results similar to those obtained in preceding studies.

The observation of digester C throughout the experiment indicated that the potential at which the digester was poised caused no serious difficulty. The gas rate and volatile acids were similar to those reported in the control digester. Alkalinity gradually decreased to about 2400 mg/l and pH dropped to 7.0 as a result of the change in potential. The carbon dioxide content of the sludge gas produced increased to 37 percent as compared to about 32 percent in the control. When the potential was returned to a normal value, both pH and alkalinity returned to practically the same levels as before the control was imposed. During this period the

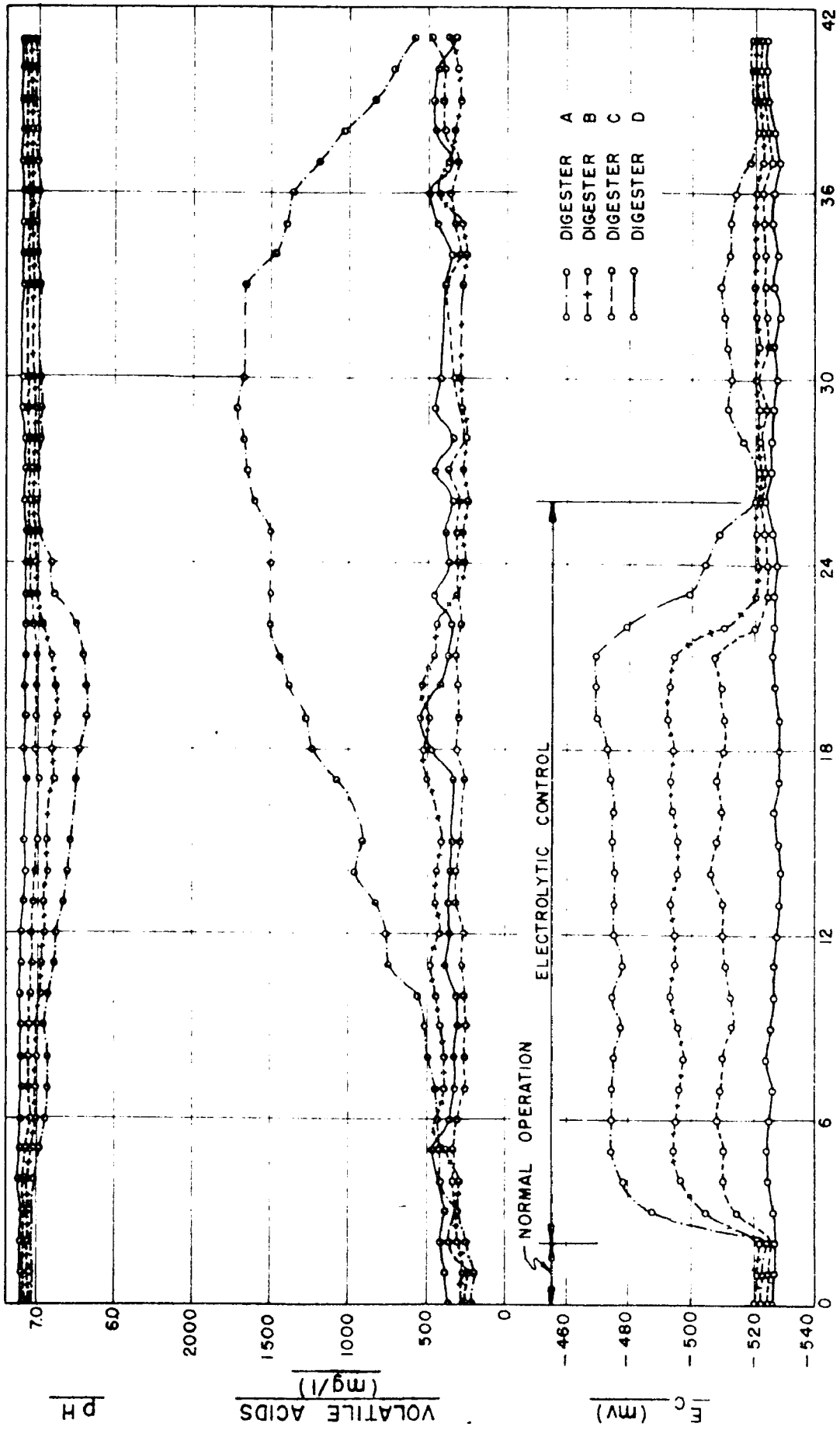


Fig. [illegible] Variation in Intermediate Acids and pH during Electrolytic Increase of Potential

carbon dioxide content returned to its original level.

Digester B presented a similar picture. At times, volatile acids were higher than might normally be expected and the daily plotted values appeared to be erratic. Throughout the run a high of 700 mg/l was recorded, although at this time the concentration of acids in the control also was high. Immediately after the potential was decreased to normal, the volatile acids fell off and remained fairly constant, between 200 and 300 mg/l. At about the same time as this decrease in volatile acids was taking place, the rate of gas production increased above the previous rate, reaching a high of 180 cc. per hr. for a period of two days. Aside from this spurt, the gas rate remained rather constant throughout. During the time the potential was being poised, the amount of carbon dioxide in the gas increased to 41 percent. After the potential had been returned to normal it decreased to 28 percent and then slowly increased to 32 percent.

The pH and alkalinity showed trends similar to those observed in digester C, but slightly more extreme. The pH decreased to 6.75 and the alkalinity dropped as low as 2000 mg/l during the control period. The pH returned to its normal level when the potential was decreased. The alkalinity increased sharply at first and then more slowly, reaching its precontrol level toward the end of the run.

Digester A reached a more critical stage. The day

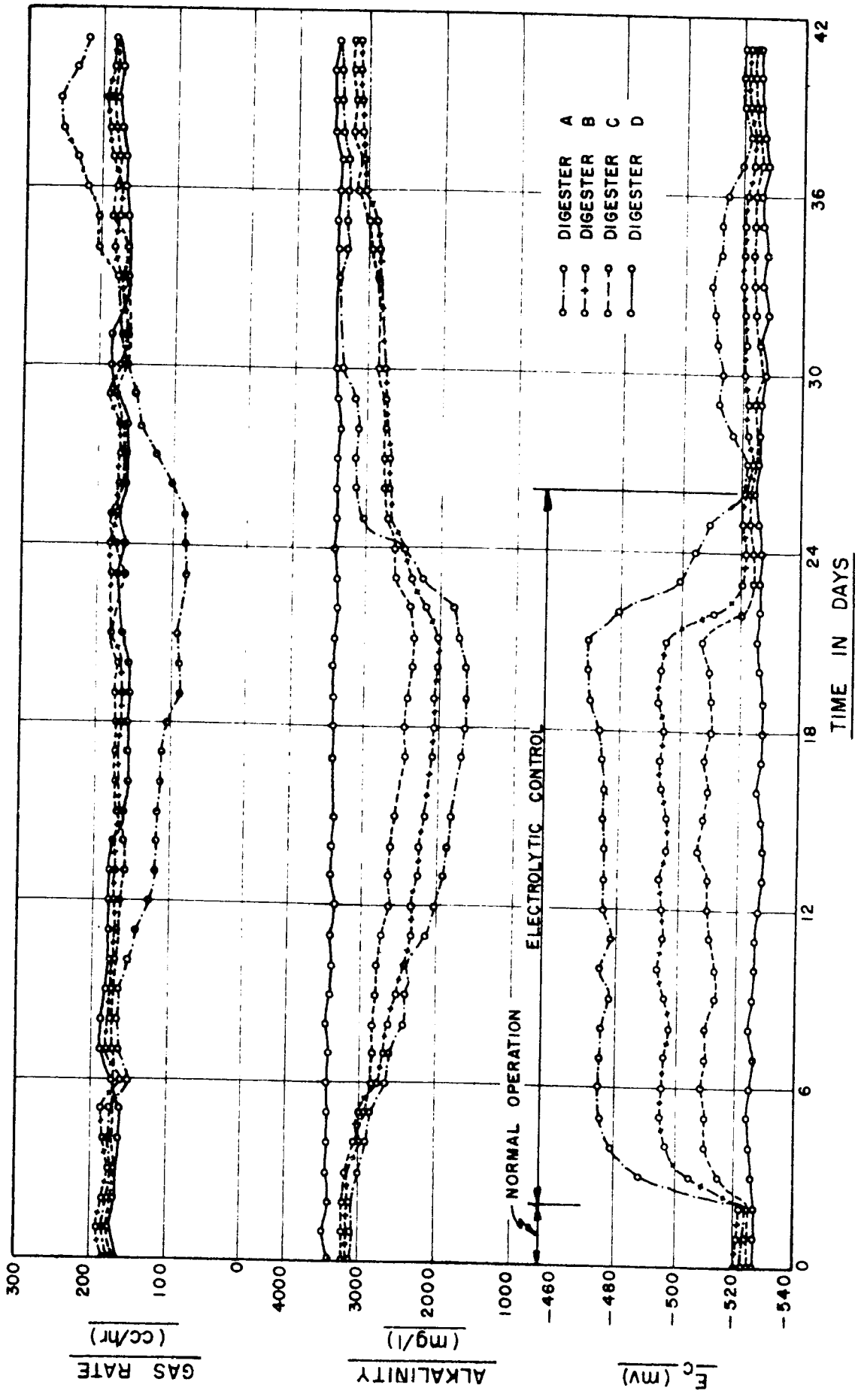


Fig. 28 Electrode Potentials, Alkalinity and Gas Rate during Electrolytic Increase of Potential

after the potential had been poised at the desired level, the acid concentration started to increase at a slow rate and continued to increase until on the twenty second day the analysis showed a concentration of 1520 mg/l. At this point and according to plan, the potentials in all digesters were returned to the normal operating range. The volatile acids increased further until the thirty third day when they began to decline. The highest concentration that was reached was 1720 mg/l. It should be noted that the electrode potential also took a decided upward trend, but did not increase enough to merit reactivating the control mechanism; however, the potential did increase to about -512 mv. The decrease in volatile acids commenced seven days after the potential had been reduced to the normal level, and it took eight days before the concentration dropped below 600 mg/l. This, along with the other parameters, indicated that recovery had taken place and the experiment was concluded.

By referring to Figs. 27 and 28 it may be seen that the gas production began to fall off at about the same time the volatile acids began to increase. The gas rate decreased gradually until the nineteenth day when it took a sharp drop down to 80 cc. per hr., where it stayed until the twenty fifth day. Then the gas production rate began to increase until it not only reached the normal value, but continued to increase until it reached a maximum of 246 cc. per hr., after which time it began a downward

trend toward normal. It should be noted that immediately after the gas production exceeded that in the control digester, a decrease in the volatile acids was initiated.

While the potential in digester A was poised at -476 mv., the carbon dioxide content of the sludge gas increased to a high of 61 percent. When the potential was electrolytically decreased, the percentage dropped to twenty six percent and then gradually increased, so that at the end of the run it was 32 percent.

The effect of the potential control on pH may be seen in Fig. 28. From the time control was begun, the pH gradually decreased reaching a low of 6.3 on the twentieth day. As usual, the pH returned to normal immediately following the electrolytic reduction of the potential in the digester.

The alkalinity of digester A varied considerably throughout the experiment. It reflected the poor condition of the digester by dropping to 1600 mg/l at one point. However, when the potential was returned to the normal range, the buffering capacity increased sharply, and the alkalinity attained its precontrol level before the digester began to recover. This wide variation in the alkalinity may be seen in Fig. 28.

In reviewing the time potential curves, it may be seen that on the nineteenth day the potential increased from -473 to -470 mv. This increase in itself was not

large, but it maintained itself even though the electrolytic control was shut off. This indicates that the potential value developed in digester A from the twentieth to the twenty second day was not maintained by the potential control mechanism, but rather by the deteriorating process. A second irregularity in the time potential curve occurred on the twenty third day of operation. The electrolytic control mechanism was accidently turned off overnight, causing the flattened portion of the curve. Neither of these irregularities affected the results to any significant degree.

The results of the preceding experiment indicate that the electrode potential may be an important tool in the evaluation of the digestion process and that a deviation from the normal digestion potential causes deterioration of the process.

Digestion at Reduced Potentials

The preceding experiment, defining digestion at increased potentials, and the following experiment, defining digestion at reduced potentials, were both essential in attempting to establish an optimum range of potentials necessary to insure good digestion.

The loading rate for this run was also set at 0.075 lb. of v.m. per cu. ft. per day. The solids fed averaged 4.15 percent, consisting of 71 percent volatile and 29 percent fixed solids. Under these conditions the average detention

time was 25 days.

The potentials were to be poised at similar levels but in an opposite direction to those in the previous experiment. This meant that the potentials in digesters A, B and C were to be poised at -575, -555 and -540 mv. respectively, with digester D again serving as the control. To obtain comparable results, the potentials were to be poised until one of the digesters, presumably digester A, developed a volatile acids concentration of 1500 mg/l. The potentials were then to be returned to normal and any further developments noted.

After the potentials reached the predetermined levels, they were controlled for a period of nine days, averaging -574, -553 and -540 mv. for digesters A, B and C respectively. While the potentials were being returned to their normal level it was found that very little control was needed. The potentials had a tendency toward returning to normal without assistance from the control mechanism. In contrast to the preceding experiment, once the potentials had returned to the normal operating range they remained between -520 and -530 mv. The electrode potentials, as well as the other digestion parameters, are shown in Figs. 29 and 30.

Digester C showed only slight deviations from the uncontrolled digestion taking place in the control. There was no build up in volatile acids and only a slight initial drop in the gas production rate. Gas production returned

to a fairly normal value soon after initiation of the experiment and remained constant during the remainder of the run. The carbon dioxide content of the gas produced showed a similar trend, first decreasing to about 24 percent and then gradually increasing to about 29 percent.

The pH and alkalinity of digester C reflected the change in potential more directly. The pH increased to about 7.3 while the alkalinity rose to about 4100 mg/l during the control period. After the potential was brought back to its precontrol level, the pH did not quite return to normal and the alkalinity remained high, showing that a greater buffering capacity had been established in the digester.

The observations made on digester B, whose potential was decreased to -553 mv., were similar to those obtained from digester C. The same consistency of a desirable concentration of volatile acids was recorded. Gas production fell off slightly more than in digester C and the carbon dioxide content dropped as low as 19 percent at one point.

The pH in digester B increased to 7.55 and the alkalinity remained high after the digester potential was returned to normal.

Digester A, on the other hand, appeared to be in trouble immediately after its potential was poised at -575 mv. Volatile acids began to increase on the sixth day and, except for the analysis on the tenth day, would have shown a curve somewhat approximating an exponential increase.

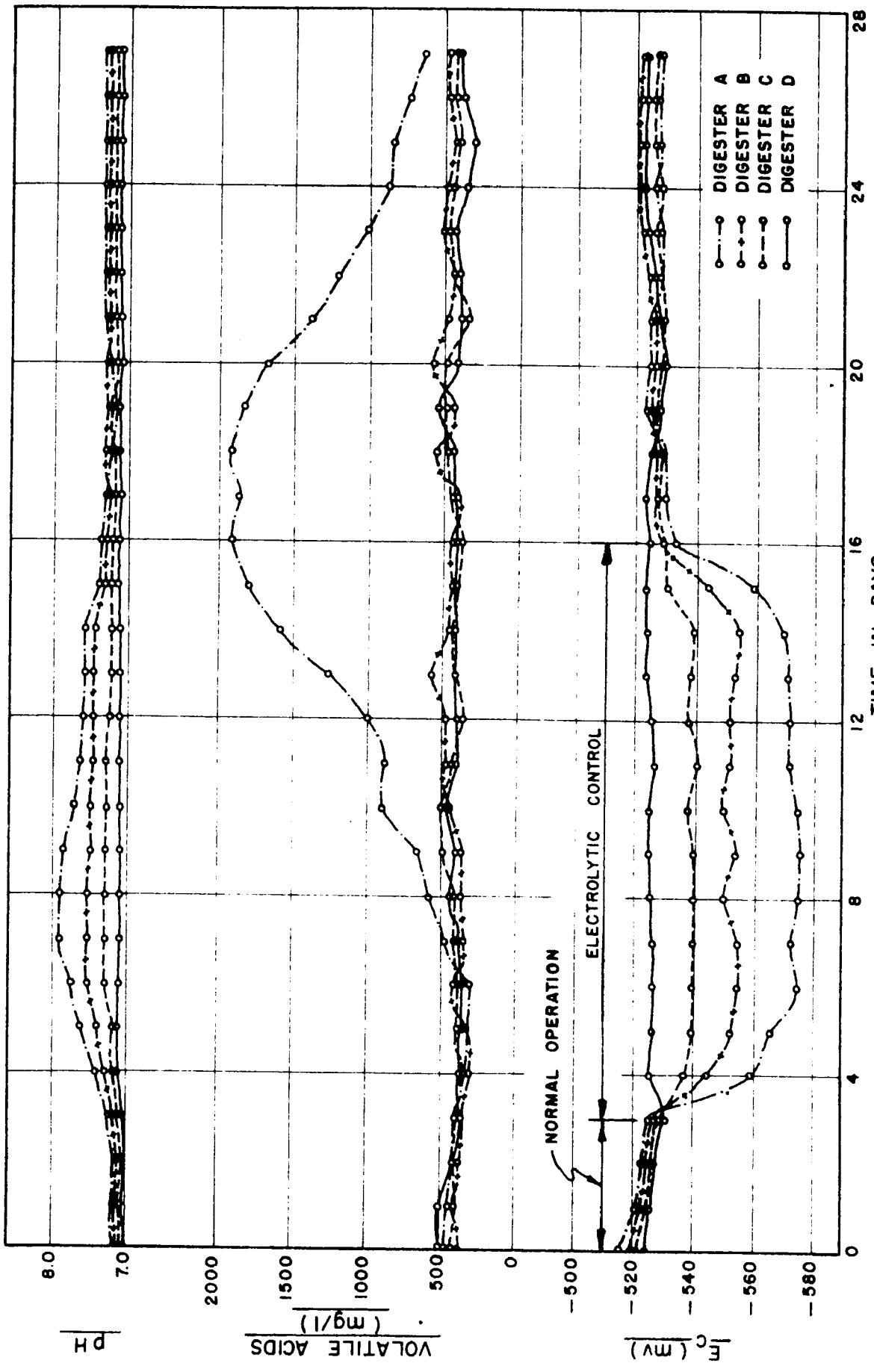


Fig. 29 Electrode Potentials, Volatile Acids and pH during Electrolytic Decrease of Potential

According to the predetermined plan, the potential in all digesters were returned to normal on the fourteenth day when the concentration of volatile acids in digester A reached 1570 mg/l. The acid concentration, however, continued to increase until it reached a high of 1920 mg/l before it began its decrease, which continued until the end of the experiment.

The gas rate in digester A was also greatly affected. A gradual drop was recorded up to the eighth day when gas was being produced at a rate of 112 cc. per hr. The following day the gas production rate was only 48 cc. per hr., continuing at this rate until the twelfth day, when it exhibited an increase to 65 cc. per hr. This upward trend in the rate of gas production continued when the potential in digester A was increased to its precontrol level. As in the previous experiment, the gas rate then increased up to and beyond the normal rate. As soon as the gas rate was higher than that of the control, the volatile acids in digester A began to decrease. The gas rate then reached a peak of 185 cc. per hr. and began a downward trend as the volatile acids in the digester fell below 1000 mg/l. Throughout the electrolytic control period the amount of carbon dioxide in the sludge gas decreased to as low as 11 percent on the eighth day of operation. It should be noted that the gas rate also fell off sharply on the eighth day.

The pH and alkalinity in digester A, as in digesters

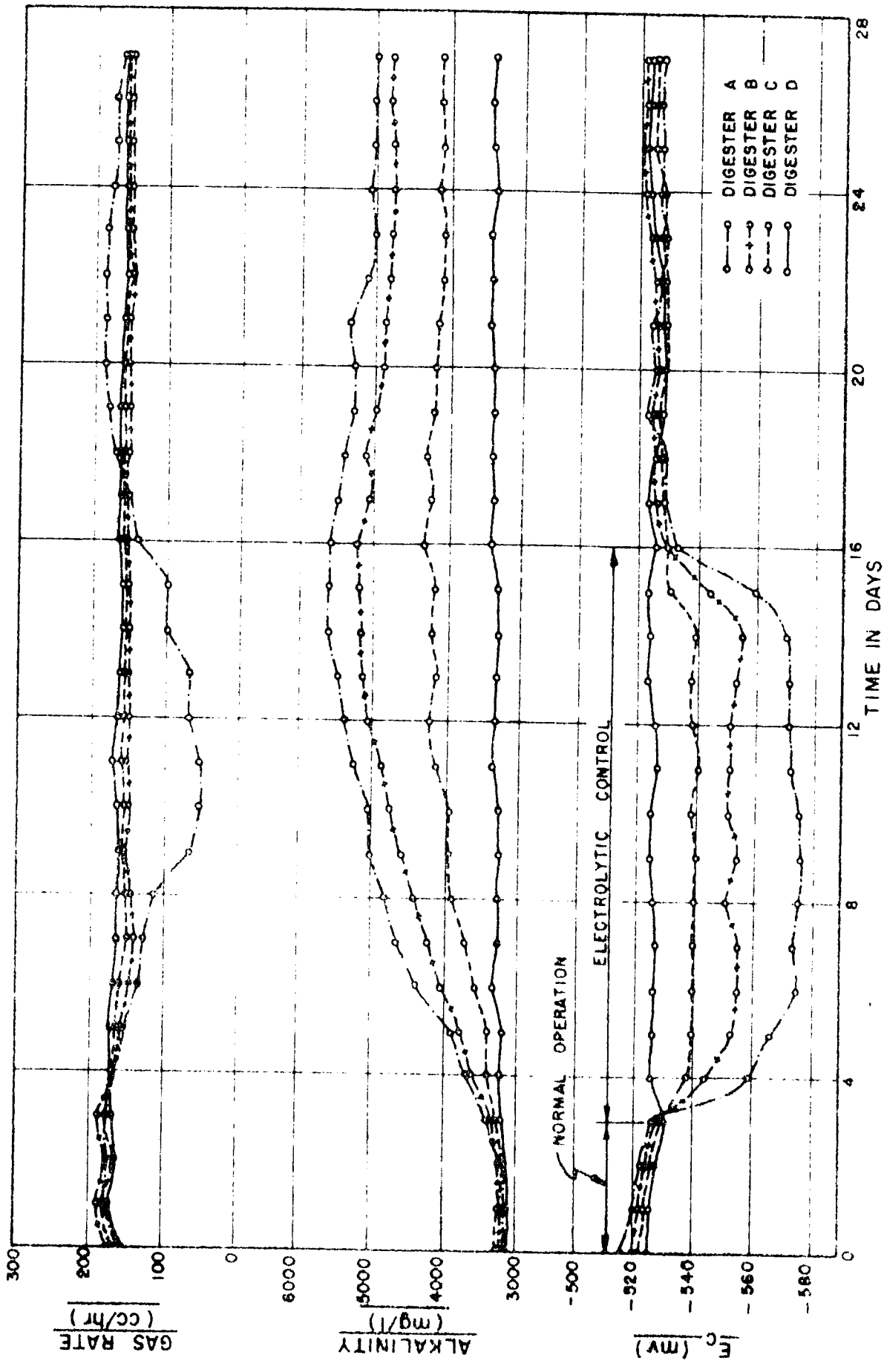


Fig. [illegible] Electrode Potentials, Alkalinity and Gas Rate During Electrolytic Decrease of Potential

B and C, increased during the control period, with the pH attaining a value of 7.92 while the alkalinity rose to over 5550 mg/l.

The results of the experimental work have been presented in the preceding sections. An attempt was made to present the data in three separate sections although complete differentiation is impossible. The first group of experiments dealt with electrode potentials developed during uncontrolled or normal digestion. The second group of experiments consisted of preliminary studies using electrolytic control of the potential. It was also aimed at comparing the results obtained by electrolytically poising the potential with those obtained from the overloading of a digester. The third section reported the results obtained when potentials are poised at levels above and below that usually developed in uncontrolled digestion.

The data thus presented will enable a thorough discussion of the use and control of electrode potentials during the anaerobic digestion of sewage sludge.

DISCUSSION

The results presented in the preceding sections will be discussed in the same order in which they were observed. In this way, the subject will be discussed first with respect to the electrode potential levels developed during normal digestion, followed by some factors concerning electrolytic potential control and finally the effect of this control on the digestion process.

It is apparent from the observations made during the experimental work that electrode potentials, when properly taken and interpreted, can be of great value in evaluating the progress of sludge digestion. Since the derivation of the oxidation-reduction potential equation is based on the assumptions that the reaction is reversible and that thermodynamic equilibrium exists, and since sludge digestion is a steady state condition producing a product from the starting material, the term "electrode potential" instead of "oxidation-reduction potential" has been used throughout this dissertation. Although oxidation-reduction potentials have no meaning in sludge digestion, electrode potentials can provide a certain amount of knowledge regarding the state of the digestion process. Inasmuch as most laboratory potential readings are made using the standard calomel reference electrode, all potential values given in this thesis have been referred to the calomel electrode.

The potential values reported have been obtained with clean surface platinum and gold electrodes. A proper potential reading can only be attained with a clean electrode and as a result all electrodes were cleaned by scouring with levigated alumina followed by soaking in a cold ten percent nitric acid solution and distilled water. Each electrode was cleaned once every two weeks. Two further conditions which affect the interpretation of electrode potentials are clogging of the salt bridge and accumulation of sludge on the tip of a metallic electrode. Clogging of the salt bridge may result in electrode potential readings that are somewhat higher than those that actually exist. A difference of as much as fifteen mv. has been observed and had the condition not been rectified, greater differences probably would have resulted. The accumulation of sludge particles on the electrode surface will cause the potential observed to drop from 50 to 100 mv. lower than it actually is. This is the difficulty occurring most often and can only be remedied by removing and cleaning the electrode. If, however, three or preferably four electrodes are used, then the reading from the electrode on which sludge has been caught can be discounted while averaging the remaining readings. Most often this condition is not permanent and after the sludge is dislodged the electrode reading will return to normal.

The electrodes which had been removed from the digester,

cleaned and replaced did not give stabilized readings until six to ten hours after reinsertion. Inasmuch as each digester contained four electrodes and only two were cleaned at any one time no serious problem was created. It is to be assumed that an instantaneous electrode potential measurement of a sample would be difficult to determine. This becomes apparent when it is noted that while the electrodes are attempting to come into equilibrium, the potential of the sample is changing.

With the above considerations in mind, electrode potentials in sludge digestion are reproducible to within 5 mv. and are definite indicators of the process.

Electrode Potentials During Sludge Digestion

The electrode potentials developed in the normal digestion of sewage sludge in all the experiments carried out ranged between -520 and -530 mv. This is the potential which exists when the process has reached equilibrium.

In the case of a slow start-up the electrode potentials increased at first and then began to fall. When the potential dropped to the normal range digestion approached equilibrium, indicating that electrode potentials bear a relationship to the other digestion parameters.

During normal digestion, the electrode potential curve is practically parallel to the volatile acids plot. This is exceptionally well represented in Fig. 12. The increase in volatile acids immediately after start-up is accompanied

by an increase in potential. Once the potential declined to a level between -520 and -530 mv., the concentration of volatile acids remained constant. It would appear that the initial rise in volatile acids is caused by the increased activity of the acid formers while the methane producers are still in what might be termed the lag phase. The rise in acids results in a higher ratio of oxidant to reductant and must be associated with an increase of potential. As the concentration of volatile acids is reduced the oxidant is being removed by its conversion to gas and a different equilibrium is established. As long as the acids produced are continually being broken down to gas this equilibrium will be maintained and a constant potential will result.

Morgan (80) has studied the variation of gas rate and volatile acids after feeding. Both parameters are reported to reach a peak within the range of three to five hours after feeding with subsequent return to their prefeed levels. The results obtained in this thesis have shown a similar relationship between gas rate and electrode potentials although the change in potential is small compared to the change in the rate of gas production. It may be deduced, therefore, that the daily variation in potential is similar to the daily variation in volatile acids. However, as long as the acids are being converted to gas the change in potential is insignificant. If, on the other hand, gasification is not taking place there is an immediate

increase in volatile acids and electrode potential levels. This, therefore, identifies one real value of the electrode potential. It immediately reflects an increase in volatile acids and is a much easier and less time consuming measurement to make. It has also been found that poising the potential outside the desirable range stated above results in the inhibition of the methane producers and an accumulation of volatile acids.

The experiments also showed that gas production did not reach its normal level until electrode potentials had fallen to the desirable level. Any change in potential results in a change in the rate at which gas is produced. In one instance when the digestion temperature was increased from 32°C to 35°C an immediate drop in potential took place, and simultaneously an increase in gas rate was observed, probably due to a temporary increase in the activity of the methane producers.

Alkalinity and pH have shown a direct relationship to the potential. The results obtained show that there is a change of one pH unit for each 70 mv. change in the potential, and a 60 mg/l change in alkalinity for a 10 mv. change in potential.

The correlations presented above occurred repeatedly throughout the experimental work. During one run three similar digesters operating under identical conditions resulted in highly reproducible results.

Five different municipal sludges were digested under identical contitions. Extensive electrode potential measurements were taken during the course of the digestion. In all cases the normal potential fell within the range described previously. The lowest millivolt reading was developed in the Saline sludge, while the highest occurred in the Ypsilanti sludge. These two values were -528 and -521 mv. respectively. It was found that sludges from sewages containing industrial wastes resulted in a higher daily variation of potential. If the potential reading was taken at the same time each day, however, the potential was found to be relatively constant day after day. Since the sludges digested covered a wide range, it appears that most sludges must develop essentially the same potential under normal digestion conditions.

In contrast to earlier work (76)(95)(126), of special significance is the highly consistent and reproducible electrode potential measurements recorded throughout the experimental work. This emphasizes the importance of certain precautions in measurements to assure reliability. The contribution by Molof (75) in this regard is, therefore significant.

Potential Control in Sludge Digestion

It has been shown that the potential within a laboratory digester can be increased, decreased or held constant using the electrolytic control mechanism previously described.

Experimental results indicate that when the potential is poised outside the range usually developed in sludge digestion, the process begins to deteriorate, as shown by the various parameters observed.

Deterioration of the process was induced by electrolytically poising the potential and also by overloading a digester, and in addition a comparison was made of the observations. Results of both methods of changing the potential would have to give similar results in the electrolytic method of control is to be fruitful in further laboratory studies.

Inasmuch as the electrolytic control was impressed on the digester through a saturated salt solution, it was necessary to determine whether or not the chloride ions passing into the digester were significant and, if so, what effect did such a transfer have on the process. For this reason chloride determinations were made and it was found that chloride ions did in fact accumulate in the digesters. However, under the worst condition imposed, that is, with the digester that received the most adverse control, a chloride concentration of just under 1000 mg/l was induced. At the same time, the digester in the next worst condition showed a chloride concentration of 685 mg/l while that with the least amount of control accumulated chloride ions to the extent of 466 mg/l. The control digester carried a concen-

tration of chloride ions of 328 mg/l. The accumulation of chloride ions in the digesters to which electrolytic control was applied eventually reached an equilibrium state. The attainment of such an equilibrium was possible because of periodic feedings and withdrawals. The highest chloride level attained could not be inhibitory to the process, since Buswell et al (60) showed that chloride concentrations under 10,000 mg/l had little or no effect on a normal digestion process.

During the times when the potential was increased the problem could be compounded. Since an electrolytic increase in the potential leaves hydrogen ions in the digester, it was thought that a combination of the hydrogen ions and chloride ions might produce a mineral acid, thus reducing the pH in a manner unlike that produced under normally occurring digestion phenomena. Inasmuch as the pH and potential values were recorded daily, a correlation between these two parameters could be obtained during both the electrolytic control and overloading runs. The data have been plotted in Fig. 31 and indicate that the relation between E_c and pH are similar in both cases.

Thus, it may be said that the electrolytic method of control can alter and poise the potential in the digester without producing anything unusual or anything that might be considered detrimental to the process.

The correlation of electrode potentials with the other monitoring parameters seems to strengthen the argument

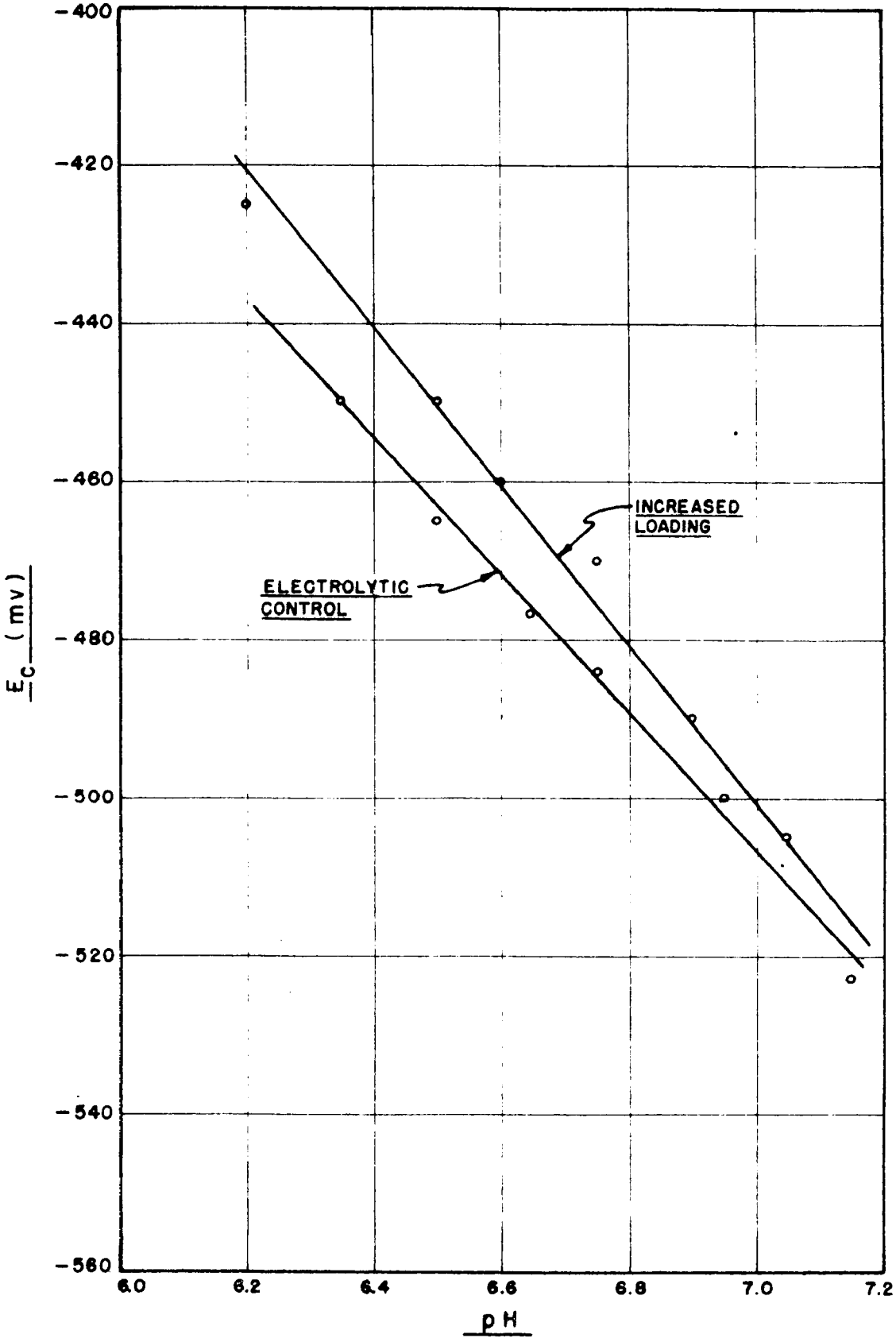


Fig. 31 Relation between E_c and pH under Two Different Conditions

presented above. During the experiment when electrolytic control was maintained, the volatile acids increased after the potential was poised at a critical level, indicating that the potential was unfavorable to the proliferation of methane producers and an accumulation of acids follows. The accumulation of acids in each case was accompanied by a decrease in gas rate, as would be expected.

When the potential was far enough away from the normal value, the acid formers are inhibited, however slightly, and a much more serious condition exists. This condition shows a decreasing rate of volatile acids formation as a result of the reduced activity of the acid formers. When the environment is returned to normal the acid formers rapidly become active and convert the organic matter, previously unconverted, to volatile acids, and the concentration of acids begins to soar. This induces a hazard to the methane producers, which are known to be inhibited by a high acid concentration, the net result being a digester that is hard to recover. This phenomenon may be seen in Figs. 23 and 25.

The above discussion shows that the monitoring parameters behave in the same manner whether the digester is made to fail by excessive additions of raw sewage solids, or by altering the potential electrolytically. As a result, electrolytic control can be considered an excellent method for evaluating the digestion process in laboratory studies.

During these studies, additional information on digestion at increased solids loading was made available. It was found that digester loadings up to 0.225 lb. of v.m. per cu. ft. per day at a detention time of 8.6 days produced good digestion, according to the monitoring parameters studied herein. It may be seen (Figs. 25 and 26) that under this condition the electrode potential was the most sensitive parameter. Although the concentration of volatile acids remained fairly constant, the increased loading was reflected by a 10 mv. increase in the potential. Gas production was slightly less than what might be expected but could be attributed to the shorter detention time.

On the other hand, a loading rate of 0.300 lb. of v.m. per cu. ft. per day at a detention time of 5.7 days showed a highly unstable condition, driving the potential up by about 30 mv. The concentration of volatile acids was erratic at about 1400 mg/l but digestion, although poor, was taking place throughout this 16 day period.

At a loading rate of 0.375 lb. of v.m. per cu. ft. per day with a detention time of 4.1 days, the process failed completely. It may be seen (Fig. 25) that this failure was accompanied by a steadily increasing potential.

It would appear from the preceding that, under conditions of continuous mixing and twice daily additions of raw sludge, digestion can take place at a loading rate of 0.300 lb. of v.m. per cu. ft. per day if the detention time is increased to about 10 days.

The observations made in this portion seem to indicate that increased solids loadings may be feasible with electrode potential control. The basis for this statement is that digesters which had gone "sour" were made to recover by impressing a desirable potential on the units even though loading was continued. How effective this method will be and to what extent loadings may be increased must be determined in future studies.

Potential Range Required for Digestion

The data observed indicate that good digestion takes place within a limited range of potentials and that digestion is feasible at somewhat less limited range while the process deteriorates when the potential is very much different from the normal value. All results point up the fact that during good digestion the potential developed is the optimum. The studies made here determined how far from the optimum the potential must be before deterioration takes place.

With the potentials poised on the positive side of normal, it appears as though favorable digestion will take place up to -505 mv. and a less favorable digestion can occur at potentials as high as -495 mv. Anything higher than -495 mv. will result in a "souring" of the digester. When the potential of the digester was poised at -475 mv. (Figs. 27 and 28) a gradual build up of volatile acids occurred, the condition becoming steadily worse with time. When the optimum environment was recreated after the volatile

acid concentration increased to 1520 mg/l the digester recovered. Before recovering, however, the acid concentration increased to 1720 mg/l, indicating that the acid formers were recovering much faster than the methane formers. It is well known that methane producing organisms require more time to develop an active culture. Thus it was shown that a digester can be recovered after the volatile acid concentration had surpassed 1500 mg/l, even with continuous feeding, if an optimum environment is maintained. It should be remembered, however, that the process will become slightly worse before recovery begins.

Similar results were obtained when the potential was poised on the negative side of the normal digestion potential. Poising at -540 mv. did not seem to retard digestion while poising at -553 mv. resulted in a condition which may be called less desirable. Poising at a potential of -573 mv. results in a rapid deterioration of the process, more so than that which developed on the positive side. The concentration of volatile acids increased to 1600 mg/l in only eleven days. However, when a proper environment was created, recovery was also more rapid although the volatile acid concentration did reach 1920 mg/l before recovery began.

It may be concluded that the effect on the digestion process is the same whether the potential is poised on the positive or negative side of the normal digestion potential. When the potential was between -520 and -530 mv. optimum

digestion took place. Good digestion was indicated when the potential fell between -510 and -540 mv. A poorer quality digestion will occur between -495 and -555 mv. while deterioration of the process will result when the potential is greater than -495 and less than -555 mv.

SUMMARY

A study was made on the electrode potentials developed during the anaerobic digestion of sewage sludge. Reproducible results were obtained when three digesters were operated in parallel under identical conditions. A study of the digestion potential of five different sludges was made and in each case the potential value was found to lie within an eight mv. range.

An electrolytic method of potential control was adapted for use in laboratory scale digesters. With this type of control it was possible to increase, decrease and poise the potential at any desired level for any period of time. A study of the effect of poised potentials on the digestion process was carried out.

As a consequence of the preceding study, additional information on digestion at increased solids loading became available. The sensitivity of electrode potentials to increased loading rates was determined. It was found that electrode potentials are as sensitive as any of the monitoring parameters presently being used, if not more so.

Ranges of potential values that would permit optimum, good, poor digestion were established. It was found that if the potential was outside the above ranges the digestion process would deteriorate. Recovery of digestion after an

accumulation of volatile acids exceeding 1500 mg/l was successfully attempted even though continuous feeding was practiced.

CONCLUSIONS

1. Electrode potentials are a sensitive indicator of the sludge digestion process and may be used as a monitoring parameter.
2. Changes in gas production, volatile acids concentration, pH and alkalinity have been shown to take place after certain changes in the electrode potential.
3. The electrode potentials developed in five sewage sludges from widely different municipal sources were essentially the same.
4. An electrolytic method of potential control capable of increasing, decreasing and poising the potential was adapted for use in the laboratory scale digesters. The results produced are similar to those which occur naturally in the practice of sludge digestion.
5. By permitting precise control of electrode potentials the electrolytic method of control can be of invaluable assistance in laboratory studies.
6. Whether or not this control mechanism can be adapted to field practice cannot be concluded at this time although the possibility does exist.
7. From the studies carried out using the electrolytic method of control, four ranges of electrode potential values are proposed. These are:

E_c in mv.	Digestion
-520 to -530	optimum
-510 to -540	good
-495 to -555	fair to poor
$-495 < E_c < -555$	not possible

8. It is proposed that a loading rate of 0.300 lb. of v.m. per cu. ft. per day at a detention time of 10 days is feasible if feedings are made twice daily and the contents of the digester are continually mixed.
9. If the electrode potential is maintained within the optimum range defined above, still higher loading rates may be possible.

BIBLIOGRAPHY

1. Lohmeyer, G. T. "A Review of Sludge Digestion," Sewage and Industrial Wastes, 31, 221 (1959).

2. Buswell, A. M. and Neave, S. L. "Laboratory Studies of Sludge Digestion," Illinois State Water Survey Bulletin, 30, (1930).

3. Heukelekian, H. and Mueller, P. "Transformations of Some Lipids in Anaerobic Sludge Digestion," Sewage and Industrial Wastes, 30, 1108 (1958).

4. Heukelekian, H. "Basic Principles of Sludge Digestion," Biological Treatment of Sewage and Industrial Wastes, Vol. 2, 25, Reinhold Publishing Co., N. Y., (1954).

5. Heukelekian, H. and Balmat, J. L. "Chemical Composition of the Particulate Fractions of Domestic Sewage," Sewage and Industrial Wastes, 31, 413 (1959).

6. Kozma, A. B. "Sludge Digestion-Operation and Control," Sewage Works Journal, 16, 700 (1944).

7. "Sewage Treatment Plant Design," Federation of Sewage and Industrial Wastes Association Manual of Practice No. 8, (1959).

8. Chanin, G. "Fundamentals of Sludge Digestion. II. Biology and Operation," Water and Sewage Works, 108, 85 (1961).

9. Schulze, K. L. and Raju, B. Naga "Studies on Sludge Digestion and Methane Fermentation. II. Methane Fermentation of Organic Acids," Sewage and Industrial Wastes, 30, 164 (1958).

10. Chanin, G. "Fundamentals of Sludge Digestion. I. Biochemical Background," Water and Sewage Works, 108, 55 (1961).

11. Simpson, J. R. "Some Aspects of the Biochemistry of Sludge Digestion," Waste Treatment, Pergamon Press, N. Y., 1960.

12. Heukelekian, H. "A Discussion of the Symposium on Sludge," Sewage Works Journal, 16, 715 (1944).

13. Nickerson, Walter J. "Transformations of Carbon Compounds by Microorganisms," Ind. and Eng'g. Chem., 48, 1411 (1956).

14. Lackey, J. B. and Hendrickson, E. R. "Biochemical Bases of Anaerobic Digestion," Biological Treatment of Sewage and Industrial Wastes, Vol. 2, 9. Reinhold Publishing Corp., N. Y., 1958.

15. Oginsky, E. L. and Umbreit, W. W., An Introduction to Bacterial Physiology, W. H. Freeman and Co., San Francisco, 1959.

16. Wood, W. A. "Fermentation of Carbohydrates and Related Compounds," The Bacteria. II. Metabolism, edited by Gunsalus, I. C. and Stanier, R. Y., Academic Press, N. Y., 1961.

17. Haseltine, T. R. "Preconditioning and Digestion of Sewage Sludge," Water and Sewage Works, 96, 271 (1949).

18. Tarvin, D. and Buswell, A. M. "The Methane Fermentation of Organic Acids and Carbohydrates," Journal American Chemical Society, 56, 1751 (1934).

19. Stadtman, T. C. and Barker, H. A. "Studies on Methane Fermentation. VIII. Tracer Experiments on Fatty Acid Oxidation by Methane Bacteria," Jour. Bacteriology, 61, 67 (1951).

20. Bloodgood, D. E. "Sludge Digestion," Water and Sewage Works, 104, 38 (1957).

21. Rudolfs, Willem "Decomposition of Grease during Digestion, Its Effect on Gas Production and Fuel Values of Sludge," Sewage Works Journal, 16, 1125 (1944).

22. Delwiche, C. C. "Biological Transformations of Nitrogen Compounds," Ind. and Eng. Chem., 48, 1421 (1956).

23. Waksman, S. A. Principles of Soil Microbiology, Williams and Wilkens Co., Balt., Md., 1952.

24. Stadtman, T. C. and Barker, H. A. "Studies on Methane Fermentation. IX. The Origin of Methane in the Acetate and Methanol Fermentations by Methanosarcina," Jour. Bacteriology, 61, 81 (1951).

25. Stadtman, T. C. and Barker, H. A. "Studies on Methane Fermentation. X. A New Formate-Decomposing Bacterium, Metanococcus Vaniellii," Jour. Bacteriology, 62, 269 (1951).

26. Barker, H. A. "Biological Formation of Methane," Ind. and Eng'g. Chem., 48, 1438 (1956).

27. Heukelekian, H. and Heinemann, B. "Studies on the Methane-Producing Bacteria. I. Development of a Method for Enumeration," Sewage Works Journal, 11, 426 (1939).

28. Heukelekian, H. and Heinemann, B. "Studies on the Methane-Producing Bacteria. II. Enumeration in Digesting Sewage Solids," Sewage Works Journal, 11, 436 (1939).

29. Heukelekian, H. and Heinemann, B. "Studies on the Methane-Producing Bacteria. III. Digestion of Sewage Solids by the Addition of Enriched Cultures of Methane-Producing Organisms," Sewage Works Journal, 11, 571 (1939).

30. Heukelekian, H. and Heinemann, B. "Studies on the Methane-Producing Bacteria. IV. Growth of Sludge Liquors," Sewage Works Journal, 11, 965 (1939).

31. Mylroie, R. L. and Hungate, R. E. "Experiments on the Methane Bacteria in Sludge," Canadian Journal of Microbiology, 1, 55 (1954).

32. Buswell, A. M. and Sollo, F. W., Jr. "The Mechanism of Methane Fermentation," Journal American Chemical Society, 73, 1809 (1951).

33. Buswell, A. M., Fina, L., Mueller, H. and Yahiro, A. "Use of C^{14} in Mechanism Studies of Methane Fermentation. II. Propionic Acid," Journal American Chemical Society, 73, 1809 (1951).

34. Kluyver, A. J. and Schnellen G. T. P. "On the Fermentation of Carbon Monoxide by Pure Cultures of Methane Bacteria," Archives of Biochemistry, 14, 57 (1947).

35. Salle, A. J. Fundamental Principles of Bacteriology, McGraw-Hill, Inc., N. Y., 1954.

36. Fair, G. M. and Moore, E. W. "Time and Rate of Digestion and Their Variation with Temperature," Sewage Works Journal, 6, 3 (1934).

37. Fair, G. M. and Moore, E. W. "Observations on the Digestion of a Sewage Sludge over a Wide Range of Temperatures," Sewage Works Journal, 9, 3 (1937).

38. Golueke, C. G. "Temperature Effects on Anaerobic Digestion of Raw Sewage Sludge," Sewage and Industrial Wastes, 30, 1225 (1958).

39. Sprague, J. T. "Operation of Sludge Digesters," Wastes Engineering, 23, 461 (1952).

40. Mueller, L. E., Hindin, E., Lunsford, J. V. and Dunstan, G. H. "Some Characteristics of Anaerobic Digestion. I. Effect of Loading," Sewage and Ind. Wastes, 31, 669 (1959).

41. Gould, R. H. "Economical Practices in the Activated Sludge and Sludge Digestion Processes," Sewage and Industrial Wastes, 31, 399 (1959).

42. Wooten, J. L. "Proper Sludge Digestion," Water and Sewage Works, 104, 278 (1957).

43. Cassell, E. A., and Sawyer, C. N. "A Method of Starting High Rate Digesters," Sewage and Industrial Wastes, 31, 123 (1959).

44. Orford, H. E., Egan D. D. and Foley, J. P. "Rapid Start Up of Digesters at a Small Treatment Plant," Sewage and Industrial Wastes, 31, 1230 (1959).

45. Etzel, J. E. and Pohland, F. G. "Volatile Acid Formation during Sludge Digestion," Public Works, 91, 105 (1960).

46. American Public Health Association, Inc., "Standard Methods for the Examination of Water, Sewage and Industrial Wastes," Waverly Press Inc., Balt., Md., 1950.

47. Buswell, A. M. "Fundamentals of Anaerobic Treatment of Organic Wastes," Sewage and Industrial Wastes, 29, 717 (1957).

48. Buswell, A. M. "Important Considerations in Sludge Digestion. II. Microbiology and Theory of Anaerobic Digestion," Sewage Works Journal, 19, 28 (1947).

49. Backmeyer, D. P. "How to Avoid Sour Digesters," Water and Sewage Works, 102, 369 (1955).

50. Morgan, P. F. and Neuspiel, P. J. "Environment Control of Anaerobic Digestion with Gas Diffusion," Biological Treatment of Sewage and Industrial Wastes, Vol. 2, 61 Reinhold Publishing Corp., N. Y., 1958.

51. Chmielowski, J., Simpson, J. R. and Isaac, P. C. G. "Use of Gas Chromotography in Sludge Digestion," Sewage and Ind. Wastes, 31, 1237 (1959).

52. Schlenz, Harry E. "Important Considerations in Sludge Digestion. I. Practical Aspects," Sewage Works Journal, 19, 19 (1947).

53. Sawyer, C. N., Howard, F. S. and Pershe, E. R. "Scientific Basis for Liming of Digesters," Sewage and Industrial Wastes, 26, 935 (1954).

54. Heukelekian, H. "Volatile Acids in Digesting Sewage Sludge," Ind. and Eng'g. Chem., 20, 752 (1928).

55. Shafer, S. W. "Initial Digester Start-Up at Alexandria, Virginia," Sewage and Industrial Wastes, 29, 1190 (1957).

56. Giles, H. L. "Liming of Sludge Digesters or Digestion Compartments," Sewage Works Journal, 21, 1072 (1949).

57. McCarty, P. L. and McKinney, R. E. "Volatile Acid Toxicity in Anaerobic Digestion," Jour. Water Pollution Control Federation, 33, 223 (1961).

58. McCarty, P. L. and McKinney, R. E. "Salt Toxicity in Anaerobic Digestion," Jour. Water Pollution Control Federation, 33, 399 (1961).

59. Sawyer, C. N. and Grumbling, J. S. "Fundamental Considerations in High Rate Digestion," Proceedings American Society of Civil Engineers, Sanitary Engineering Division, 86, SA2 49 (1960).

60. Buswell, A. M., Pagano, J. F. and Sollo, F. W., Jr. "Effect of Sodium Sulphate and Chloride on Anaerobic Digestion," Industrial and Eng'g Chemistry, 41, 596 (1949).

61. Sawyer, C. N. "A Laboratory Evaluation of High-Rate Sludge Digestion," Sewage and Industrial Wastes, 27, 1356 (1955).

62. Torpey, W. N. "High-Rate Digestion of Concentrated Primary and Activated Sludge," Sewage and Industrial Wastes, 26, 479 (1954).

63. Hindin, E. and Dunstan, G. H. "Some Aspects of Sludge Digestion," Water and Sewage Works, 107, 457 (1959).

64. Rankin, R. S. "Digester Capacity Requirements," Sewage Works Journal, 20, 478 (1948).

65. Rudolfs, W. "Gas Yield from Sewage Sludge," Sewage Works Journal, 4, 444 (1932).

66. Morgan, P. F. "Studies of Accelerated Digestion of Sewage Sludge," Sewage and Industrial Wastes, 26, 472 (1954).

67. Buswell, A. M. "Design and Loading Factors for Anaerobic Fermentation Plants," Proc. of the Fifth Industrial Waste Conference, Purdue University, 168 (1949).

68. Neave, S. L. and Buswell, A. M. "The Anaerobic Oxidation of Fatty Acid," Journal American Chemical Society, 52, 3308 Aug. (1930).

69. Bloodgood, D. E. "Gas from Sewage Sludge," Water and Sewage Works, 101 512 (1954).

70. Mahlie, W. S. "Sulphur in Sewage," Sewage Works Journal, 6, 547 (1934).

71. Aulenbach, D. B. and Heukelekian, H. "Transformation and Effects of Reduced Sulphur Compounds in Sludge Digestion," Sewage and Ind. Wastes, 27, 1147 (1955).

72. Lackey, J. B. "Biology of Sewage Treatment," Sewage Works Journal, 21, 659 (1949).

73. Miller, F. H. and Barron, W. T. "The CO_2 Alarm in Digester Operation," Water and Sewage Works, 104, 362 (1957).

74. Walker, H. H. "Carbon Dioxide as a Factor Affecting Lag in Bacterial Growth," Science, 76, 602 (1932).

75. Molof, A. H. A Study of Oxidation-Reduction Potentials Applied to Sewage Sludge Digestion, Ph. D. Thesis, University of Michigan, 1961.

76. Grune, W. N. and Chueh, Chun-Fei "Redox Potentials in Waste Treatment-Laboratory Experiences and Applications," Sewage and Ind. Wastes, 30, 479 (1958).

77. Symons, G. E. and Buswell, A. M. "The Methane Fermentation of Carbohydrates," Journal American Chemical Society, 55, 2028 (1933).

78. Sawyer, C. N. "High Rate Digestion," Water and Sewage Works, 105, 255 (1958).

79. Estrada, A. A. "Design and Cost Considerations in High Rate Digestion," Proceedings American Society of Civil Engineers, Sanitary Engineering Division, 86, SA3 111 (1960).

80. Morgan, P. F. "Efficient Utilization of Digester Capacity," Sewage and Industrial Wastes, 26, 1340 (1954).

81. Furhrman, R. E. "Scum Control in Sludge Digestion," Sewage and Industrial Wastes, 26, 453 (1954).

82. Langford, L. L. "Digester Net Effective Capacity," Water and Sewage Works, 105, 435 (1958).

83. Schreiber, H. A. "Scum Control and High Rate Digestion at the District of Columbia," Sewage and Industrial Wastes, 31, 729 (1959).

84. Blodgett, J. H. "Accelerated Sludge Digestion Successful at Columbus, Ohio," Wastes Eng'g., 24, 608 (1953).

85. Schulze, K. L. "Studies on Sludge Digestion and Methane Fermentation. I. Sludge Digestion at Increased Solids Concentrations," Sewage and Industrial Wastes, 30, 28 (1958).

86. Schlenz, H. E. "Controlled Digestion," Sewage Works Journal, 16, 504 (1944).

87. Torpey, W. N. "Loading to Failure of a Pilot High-Rate Digester," Sewage and Industrial Wastes, 27, 121 (1955).

88. Keefer, C. E. "Effects of Premixing Raw and Digested Sludge on High-Rate Digestion," Sewage and Industrial Wastes, 31, 388 (1959).

89. Stanier, R. Y., Doudoroff, M. and Adelberg, E. A. The Microbial World, Prentice-Hall, Inc., Englewood Cliffs, N. J., 1959.

90. Hewitt, L. F. Oxidation-Reduction Potentials in Bacteriology and Biochemistry, 4th Edition. London County Council, London, 1936.

91. Clark, W. M. Oxidation-Reduction Potentials of Organic Systems, Williams and Wilkens Co., Balt., Md., 1960.

92. Daniels, F. and Alberty, R. A. Physical Chemistry, John Wiley and Sons, Inc., N. Y., 1958.

93. Conant, J. B. and Lutz, R. E. "The Irreversible Reduction of Organic Compounds. I. The Relation between Apparent Reduction Potential and Hydrogen Ion Concentration," Journal American Chemical Society, 46, 1254 (1924).

94. Rohlich, G. A. "Discussion--'Measurement and Control of Sewage Treatment Process Efficiency by Oxidation-Reduction Potential,' by Hood, J. W., Sewage Works Jour., 20, 640," Sewage Works Journal, 20, 650 (1948).

95. Grune, W. N. and Peek, R. C., Jr. "New Parameters for Improving Control of Sludge Digestion. III. Oxidation Reduction Potentials for Checking Digester Activity," Wastes Eng'g., 29, 468 (1959).

96. Tobin, L. C. "Convenient Measurement of Oxidation-Reduction Potentials in Fermentation Studies," Chemist. Analyst., 35, 63 (1946).

97. Ward, W. E. "The Apparent Oxidation-Reduction Potentials of Bright Platinum Electrodes in Synthetic Media Cultures of Bacteria," Journal of Bacteriology, 36, 337 (1938).

98. Morgan, J. L. R. and Lammert, O. "The Quinhydrone Electrode III," Journal American Chemical Society, 53, 2154 (1931).

99. Longsworth, L. G. and MacInnes, D. A. "Apparent Oxidation-Reduction Potential, Acid and Population Studies of L Acidophilus under Anaerobic Conditions," Jour. of Bacteriology, 32, 567 (1936).

100. Henry, Clarence R. "Measuring the ORP of Sewage," Jour. Water Pollution Control Federation, 32, 897 (1960).

101. Hood, J. W. "Measurement and Control of Sewage Treatment Process Efficiency by Oxidation-Reduction Potential," Sewage Works Journal, 20, 640 (1948).

102. Potter, M. C. "Electrical Effects Accompanying the Decomposition of Organic Matter," Proc. Royal Society of London, 84, 260 (1911).

103. Moore, W. A., Ruchhoft, C. C. and Wattie, E. "Oxidation-Reduction Studies. I. Oxidation-Reduction Potentials Developed by Pure Cultures in Sewage," Sewage Works Journal, 14, 980 (1942).

104. Kehoe, T. J. and Jones, R. H. "ORP Measurement in Waste Treatment," Water and Sewage Works, 107, 305 (1960).

105. Eckenfelder, W. W. and Hood J. W. "The Application of Oxidation-Reduction Potential to Biological Waste Treatment Process Control," 6th Industrial Waste Conference, Purdue University, 221 (1951).

106. Rohlich, G. A. "Oxidation-Reduction Potential Measurements in Activated Sludge and Activated Sludge-Sewage Mixtures," Sewage Works Journal, 16, 540 (1944).

107. Reed, G. B. and Orr, J. H. "Cultivation of Anaerobes and Oxidation-Reduction Potentials," Journal of Bacteriology, 45, 309 (1943).

108. Vennesland, B. and Hanke, M. E. "The Oxidation-Reduction Potential Requirements of a Non-Spore-Forming; Obligate Anaerobe," J. of Bacteriology, 39, 139 (1940).

109. Hanke, M. E. and Katz, Y. J. "An Electrolytic Method for Controlling O-R Potential and Its Application in the Study of Anaerobiosis," Arch. of Biochemistry, 2, 183 (1943).

110. Langlykke, A. F., Van Lanen, J. M. and Fraser, D. R. "Butyl Alcohol from Xylose Saccarification Liquors from Corncobs," Industrial and Eng'g. Chem., 40, 1716 (1948).

111. Squires, R. W. and Hosler, P. "Pilot Plant Fermentor with a Continuous Electrode Potential Measurement," Ind. and Eng'g. Chem., 50, 1263 (1958).

112. Tengerdy, R. P. "Redox Potential Changes in the 2-Keto-L-gluconic Acid Fermentation. I. Correlation between Redox Potential and Dissolved Oxygen Concentration," Journal of Biochemical and Microbiological Technology and Engineering, Vol. III, 241 (1961)

113. Tengerdy, R. P. "Redox Potential Changes in the 2-Keto-L-gluconic Acid Fermentation. II. Relationship between Redox Potential and Product Formation," Journal of Biochemical and Microbiological Technology and Engineering, Vol. III, 255 (1961).

114. Hall, I. C. "A Review of the Development and Application of Physical and Chemical Principles in the Cultivation of Obligatory Anaerobic Bacteria." Journal Bacteriology, 17, 255 (1929).

115. Knight, B. C. J. G. "Oxidation-Reduction Studies in Relation to Bacterial Growth. II. A Method of Poising the Oxidation-Reduction Potential of Bacteriological Culture Media," Biochemical Journal, 242, 1075 (1940).

116. Scheff, G. J., Proctor, Charles and Cohen, Philip "Use of the Dropping Mercury Electrodes for Measuring Oxygen Changes in Treponema and C. Sporgenes Cultures," Arch. of Biochemistry, 61, 20 (1956).

117. Backmeyer, D. P. and Drautz, K. E. "CRP and Operation." Jour. Water Pollution Control Federation, 33, 906 (1961).

118. Bargman, R. D., Betz, J. M. and Garber, W. F. "Aeration Requirements of a High Oxygen Demand Sewage," Sewage and Industrial Wastes, 29, 768 (1957).

119. Moore, W. A. and Ruchhoft, C. C. "Oxidation-Reduction Studies. II. Oxidation-Reduction Potentials Developed in Sewage and Sewage-Activated Sludge Mixtures," Sewage Works Journal, 15, 880 (1943).

120. Nussberger, F. E. "Application of Oxidation-Reduction Potentials to the Control of Sewage Treatment Processes," Sewage and Ind. Wastes, 25, 1003 (1953).

121. Goodman, B. L. "Activated Sludge Process Control," Water and Sewage Works, 108, 173 (1961).

122. Shapiro, R. "Oxidation-Reduction Potential," Water and Sewage Works, 101, 185 (1954).

123. Hoot, R. A. "Automatic Control of Raw Sewage Chlorination," Water and Sewage Works, 96, 267 (1949).

124. Keefer, C. E. and Meisel, J. "Oxidation-Reduction Potential of Chlorinated Sewage," Sewage and Ind. Wastes, 25, 759 (1953).

125. Langley, H. E., McKinney, R. E. and Campbell, H. "Survival of Salmonella typhosa during Anaerobic Digestion. II. The Mechanism of Survival," Sewage and Industrial Wastes, 31, 23 (1959).

126. Grune, W. N. and Lotze, T. H. "Redox Potentials in Sludge Digestion," Water and Sewage Works, 105, 37 (1958).

127. Grune, W. N. and Sload, R. Q. "Biocatalysts in Sludge Digestion, " Sewage and Industrial Wastes, 26, 1425 (1954).

128. White, W. P. "Leakage Prevention by Shielding, Especially in Potentiometer Systems," Journal American Chemical Society, 36, 2011 (1914).

129. DiLallo, R. and Albertson, O. "Volatile Acids by Direct Titration," Journal Water Pollution Cont. Fed., 33, 356 (1961).

130. United States Public Health Service. 1957 Inventory Municipal and Industrial Waste Facilities, Vol. 5, Public Health Service Publ. No. 622 (1958).