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A STUDY OF OXIDATION-REDUCTION POTENTIALS APPLIED TO SEWAGE SLUDGE DIGESTION

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INTRODUCTION

The cost of sludge digesters under present day construction prices comprises a substantial portion of the total first cost of sewage treatment plants. To reduce this cost, efforts have been made to diminish the required tank volume or digestion time by improving present sludge digestion practices. More efficient use of digester capacity has been accomplished by such techniques as higher feeding levels and lower detention times in conjunction with adequate agitation of the digester contents and prethickening of the raw sludge.

The increased trend toward maximum utilization of digester capacity has resulted in a need for more adequate knowledge of the process and its control. This is due to the increased sensitivity of the digesting sludge to adverse conditions. Like many process developments, the understanding of its mechanism and control has lagged behind its use. Knowledge of the factors affecting the process will not only aid in the understanding of its mechanism and control, but will also stimulate further process improvements.

Sludge digestion has been extensively studied by the use of such parameters as pH, quantity and quality of the gas production, volatile acids, volatile solids and methane-forming bacteria. These parameters help define the necessary conditions for successful sludge digestion as well as aid in the evaluation of the bacteriological, chemical, and physical processes taking place during the digestion. However, because of the complex biochemical and biological systems present, the entire mechanism of the digestion has not been completely established.

The digestion of sewage sludge is a process involving the anaerobic degradations of complex organic materials. A succession of bacterial systems produce enzymes which enable the degradation reactions to proceed. The many steps involved in the breakdown of these complex compounds to simpler materials include various oxidation-reduction reactions.

Since an oxidation-reduction reaction involves an electron transfer, it is possible to make quantitative studies of these reactions by measuring the resulting potential change. This technique has been used so successfully in pure bacteriological and biochemical systems that it would appear possible to apply the same techniques to the mixed cultures of sludge digestion with some degree of success. If such would be the case, a better understanding permitting better control of the process might result.

The measurement of oxidation-reduction potentials in digesting sewage sludge has never been investigated on a continuous basis. In a few instances data has been published giving a few potential values, but the information was so meager that its value was limited.

The objectives of this thesis are to present and evaluate methods of measuring oxidation-reduction potentials in anaerobic sludge systems, to study the potential changes in a digesting sludge, and to contribute to the further understanding of oxidation-reduction potentials and their application to sludge digestion. The research included in this dissertation was begun in September 1953 and concluded in June 1957.

SLUDGE DIGESTION

Sludge digestion is the biochemical process by which complex organic materials in sewage sludge are broken down into simpler substances. This organic matter is gasified, liquified, mineralized or converted into more stable organic products. The result is a residue which can be economically disposed of by drying or burning without creating a nuisance. A valuable by-product of the digestion is the production of methane gas. This is used mainly as a fuel, but also has been employed as a raw material for chemical synthesis.

The biological, chemical and physical changes occurring in sludge digestion have been the subject of many investigations. A complete review of all this work would be beyond the scope of this thesis. There are, however, many descriptions of sludge digestion available in books and review articles concerning sewage treatment(1)(2)(3)(4). The anniversary book of the Federation of Sewage Works Associations(5) is an outstanding reference with contributions by several authors. Because of these comprehensive references, this presentation of the sludge digestion process will be reduced to a brief summary.

The sludge digestion process has been studied on both a batch and a continuous basis. In the former process the digestion of sewage sludge is divided into three well-defined stages: acid production, acid regression, and alkaline fermentation. At a temperature of 60°F, the acid production phase lasts about two weeks. The bacteria attack easily available substances such as carbohydrates and soluble nitrogenous compounds releasing small quantities of gas, organic acids and acid carbonates. The gas is composed chiefly of carbon dioxide, with some methane and hydrogen sulfide present. The pH is around six or lower.

Acid regression lasts about three months. In this phase, the organic acids and nitrogenous compounds are attacked, thereby producing ammonia compounds, acid carbonates and gas. The small quantity of gas produced is composed chiefly of carbon dioxide and methane, along with some hydrogen. The pH gradually rises to around 6.8 and the sludge odor is very offensive.

With the rise of the pH, alkaline fermentation sets in. This phase lasts about one month, during which the organisms attack the more resistant materials such as proteins and organic acids. The pH continues to rise, reaching pH 7.0 or above, and the decrease in organic acids which results makes a more favorable enviroment for proteolysis. The resulting mixture of reactants is a well-buffered system in which acids are neutralized by the previously formed products of alkaline decomposition. Large volumes of gas are released consisting of methane, along with some carbon dioxide. When the bulk of the digestible material is exhausted, the sludge becomes stable and a gradual cessation of bacterial activity sets in. During the phases outlined above, there exists a succession of bacterial agents which are influenced both by intermediate and final chemical products and also are greatly affected by the changing environmental conditions.

Additions of small quantities of fresh solids to the sludge in the alkaline fermentation period result in a continuous type of digestion where the acid production and regression periods are not distinct and the gas production is high. This is due to the well buffered, highly developed bacterial culture developed within the sludge. At 60°F the time for comparable digestion is reduced to one-tenth of that of the batch process.

On a continuous basis sludge digestion can be divided into two phases. The first is the breakdown of complex materials by hydrolytic enzymes. This includes protein breakdown to amino acids, carbohydrate breakdown to simple sugars and lipid breakdown to glycerol and fatty acids. The amino acids are in turn converted to organic acids, alcohols and amines, while the sugars are converted to organic acids. The formation of these organic acids is considered a primary end product. The second phase involves the breakdown of lower fatty acids, alcohols and other molecular fragments with the production of methane and carbon dioxide. This is completed by a group designated as methane-producing bacteria.

The gas produced from a continuously digesting sludge can include methane, carbon dioxide, hydrogen, hydrogen sulfide, and nitrogen. The analysis of this gas under normal digestion would be about 70 to 75 percent methane, 23 to 28 percent carbon dioxide and 1.5 percent nitrogen. Hydrogen and hydrogen sulfide comprise the remaining small portion of the total.

The amount of gas produced by digesting sludge was reported throughout the literature and also summarized in many texts on the subject, i.e., Imhoff and Fair(3). More detailed studies have been concerned with the composition of the gas(6)(7)(8), the gas yield from fat, protein and carbohydrate(6), the time required to produce a certain percentage of the total yield(9)(10)(11)(12), and gas production rates(13).

The production of hydrogen was of particular concern to this research since the effect of this gas on the platinum electrode could be appreciable(14)(15)(16)(17). Reports of sludge gas analysis did not always include hydrogen, although most authors reported that hydrogen was usually present. Buswell and Neave(18) found an average of approximately two percent hydrogen, Sawyer and Roy(19) reported two to three percent in high rate laboratory tests, and Steel(20) reported from one to three percent. Imhoff and Fair(3) have stated that hydrogen was produced in the acid regression period of a batch digestion of raw sludge. There were other authors however, who did not feel that hydrogen was a normal component of sludge gas or, if present, would be so only in very small amounts. Hawkes and Jenkins(21) found that hydrogen was sometimes produced in immature digesting sludge and Rudolfs(22) stated that the gas production included hydrogen only under certain conditions. Fulweiler(23) reported that there was little, if any, hydrogen in the sludge gas and Phelps(24) stated that hydrogen did not appear in any quantity.

The question of whether or not hydrogen was present in sludge gas was discussed by Buswell and Neave(18) and Hawkes and Jenkins(21). Possible sources of this gas were presented by Buswell et al.(25). From the above information it appeared that hydrogen was usually, but not always, present in sludge gas. Large ratios of raw to digested sludge appeared to favor hydrogen production.

Conditions more favorable to the production of hydrogen have been created by the recent trend toward higher feeding levels. This condition has been created by the attempt of engineers to utilize more of the available capacity of the sludge digesters. On a plant scale, gas recirculation was used by Morgan(26) to agitate the sludge; pre-thickening in conjunction with continuous feeding was tried by Torpey(27). In a pilot digester Torpey used continuous mechanical agitation, pre-thickening and feeding every two hours. Laboratory scale experiments have been performed by Sawyer and Roy(19) utilizing continuous gas agitation and two feedings per day.

This experimental work helped to define certain of the factors involved in successful high rate feeding. These were:

1) concentrating the sludge feed,
2) continuous feeding of the sludge, and
3) continuous agitation to get effective utilization of the tank volume.

Higher feeding levels created a need for better process control than was necessary with lower loadings since the digestion was more susceptible to overloading, and hence failure. Because of their sensitive environmental pattern, the methane-producing bacteria might determine the point in the digestion where failure was most likely to occur. These bacteria have been extensively investigated by Stadtman and Barker(28)(29)(30)(31), Heukelekian and Heineman(32)(33)(34)(35) and Buswell et al.(36)(37)(38)(39)(40). The work of Heukelekian and Heineman was concerned with sewage sludge, while the other investigators concentrated on the properties of the bacteria per se.

The effect of volatile acids on these bacteria was evidenced from the fact that an acid accumulation could retard or completely stop the action of these methane-producing bacteria. The temperature effect could be appreciable since a drop of 5°C will frequently lower the gas production without materially affecting the production of acid according to Buswell(37).

The effect of volatile acids on the digestion, particularly the gas producing phase, has resulted in many studies of these acids(37)(25)(13)(41)(42)(43)(44)(45)(46). It was found that volatile acids were produced by the first or hydrolytic phase of the digestion, and destroyed by the second or methane-producing bacterial phase. In regard to this, Kaplovsky(43) has stated that a lowering of the acid content was due to a greater rate of destruction, not a lower rate of production. This indicated that the acid balance was controlled by the methane-bacterial phase and not by the hydrolytic phase.

Control of the sludge digestion process has usually been based on the factors affecting the methane bacteria since this bacterial system was the most sensitive link in the chain of reactions. These factors included volatile acids, pH and temperature. The reduction of volatile matter, alkalinity, and composition and quantity of the gas have also been used as parameters since they reflect the condition of the bacterial environment. Although it was found in one plant that a rise in the carbon dioxide content preceded by at least one week a reduction in the gas rate(47), the volatile acid content has been considered by most authorities to be the most sensitive indicator of proper digestion(25)(26)(47). Apparently it was not the complete answer, since Kaplovsky(43) stated that the volatile acid accumulation was only a secondary factor because without the proper bacterial flora, trouble would be encountered even at low acid levels.

The length of time necessary to determine the volatile acid content of a sludge has been a disadvantage for process control. The approximate analytical determination of volatile acids required over an hour, while the more precise tests lasted several hours. If oxidation-reduction potentials would indicate the condition of the digesting sludge, it would make available a rapid test for control purposes and thus provide a new tool in sludge digestion operation.

OXIDATION-REDUCTION POTENTIALS

The digestion of sewage sludge involves oxidation-reduction reactions which play an important role in the degradation of complex biochemical materials. There is a chain of steps from the initial reactant to the final product, many of which are imperfectly understood. Included in this chain are oxidation-reduction reactions, some reversible and some irreversible. The reversible reactions enable the living cell to store energy for future utilization. Hewitt(48) states that oxidation-reduction systems are so essential that life might be defined as a continuous oxidation-reduction reaction.

These reactions can be studied by the use of electrode potential measurements. However, their quantitative interpretation depends upon the reaction being reversible. Michaelis(16) states that the use of potential measurements has provided a more clear and thermodynamically correct approach to cell energetics and the metabolism of the living cell. The potential measurement is termed electrode potential, oxidation-reduction potential, ORP, or redox potential by different authors and these terms are generally used synonymously.

A complete review of the basic principles of oxidation-reduction potentials would be beyond the scope of this thesis. Several sources of this information are available, of which Michaelis(16), Clark et al.,(49) and Hewitt(48) are outstanding. Because of these references, the presentation of the basic principles of oxidation-reduction potentials is reduced to a brief summary.

Oxidation signifies more than simply the gain of oxygen by an element or compound such as the formation of carbon dioxide from carbon or acetic acid from acetaldehyde.

$$C + O_2 = CO_2$$

$$HCHO + O = HCOOH$$

It also denotes the loss of hydrogen or dehydrogenation and the loss of an electron. These comprise the three methods of oxidation. Dehydrogenation of ethane to ethylene and a gain of an electron by ferric from ferrous iron are examples of the latter two methods.

$$CH_3-CH_3 = CH_2=CH_2 + H_2$$

$$Fe^{++} = Fe^{+++} + e$$

The modern definition of dehydrogenation by Michaelis(16) involves the loss of an electron with the simultaneous loss of a proton or hydrogen ion. The proton is not involved in the oxidation process and the proton attachment is termed the level of acidic ionization. Referring to the chain of respiratory processes, he states that the process is not entirely a transfer of hydrogen to another molecule, but is a transfer of electrons with or without protons.

It is important to note that for every oxidation, there must be a corresponding reduction process. The oxidation of ferrous chloride to ferric chloride illustrates this:

$$FeCl_2 + Cl = FeCl_3$$

or in ionic form:

$$Fe^{++}\ 2Cl^- + Cl^\circ = Fe^{+++}\ 3Cl^-$$

From this can be seen the oxidation and corresponding reduction.

$$\text{Oxidation: } Fe^{++} = Fe^{+++} + e$$

$$\text{Reduction: } Cl^{\circ} + e = Cl^{-}$$

Various methods are presented by different authors which relate the transfer of electrons in an oxidation-reduction reaction to the potential by the use of a quantitative equation. These include Clark et al.(49), Michaelis(16), Glasstone(50) and Hewitt(48). All of these methods lead to the same equation for which the derivation is illustrated in Appendix A.

$$E_h = E_o + \frac{RT}{nF} \ln \frac{(\text{Oxid})}{(\text{Red})}$$

This is the basic equation under reversible conditions which quantitatively relates the oxidative state of the system with the oxidation-reduction potential. E_h is the potential of the system referred to the normal hydrogen electrode and E_o is a specific constant for the system being measured. They are measured in volts. R is the universal gas constant, T is the absolute temperature, F is the Faraday constant and n is the number of electrons transferred in the oxidation-reduction reaction.

If the ratio of oxidant to reductant gets larger, the potential becomes more positive and if the ratio of oxidant to reductant gets smaller, a more negative potential results. A high positive is shown by chlorine, an excellent oxidizing agent. Conversely, hydrogen as a good reducing agent will exhibit a high negative potential. We can then speak of an aerobic solution in the positive potential range and an anaerobic solution in the negative potential range.

It can be seen that the potential is dependent only on relative amounts and not absolute quantities. Thus, oxidation-reduction potentials determine the level of intensity, not capacity of the oxidizing system.

Intensity resembles the pH and temperature of a solution in that nothing is indicated about the buffering ability or heat content, respectively. The ability to resist change in oxidation-reduction systems is called the "poise" of the system. As temperature alone does not allow prediction of the total cooling or heating ability of the solution, neither does the electrode potential yield any information of the total oxidizing or reducing ability of the solution. This factor is especially important in biological systems where many have well-defined potentials but are poorly poised.

A typical oxidation-reduction curve as shown in Figure 1 illustrates the poising effect. The maximum stability or poise of a solution will be found at the point where the curve is flattest and most resistent to change. By mathematical means Michaelis$^{(16)}$ shows this point to be located where there are equal concentrations of oxidant and reductant. Thus a system with small quantities of either the oxidized or reduced state is poorly poised and its potential is very susceptible to other redox

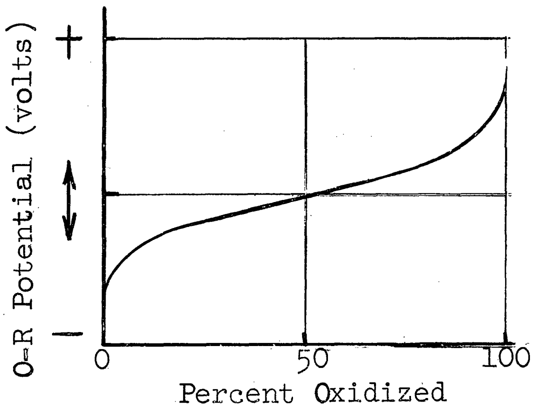


Figure 1. Relation Between the Oxidation-Reduction Potential and the Percentage Oxidation of the System

systems which may have lower concentrations but are in a more poised state. The effect of concentration on the capacity of the solution is based on the law of mass action. If the solution is poorly poised, based on the above definitions, it still could resist changes of potential if the concentration is sufficiently high.

The effect of pH on the potential is due to the altering of ionic equilibria. Because of the fact that acid or basic groups are created or destroyed in redox reactions, it follows that oxidation-reduction is an interdependent factor in the acid-base equilibria. The dissociation constants can be affected and this plus the pH may have a considerable influence according to Clark et al.(49).

The formulation of a general rule for the pH effect was very complicated in many cases. Hewitt(48) felt that for biological systems it was impossible to formulate a general rule since the pH effect varied in different ranges of pH. With systems that were not exhaustively studied, the E_h as well as the pH should be noted. Hewitt stressed that even though the effect of pH on E_h was complex, it did not imply that the effect was necessarily great. A usual E_h to pH ratio of 0.03 for biological systems at a pH near seven meant a difference of three mv for 0.1 pH unit change.

The derivation of the electrode equation presented previously was based on a thermodynamically reversible reaction. The equation, therefore, could not theoretically be applied to an irreversible reation and was independent of any time considerations. However, there have been attempts to relate the potential to irreversible reactions and kinetics.

A convenient, but empirical, method of characterizing irreversible systems by potential measurements was developed by Conant and Lutz(51). The measured potential was referred to as "the apparent reduction potential," which was defined as "the oxidation-reduction potential of a particular reducing agent which will just cause an appreciable amount of reduction of the substance in question." In this way it was possible to treat irreversible organic reductions by the use of potential measurements and place them on a scale based on the standard hydrogen electrode.

Gershinowitz(52) has pointed out that Conant and co-workers have shown that there was a definite relationship between rates of an irreversible reaction and OR potential, and as a result they have derived an equation for this condition which gave satisfactory experimental agreement. He concluded from this and other work that there was some connection between kinetic rate constants and thermodynamic quantities; and he derived theoretical equations relating these. This work was based on the assumption of the formation of an activated complex and a reversible first step. In regard to this assumption it was of interest to note that LuValle and Goddard(53), in discussing the mechanisms and kinetics of enzymatic oxidation-reduction, assumed that a complex was formed between the enzyme, electron donor and the electron acceptor; and that the reactions proceeded through a series of univalent electron exchanges.

Longsworth and MacInnes(54) found a connection between E_h and the rate of acid production in a growing culture. They used the term "apparent ORP" and said the E_h measured was not an equilibrium potential but the result of several kinetic processes. Kinetic properties of potential measurements have also been observed by others(55)(56).

METHODS OF MEASURING THE POTENTIAL

There are two methods of obtaining the oxidation-reduction potential: inert metal electrodes and oxidation-reduction dyes. Much of the early work was done with dyes due to the success and simplicity of the use of pH colorimetric indicators. Clark et al.(49) made an extensive study of dye systems but no simple reliable method was found which compared to pH measurements. The methods of obtaining pH and oxidation-reduction potentials are identical except that one uses a dye which reacts to pH in the first case, while in the other a dye is used which reacts to the oxidative state of the system.

The majority of dyes used are indophenols or derivatives of indigo and their color is due to the quinoid structure of the benzene ring. Methylene blue used in the "relative stability" of sewage is an example of this technique. But the disadvantages for biological systems are many. Dyes can poise the solution by oxidizing a system of low capacity without being reduced appreciably. The time lag may be very great and the system may be changing. There can be catalytic as well as toxic effects on the system. A great disadvantage lies in the small range the dye can span and when potential changes are great, more than one dye system would be needed.

Metal electrodes provide the most reliable method of obtaining oxidation-reduction potentials. The measurement reflects the difference in potential between an inert metal electrode, i.e., platinum or gold, and a reference electrode, such as a calomel cell. Since the metal electrode is only one-half a cell, the reference electrode is needed to complete the measuring circuit. Potential measurements are identical to pH electrometric determinations except for the measuring electrode. The glass electrode is replaced by an inert metal for the redox potential.

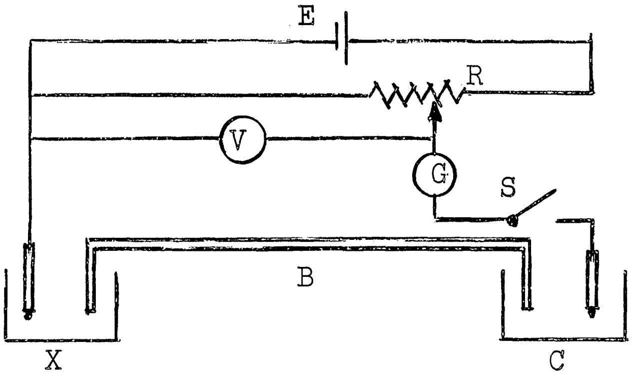
The metal electrode must be inert to the system in which it is used. An inert electrode can be defined as one that does not participate in the reaction but merely acts as a conductor of electrons other than its own. It is important that the inherent characteristics of the metal do not affect the potential measurements.

There are various types of reference electrodes but the most commonly used is the calomel electrode. The hydrogen electrode is not very convenient to construct or use, and it is used only as a standard for the other reference electrodes. The values obtained with the calomel electrode can be referred to the normal hydrogen scale since these electrodes are standardized against the hydrogen electrode at different ion concentrations and temperatures. The reversible oxidation-reduction equation for the calomel or mercurous chloride-mercury-potassium chloride cell is as follows:

$$Hg_2Cl_{2(s)} + 2e = 2Hg_{(l)} + 2Cl^-$$

In order to join the reference electrode with the solution to be measured, maintain electrical neutrality between the solutions involved, and to reduce the liquid junction potential (caused by the contact of two different solutions), a salt bridge is used. Potassium chloride is generally used for this connecting bridge because the liquid junction is minimized due to the almost identical mobilities of the potassium and chloride ions. This does not eliminate completely the junction potential, but its value is negligible where measurements do not have to be of the highest accuracy.

The principle generally used in the measurement of potentials is based on the Poggendorff compensation method. The voltage of the cell is measured when no current is being produced due to balancing of the resistances. Since a cell behaves reversibly only when an infinitesimally small current is produced, this open circuit where no current flows is ideal for determining the reversible potential. This is accomplished as shown in Figure 2.



E-Cell of known EMF
R-Variable resistance
G-Galvanometer
V-Voltmeter
X-Solution Half Cell
C-Reference Half Cell
B-Salt Bridge
S-Switch

Figure 2. Circuit for the Measurement of the Electrode Potential

In order to obtain the potential of the solution, X, the switch, S, is closed and the resistance, R, is balanced so that the Galvanometer, G, shows no current flowing. The potential is then read from the potentiometer. At this point the potential from the known cell, E, is exactly compensated by the measuring system, X and C.

Since the current drawn during the balancing of the circuits must be kept very small in order to avoid polarization of the metal electrode, a very high resistence galvanometer must be used. Vacuum tube potentiometers with very high resistances are presently used to minimize or completely eliminate this problem. This is especially important in biological systems where slight polarization of the electrode can cause errors in the readings.

FACTORS TO BE CONSIDERED IN THE USE OF METAL ELECTRODES

Of the previously described components required for potential measurement, the metal electrode presents the most complications. This is a result of the requirement that the metal be inert and the fact that no metal actually is inert. From the initial selection of the metal to be used as the electrode to the final evaluation of the potential measurements, the investigator will require a knowledge of the factors involved. These factors are: the metal to be used in the electrode, the size and shape of electrode required, the method of cleaning the metal surface, the effect of cleaning on the metal, both from the physical and the electrical viewpoint, the effect of the experimental conditions on the electrode, i.e., gas adsorption, and finally the characteristics of potential measurements in various systems.

The literature survey conducted by the author failed to reveal an adequate coverage of the various factors outlined above and in no instance was there a compilation of what is presently known about the subject. One of the purposes of this dissertation, therefore, was to summarize what could be found in the literature regarding the factors influencing a potential measurement.

Types of Electrodes

Many different metals have been used in oxidation-reduction studies. Platinum has been the most popular, with gold in a secondary position. Other choices have included iridium(57), tungsten(58), graphite(59), mercury, rhotanium alloy(49) and palladium(60). Clark(49) used a wide variety of electrodes which included platinum wire and foil, gold foil, gold plated wire and foil, rhotanium alloy, burnt-on platinum, gold plated and amalgamated burnt-on platinum and mercury. Electrodes have been used in the form of straight wire, spiral wire, gauze, foil, and plated glass.

The first type of oxidation-reduction electrode was the hydrogen electrode used in pH measurements. In this electrode, platinum was used as the base metal for the plating of platinum black. The metal deposit was necessary to attain rapid equilibrium with the hydrogen gas atmosphere. Gold was in some cases used as the base metal. With the development of the quinhydrone oxidation-reduction system as used in measuring pH, more attention was paid to the electrode base metal. An inert metal surface was essential in this technique, and platinum and gold were the common metals used for the electrode. The electrode most commonly used in other oxidation-reduction systems, both inorganic and organic, was platinum. The other metals mentioned previously, except for gold, were used only in isolated instances.

The use of electrodes in bacteriological and biochemical systems presented a more difficult problem to many workers since these systems often yielded erratic potential results. Many types of metal were tried, but platinum was the most popular with gold in a secondary position. For sewage treatment systems, platinum was used by all workers. Since sludge digestion presented problems similar to the bacteriological systems, it was decided by the author that either platinum or gold should be used, no better metal having yet been discovered. The following discussion was therefore limited to these two metals.

Cleaning the Electrode

In order to achieve reproducibility of an electrode and agreement between different electrodes, various techniques have been employed to clean the metal surface. A lack of agreement existed between various workers regarding which technique was best, and the reasons for a particular preference were frequently not mentioned. Methods employed in cleaning have ranged from a water rinse(61) to replating the surface(62). However, most of the methods for cleaning involved the use of an acid, an oxidizing solution, heat, or an abrasive. Often two or more of these methods were used in conjunction with each other.

One of the most frequently used techniques has been nitric acid cleaning. This acid has been used concentrated or diluted, hot or cold. Another popular cleaning method required a potassium dichromate-sulfuric acid mixture, or chromic acid solution. Hydrochloric acid has been used alone or in combination with nitric acid to form aqua regia. In addition to the frequent use of water as a rinse, it has also been used as the sole cleaning agent. Heating of the metal to redness by an alcohol flame has been a common technique, while polarization was mentioned in many research papers. Abrasive cleaning was done by rubbing the metal surface with filter paper, sand paper, or materials such as levigated alumina or Bon Ami.

A few authors have compared some of these methods in an attempt to find a superior process for cleaning the electrode. Borchardt(63) tried the alcohol flame, a hot chromic-sulfuric acid mixture, hot nitric acid, and levigated alumina for platinum and gold electrodes. The alumina was preferred for measurements in quinhydrone since the other methods resulted in poor electrode agreement. In addition, he found that when using the gold electrodes in amino acid-chlorination studies, it was necessary to clean with alumina before reuse. However, if the electrode was used in quinhydrone, a water rinse was sufficient.

Remington and Trimble(64) found that the potential in hypochlorite solutions showed no indication of equilibrium, rarely or never was twice the same value, fell lower and lower in successive experiments and that different electrodes behaved in the same manner. Treatment with chromic acid, alkaline potassium permangenate and nitric acid did not improve the performance. They found cleaning with hot nitric acid, washing, drying, heating to cherry red and cooling before immersion and reading, yielded fairly consistent results in successive experiments. These investigators felt that the heating degasified the electrode. To achieve the cherry red heat, an electric current was preferred to a gas burner due to possible gas contamination and cracking of the glass-metal seal. Similarly, Clark(65) used an alcohol flame to prevent contamination by the sulfur in ordinary gas.

Ward(66) tried hot chromic acid, nitric acid, and aqua regia for platinum electrodes in sterile and cultured synthetic media working with E. coli. Although none of these cleaning methods proved to be superior, nitric acid was adopted since its action was less vigorous than aqua regia. Tobin(67) found that a hot potassium dichromate-sulfuric acid mixture followed by a water wash was theonly method which would give reproducible results with platinum electrodes in yeast fermentations.

As may be concluded from above, a divergence of opinion was the usual situation found in the literature with regard to the preference for a cleaning method. Although different test solutions were used in the above citations, the same divergence of opinion existed for various authors using the same metal in the same solution. It was therefore felt that a knowledge of the effect of the cleaning methods on the metal electrode would be an invaluable aid in the selection of a cleaning technique to be used in this research as well as contributing to the understanding and evaluating of the potential measurements obtained. This literature study concerning the effect of cleaning methods on the metal included the effect of acids and other chemicals, heat, abrasives, and electrolysis with regard to their influence on the surface structure from the physical and electrial viewpoints. The presentation of this study as Appendix B was considered desirable since a compilation of information on this important subject did not exist.

The results of the above study indicated that cleaning methods can change the metal surface, can create catalytic activity, can react with the metal, can only with great difficulty degasify the surface, and can affect the function of the metal as an electrode. Although these were all possibilities, the actual effect on the electrode potential by the usual cleaning techniques could not be definitely ascertained. A very important objective of this discussion would be achieved if it made the investigator more aware of the possible effects of different cleaning procedures on the electrode.

Effect of Gases on the Electrode

Because of the production of various gases from the sludge digestion process, it was necessary to determine if any or all of these gases would affect the potential measurement by producing a gas-metal effect. In addition, the effect of oxygen was also of interest due to the procedure used in measuring the potential. As was the case in the previous discussion, this summary presented as Appendix C was concerned only with the metals platinum and gold.

The information presented established the possibility of the sludge gas affecting the potential measurement. This was especially true for the platinum electrode although the gold was not inert to the gas-metal effect. It would seem that the differences between the two types of electrodes was substantial and it might be indicated that gold was more inert to gas effects in digesting sludge.

OXIDATION-REDUCTION POTENTIALS IN BACTERIOLOGY AND BIOCHEMISTRY

The fields of bacteriology and biochemistry provide an excellent source of background information for the application of electrode potential measurements to digesting sludge. The usefulness of this information arises from the fact that sludge digestion is a biological process containing various bacteriological and biochemical systems. Although sludge digestion with its multitude of organisms, continuous operation, and naturally buffered media, differs somewhat from the conditions of normal bacterial cultures, potential observations derived from bacterial growth remain valuable. These observations are even more applicable to batch-type digestion because of the lack of a well-buffered sludge medium which more closely simulates the conditions of the average bacterial culture. Because of the excellent treatise on the relation of potentials and bacterial cultures by Hewitt(48), the discussion of the basic considerations involved in this relation shall be limited to a brief summary.

Anaerobic organisms cannot grow under aerobic conditions, but they can grow if aerobic organisms first reduce the potential to a given level. A distinguishing feature of aerobes and anaerobes is the potential range in which they can initiate growth. The different potential levels at which organisms multiply and the effects they produce are a reflection of their metabolic effects and the enzyme system which they possess. According to Hewitt(48) the potential (E_h) range of an aerobe is generally from 400 to -200 mv and of an anaerobe is 50 to -400 mv or lower. Facultative organisms such as E. coli span the entire potential range.

Reduction of the media is a necessary result of metabolism. In order to obtain the energy necessary for growth, any oxidizing agent such as electron acceptors, hydrogen acceptors, or oxygen is utilized by the cell and one after another of these oxidizing systems will be reduced during growth. As a result, there is a drop in the potential level. The magnitude of this fall is dependent on which enzymes or other hydrogen acceptors are reduced and this depends on the enzymes which are present and able to function. Therefore, a more carefully constituted medium is needed for anaerobic than for aerobic growth since hydrogen acceptors must be present due to the lack of oxygen.

Reducing conditions alone are not a sufficient condition for bacterial growth. This can be compared to the effect of pH where a correct value is necessary, but not sufficient for growth. It is stressed by Hewitt(48) that bacterial cultures develop reducing conditions more because of the exertion of reducing activities than due to the liberation of reducing substances.

The metabolic activities of the bacterial culture can be divided into four periods. These are the lag phase, logarithmic growth phase, stationary period and declining period. The first two are of particular interest as they add insight into the biological and potential changes that occur after adding raw sludge to the digesting solution.

During the lag phase, intense bacterial action alters the environment for the best growth and the oxidation-reduction potential begins to fall. The logarithmic phase takes place after the bacteria have altered the environment and active multiplication takes place. It is characterized by intense enzymatic and synthetic activities. The lowest potential is reached in this phase where the reducing conditions are symptomatic of the dynamic equilibrium between the enzymes and the constituents of the medium which are always in a state of change. Items which are constantly changing in this system are the potential, pH, chemical composition, number and condition of organisms, etc. The next two steps are characterized by a rising potential, a decrease in bacterial growth and activity, and the gradual death of the bacteria.

The potential characteristics of many bacterial cultures are given by Hewitt(48). Many of the biochemical reations taking place during bacterial growth or participating in other metabolic processes are also covered. A few of these potentials are given in Table I. Included in this table are potentials values from other sources(68)(69).

The values listed are the potentials of the half-reduced system, E'o at pH 7, except for bacteriological cultures. In these cases the minimum potentials reached during growth are given.

Although definite potentials are established in bacterial cultures, it is not fully known what substances are responsible for these potentials or what oxidation-reductions systems are actually being measured. Hewitt(48) states that some systems may be present in too small a quantity to affect the potential, while others may have a large poising power and therefore would act to inhibit any oxidation-reduction processes which are different since they would have to be altered themselves. Therefore, the quantity of the redox system as well as its potential level will determine

Table I

OXIDATION-REDUCTION POTENTIALS OF SOME BACTERIAL CULTURES AND BIOCHEMICAL REACTIONS

System	E (volts)
Succinate - fumarate	-0.01
Glutamate - ketoglutanate	-0.03
Amoeba in air	-0.07
Alanine - pyruvate	-0.07
Malate - oxaloacetate	-0.10
Oral lactobacillii cultures	-0.13
Pneumococcus cultures	-0.15
Ethanol - acetaldehyde	-0.16
Lactate - pyruvate	-0.18
Bacillus polymyxa cultures	-0.2
Flavines	-0.23
Glutathione (pH 7.15)	-0.233
Lactobacillus acidophilus cultures	-0.24
Amoeba in nitrogen	-0.25
Bacillus macerans	-0.27
3-phosphoglyceraldehyde: 1,3-diphosphoglycerate	-0.28
Beta-hydroxy-butyrate: acetoacetate	-0.29
Isocitrate - oxalosuccinate	-0.30
Coenzyme I (pH 7.4, 20°C)	-0.325
E. coli cultures	-0.40
Hypoxanthine-uric acid (pH 7.2)	-0.41
Glucose-gluconic acid	-0.45

the final potential. In addition there are the effects of components which do not directly affect the potential, but do so indirectly by poising, catalysis, and poisoning of the electrode surface. Finally, the oxidation-reduction systems which are irreversible or semi-reversible affect the equilibrium and complicate the results.

The irreversible systems can affect the electrode in two ways according to Michaelis(16). There can be no effect on the electrode and no direct effect on the reversible system potential. The only effect is by changing the ratio of the components of the reversible system which may oxidize or reduce the irreversible system. The other type of behavior consists of the determination of the potential at the electrode. Time is needed for the potential establishment and the potential is apparently independent of the quantitative ratio of the reduced reactant to the oxidized product.

In spite of the lack of knowledge concerning the substances responsible for the potential in bacterial cultures, the use of the electrode potential has been successful in providing a better understanding of the behavior of these cultures. In a similar fashion it can be anticipated that the electrode potentials of digesting sludge will also provide a further understanding of the sludge digestion process even though the problem of what the potential is actually measuring becomes more complex. Although the potential of a biological solution can be measured without any knowledge of what is causing the potential, the characteristic of the metal electrode in these solutions are an integral part of the potential measurement.

Many authors have had difficulty in measuring the potential of biological systems. Hewitt(48) felt that this was due to the fact that no two organisms were absolutely identical and no organism was quite the same on two different occasions. However, the large majority of investigators felt the difficulty was due to the electrode itself.

Erratic electrode behavior in biological systems resulted in an extensive study of organic oxidation-reduction dyes in relation to electrode potentials by Clark et al.(49). This work was carried on to obtain more basic data on electrode potentials in order that explanations would be more feasible for biological systems. With biological material they found disagreement between electrodes of different metals, of different surface structure or even between electrodes of the same metal. It was found that cultures, especially in the early growth phase, were not well-poised and different electrodes did not yield the same potential. Such electrodes did tend to agree after a time duration. There was no case of static equilibrium. The authors stated, "The criterion of stability with time, which is one of the most important criterions of significance in potentials observed with definite reversible systems, is lacking." They believed that mainly irreversible systems were present.

Another very extensive study of electrodes was done by Michaelis(16). He stressed that the important criterion for a potential measurement was that it must be independent of the individual electrode and show agreement in the same solution. In biological systems two apparently identical gold or platinum electrodes in the same solution differed by more than 100 mv and in such cases he felt these values could not be said to be that of the system. This divergence could be due to (1) a poisoned electrode surface or (2) a system so weakly poised that it failed to overcome the slight inherent individuality of the electrode.

The influence of the electrode metal on the potential was considered by Barron, Flexner and Michaelis(70). They stated that an answer concerning the inertness of the "unattackable" electrodes was necessary for the correct interpretation of all potentials measured in tissues and bacterial culture. They concluded that this was "of such great importance that it justifies a separate study of platinum and gold which is soon to be reported." Unfortunately, however, no record was found by the author covering this proposed study.

The question concerning which metal, platinum or gold, was best for oxidation-reduction electrodes has resulted in differences of opinion. In order to properly determine the type of electrode to be used in this research, it was considered desirable to review the work of other investigators who have studied this problem. Because of this restricted viewpoint, the following literature survey on the use of electrode potentials in bacteriology and biochemistry did not represent the large majority of cases where platinum was used as the electrode. The emphasis was on experimental work where gold and platinum were compared or where the characteristics of either metal as the electrode were discussed. Other investigations which contributed directly to the evaluation of potential measurements of the sludge digestion process were also included in the review.

It was first noted by Potter(71) in 1911 that the electrode potential of an inoculated culture was more negative than that of the sterile medium. Gillespie(72) in 1920 was the first to observe the development of reducing conditions in bacterial cultures by following the fall in potential. Although he discussed the use of gold, only mercury, platinum and platinum black were used as electrodes. Michaelis(16) stated that the germs of all later investigations were contained in this work and the ideas credited to Gillespie were: (1) interpretation of the potential as an oxidation-reduction potential, (2) comparison with the hydrogen electrode at the same pH, (3) exclusion of oxygen, and (4) the fact that the addition of glucose to the culture increased the velocity of the establishment of the maximum reduction potential.

The potential drop resulting from bacterial growth as well as the other findings of Gillespie were confirmed by Clark et al.(49) and many others. It would be beyond the scope of this thesis to even attempt to list the many authors in this field. However, an excellent summary of the quantity of work done with bacterial cultures and electrode potentials can be found in the excellent reference book by Hewitt(48).

A relationship between the oxidation-reduction potential and the hydrogen electrode potential was noticed first by Gillespie(72) with a growth of E. coli. This was also observed by Clark et al.(49) with E. coli using platinum electrodes for the redox potential and platinized platinum for the hydrogen electrode.

The curves of E_h and the hydrogen potential crossed and remained close together after one hour at approximately -380 mv and then drifted upward. In spite of a slight but repeated depolarizing current, there developed an over-voltage which was maintained. This was observed many times. The gas produced from this culture consisted of slightly more carbon dioxide than hydrogen. Thus, the partial pressure of hydrogen was less than 0.5 atmosphere. A case was cited where the addition of a hydrogen suppressor, asparagine, resulted in a potential slightly positive to that of the hydrogen electrode. Organisms of the dysentery group in media from which no hydrogen was produced brought the potential almost to the hydrogen electrode. They concluded that the evaluation of these observations was not possible until more experimental work was done.

Among the others who investigated the growth of E. coli, the work of Boyd and Reed(73) was of special interest since they published their original experimental data for each of two platinum electrodes. This provided an example of the kind of electrode agreement that might be expected. The usual practice was simply plotting the average value if more than one electrode was used. The electrodes were allowed to remain overnight in the sterile broth before inoculating the broth. For the first three hours after inoculation of the broth the electrodes differed by 70 mv. However, during the active growth period the electrodes differed by only 10 to 20 mv. After 14 hours the values began to diverge until at 50 hours they were 130 mv apart. Although this large divergence between electrodes was probably more than was the usual situation, it did illustrate how the use of one electrode could give misleading data.

Addition of glucose to the broth before inoculation induced an earlier and greater fall in the potential. The beginning of the fall was coincident with the first evolution of gas and they concluded that hydrogen was a factor in the potential change. In previous work(14) it was stated that the potential change was not due to the carbon dioxide production. The electrodes behaved similarly to those in non-glucose broth exhibiting a large disagreement at first which became less during the active growth period. At 10 hours when the readings were terminated, the electrodes differed by 35 mv.

Another instance where individual electrode values were reported was by Ward(66) in the investigation of E. coli growth in synthetic media. He found large disagreements up to 95 mv between electrodes in the same vessel and up to 450 mv between the vessels themselves. Various types of platinum electrodes such as foil, coil, gauze and straight wire were used due to "somewhat conflicting statements in the literature". With nutrient broth and agitation there was much better agreement between the electrodes and between different vessels. The electrode agreement was usually within 5 mv with an occasional 20 mv difference. Between cultures the difference ranged from 5 to 10 mv with a greater variation during the active growth period. It was concluded that potential determinations in poorly poised media in the presence of oxygen were dependent on the type of bright platinum electrode used. This was believed due to the possibility of an oxygen electrode effect.

Platinum was used almost exclusively although a few gold electrodes were tried. The use of gold was the result of the work of Longsworth and MacInnes(54) and Elema et al.(74) who reported that gold was more sensitive than platinum. However, Ward did not find any advantage in using gold, and there was no apparent sluggishness of platinum as compared to gold. Ward found that stratification caused different readings from temporary poisoning of the electrode and agitated to get better agreement by using nitrogen. When a synthetic broth was intermittently agitated, better agreement between duplicate electrodes was exhibited although a considerable difference still existed between different broths. When stirring was started or stopped there was no definite trend, some potentials rose and some fell slightly.

Nitrogen gas was used in many experiments to deaerate the culture for anaerobic growth and as a result, agitated the solution. Differences in agitation did not change the potential, but did change the time necessary to reach the ultimate potential(14)(75). Coulter(75) used gold electrodes for potential-time experiments on sterile beef bouillon. Initial potentials were variable and poorly poised and were between +250 and +150 mv. Individual electrodes might disagree by 50 mv but often by only 5 mv when purified by polarization. A common limiting value and time were found for various bouillon samples. These were between -50 and -60 mv and the time was five to six hours for a rapid rate of oxygen removal by nitrogen. This gas rate was sufficient for agitation also. With less deaeration time, the potential change was slower, taking up to five days to reach -50 to -60 mv.

Coulter found that close agreement was not possible with electrodes of the purest metals obtainable and therefore purified the gold himself. This was fused on platinum wire and enclosed in glass. Four electrodes were used simultaneously. It was frequently necessary to make the electrodes sensitive by slight polarization.

Deaeration of a sterile meat broth by nitrogen was used by Knight(62) to study the effect of pH on the potential. The final limiting value was reached in six to eight hours. Soon after the deaeration was started, large differences in the potential occurred. However, as the potential became more negative, the potential values tended to come together until they differed by 10 mv in the final value. Occasionally one of the three electrodes used in each run would behave in a different manner.

This was theorized as being due to a crack in the glass seal with the metal. The electrodes were made by freshly gilding a platinum foil electrolytically for each experiment. The foil was welded to a platinum wire and the contact made by mercury.

Of more importance to this research than the addition of nitrogen to create anaerobic conditions by deaerating the broth was the reverse case of adding oxygen to the anaerobic broth. This was because the addition of an oxidizing agent to a reduced bacterial culture or broth closely corresponded to the condition of feeding a more oxidized raw sludge to a more reduced digesting sludge. It was found by Clark, et al.(49), that an addition of an oxidant to a cell suspension caused a positive displacement of the potential followed by a recovery toward the originally more negative potential. It was concluded that cell suspensions appeared to be of low active capacity acting as if small quantities of active poising material were fed from a large reservoir. This reservoir was slowly but decidedly mobilized.

The effect of oxygen on the potential of anaerobic bacterial growth was studied by Aubel, Rosenberg and Grunberg(76). They stated that a zone of defense was set up by hydrogen and reduced substances to counteract the oxygen. Using *Clostridium saccharobutyricum* it was found that 1.4 percent oxygen merely delayed the negative potential drop, but at 2 percent the culture was unable to cause any reduction. Knight(77) used oxygen in nitrogen to poise the potential of a sterile and inoculated broth at a constant level.

Instead of varying the oxygen input, Reed and Orr(78) added a definite volume of air to anaerobic broth containing different quantities of a reducing agent and two platinum electrodes. One ml of air passed into a peptone broth caused a sharp potential rise of approximately 40 mv. The potential returned to its original value in a few hours with 0.1 percent sodium thioglycollate but continued to rise with only 0.01 percent sodium thioglycollate in the broth.

The addition of oxygen or any other gas to a bacterial culture or sterile broth could affect the potential directly by a gas-metal effect, or indirectly by changing the oxidant-reductant ratio. The direct method would depend not only on the particular gas used, but also on the type of electrode metal. Studies of the sulphydryl system, cysteine-cystine, have produced a considerable amount of information on different electrode metals due to the difficulties in obtaining potential readings by different investigators. The electrode potentials in this system did not fit the behavior of a perfectly reversible system. This system is of the type: $2RSH = RSSR + H_2$. Specifically the reaction is:

$$\underset{\text{Cysteine}}{2\ CH_2SHCHNH_2COOH} = \underset{\text{Cystine}}{COOHCHNH_2CH_2S\text{-}SCH_2NH_2CHCOOH} + H_2$$

Such compounds are present in biological systems and are involved in many vital processes. These amino acids are present in digesting sludge and it was therefore felt that the results obtained on this system could aid materially in the understanding of electrode potential behavior in digesting sludge.

Dixon and Quastel(61) tried platinum and gold in the cysteine-cystine system. The drift exhibited with platinum was explained by the hydrogen pressure. Methods that were tried to control the drift included passing a polarizing current through bright platinum and the use of platinum black. The platinum black merely slowed the drift. The bright platinum was not affected by stirring or bubbling with nitrogen and was independent of the initial state, i.e., ignited or not. The electrodes were satisfactory in alkaline solutions but not in acid solutions where they slowly reached steady values and then gave considerably different values. Since biological reactions were near pH 7 or less, they concluded platinum was unsatisfactory for this type of system. They also were not able to get extreme accuracy in a solution such as quinhydrone.

Other electrodes, gold-plated platinum and massive gold, were also investigated but the only satisfactory electrode was pure gold. It gave very steady readings independent of the rate of stirring, was good in acid or alkaline solution and returned to the intial values after slight anodic or cathodic polarization. But these results could not always be reproduced with great accuracy with definite concentrations of cysteine. Such small deviations were "in no case sufficiently large to affect appreciably the magnitude of the potential". Differences of up to sixty millivolts caused much comment by Michaelis(16) concerning the reproducibility of these electrodes. The only cleaning felt necessary was washing the electrode with water. The gold plate electrode used had a surface area of 5.35 square centimeters.

Kendall and Loewen(79) compared gold, platinum, mercury, and dyes in cysteine. With cysteine and platinum there was a six to eight hour drift to a value of -140 mv. But the reduction potential was higher and reached equilibrium quicker if the electrodes were exposed to the air for a time longer than usual. They concurred with the statement by Dixon and Quastel(61) that the reduction potential "was determined by the previous history of the platinum electrode used". It appeared that the electrodes were influenced by the nitric acid used in cleaning as well as the air.

Anodic polarization of platinum in cysteine delayed the development of the reduction potential. Cathodic polarization caused a greater reduction potential which drifted back to the original value of -140 mv. With gold and cathodic polarization the potential was obtained with a little greater speed than with platinum, and with anodic polarization gold promptly returned to the original potential. They felt the difference in behavior was the speed with which the sulphydryl group could react with oxygen on the surface of the metal.

The smaller fluctuations with gold than platinum also observed by Dixon and Quastel were explained by the traces of oxygen or oxidizing agents adsorbed on the platinum whereas gold failed or didn't adsorb oxygen or oxidizing agents as well. Tests with reducing dyes showed that gold responded more rapidly than platinum and was less affected upon the subsequent addition of hydrogen peroxide. If cysteine was then added, the gold responded more quickly to a steady potential. The final values attained less than an hour after the addition of cysteine were the same for the gold and platinum. Subsequent additions of the peroxide yielded a greater response by platinum.

In evaluating the platinum as a hydrogen acceptor for the cysteine reduction potential, they found this could not be shown to occur and they added that therefore "the probability of its occurring with the gold may be entirely dismissed". These authors therefore expressed the belief that gold was more inert to hydrogen than platinum.

Michaelis and Flexner(80) have compared platinum, platinized platinum, gold-plated platinum, and solid gold in cysteine solutions. For blank platinum a long time was necessary to establish a final, definite potential. It was four to six hours after the start of deaeration by nitrogen before they felt justified in calling it the ultimate potential. They found platinum very sensitive to oxygen. After the potential was reduced by the system in several hours, oxygen was passed through which caused the oxidation potential to rise. However, nitrogen rapidly returned the electrode to its equilibrium value. This indicated to them a change in the electrode itself with the possible formation of an oxide or suboxide on the surface which had to be reduced, and with each metal differing in this respect. With small amounts of oxygen the potential depended on the speed of bubbling gas, the concentration of cysteine, and stirring. Without oxygen the stirring effect was not noticed. They attempted to get equilibrium with hydrogen but the velocity was slow and the process was incomplete. By polarizing the return velocity was fast with cathodic and slow with anodic polarization.

Different time intervals were necessary to obtain the same final potential even though all the electrodes checked with quinhydrone. Platinized platinum drifted as long as nine hours which was longer than blank platinum. Gold plate was similar to platinum except there was less response to hydrogen and the final potential was reached more slowly. There were individual differences in the time needed to reach equilibrium. If all traces of oxygen were excluded, they found the final potential was the same for platinum, gold-plated platinum, or mercury.

Pure gold was different in that it was the quickest to reach a constant final potential and there was less variation with a change from nitrogen to oxygen than for gold plate. The difficutly was that the final potential was different for each electrode and never was as negative as with the other electrodes. They behaved as though the surfaces contained oxygen, with each electrode having a different degree of oxidation. These experimenters felt that in the work of Dixon and Quastel the Eo constant of the potential equation varied too much for different gold electrodes and there was also variation for the same electrode in different experiments. Gold was discarded since acceptance of the potential as an intrinsic property of the solution was felt to be impossible.

The long period of time necessary for the establishing of the potential with platinum and gold indicated that the mechanism of the cysteine potential was different from truly reversible systems which established their potentials almost immediately. The authors felt that sulphydryl compounds were highly responsible for the potentials of noble metal electrodes in a tissue liquid.

The cysteine potential in the presence of oxygen was discussed by Michaelis(16). Cysteine consumed oxygen slowly and differed from well-poised positive potential systems like quinhydrone where oxygen caused little change in the potential. It also differed from reduced components such as dyes in the negative potential zone which had a great affinity for oxygen and hence determined the final potential by affecting the oxidant-reductant ratio. The potential of cysteine was sensitive to the slightest trace of oxygen and therefore, oxygen was of significance in the potential measurement.

The largest variation in the platinum potential was at very low oxygen concentrations in nitrogen. For one part oxygen in 40,000 parts nitrogen the potential varied by 17 mv from pure nitrogen. The stirring effect was most noticed at very slight oxygen pressures. Without oxygen stirring was not a definitely noticeable factor. A constant oxygen consumption at all pH's indicated that oxygen was deposited on the electrode surface and not consumed by the cysteine. For the oxygen effect on the electrode, two possible explanations given were: 1) tendency to behave as an oxygen electrode, and 2) catalytic effect on hydrogen and oxygen.

Comparisons of platinum and gold were made by other investigators which resulted in differing viewpoints. Boyd and Reed(14) studied differences in platinum and gold in anaerobically aged beef extract broth at 0°C. The electrodes were polished foil in glass tubes. A gas flow speeded equilibrium slightly and slightly decreased the time to reach the limiting potential, while it did not affect the final value. Slight polarization had very little effect. For the sterile broth without a gas flow, they found slight variations in the potential in any one experiment with gold or platinum. With two or more samples under the same conditions, the potential varied considerably. A statistical study was presented to analyse these differences. An excerpt from this is shown below. All values are in millivolts.

Metal	No. of Samples	Initial Mean	Std. Dev.	Probable Error in Mean	P. E. in Std. Dev.
Platinum	14	86	77	15	10
Gold	8	122	41	11	8

Thus platinum gave a mean potential of 71 to 101 mv. with a possible variation from -100 to +163. Gold gave a mean potential of 111 to 133 mv. with a possible variation of from 73 to 171 mv.

The variation within any one sample was much less than variation from sample to sample.

Mean	No. of Readings	No. of Samples	Std. Dev. of Initial Mean	P. E. in Std. Dev.
Platinum	75	3	7.2	1.7
Gold	101	4	22.	4.4

Longsworth and MacInnes(54) compared a gold and a platinum foil electrode in a broth containing <u>Lactobaccilus acidophilus</u> under anaerobic conditions. The platinum was found more sluggish and had more lag than the gold. The gold showed symmetry to the acid production rate curve and they suggested this meant the values were nearer to the instantaneous ratio of the oxidant and reductant. They felt the difference was due to the fact that the metals attained equilibrium at different rates with the electromotively active materials in the solution. They had found previously(81) that oxygen in the nitrogen affected the potential of the gold electrodes. The gold electrodes used were foils one cm square welded to platinum.

The exposed platinum wire was covered by a thin film of gold by melting. The gold electrodes agreed closely within three mv. The maximum difference was nine mv when a rapid change occurred in the solution potential.

When the electrodes were placed in the media from the sterilizer, gold usually gave +250 mv. The platinum value was from +400 to +500 mv indicating a larger response to the atmospheric oxygen dissolved in the media. Saturating the media with a nitrogen-carbon dioxide mixture resulted in a gold potential equal to zero which corresponded to previously reported values. Platinum approached this value but in a much slower manner requiring a period of time of two days duration.

Lepper and Martin(57) found gilded platinum and mirrored iridium disagreed up to 30 mv in a cooked meat media. The meat media was autoclaved with the electrodes and allowed to stand overnight. When very fresh the potential of the media was -200 mv, but the potential usually was -174 mv. Stirring dropped the potential 50 mv at once and it took several hours to return to the original value. These electrodes were compared in the meat media following the inoculation of anaerobic bacteria(82). With no obvious evolution of gas from a culture of _B. tetani_, the gold and iridium agreed and the potential dropped to -400 mv. However, with gas evolution using _B. welchii_, the iridium rapidly dropped to a potential of -450 while the gold remained approximately constant at less than -200 mv. They explained this by stating that iridium functioned as a hydrogen electrode showing the potential of the buffer solution surrounding the meat, while the gold was inert to hydrogen and remained poised by the feeble reversible system shown previously to be at approximately -200 mv. By adding a dye of lower potential with E_0' = -0.289 they found the gold dropped to a potential of -330 mv. When they reduced the gas-forming period by adding a suppressor, the iridium started to rise in four hours and agreed with the gold in seven hours.

Clark(49) in his extensive work with many types of electrodes did not draw any conclusions regarding the best electrode metal, although he appeared to use platinum and gold-plated platinum in biological and related systems. Borsook and Schott(83) used gold-plated platinum foil in studying the succinate-enzyme-fumarate equilibrium. Platinum was also used and the results were the same for both types of electrodes. Hewitt(48) preferred platinum, and stated that with gold wire and foil he did not obtain the reliable reproducible results obtained with platinum. No quantitative information was given. After reviewing the different electrodes used in the field of biochemistry and bacteriology, he concluded "that no more suitable electrode than bright platinum has been described."

Although this discussion does not provide a definite answer to the question, "What is the best type of electrode for use in bacteriological and biochemical systems?", it does present the advantages and disadvantages of the metals, platinum and gold. From this and the general characteristics of the metal electrode in question, a much more valid basis is possible for the selection of the electrode. In addition, this information can be of assistance in the understanding of oxidation-reduction potentials as applied to sludge digestion.

ELECTRODES USED FOR THE QUINHYDRONE SYSTEM

Another source of information for the investigation of the applicability of gold or platinum as an oxidation-reduction electrode, is the quinhydrone system. This organic compound is often used in conjuction with investigations of the potentials of bacteriological, biochemical and other systems to provide a means of determining whether or not the electrode is functioning properly. Quinhydrone is an excellent reference standard for electrodes because of its potential characteristics which include stability, reproducibility, being well-poised, rapid equilibrium between the electrode and the solution, and a large capacity to resist change from environmental factors such as the dissolved oxygen content of the solution.

The impetus for the study of the quinhydrone electrode was due to its use as a pH indicator before the glass electrode was developed. The usefulness of quinhydrone resulted from the fact that the ionization of the compound in a saturated solution produced an equal concentration of oxidant and reductant which provided a linear relationship between the potential and pH. The widespread use of quinhydrone resulted in many investigations of the relative merits of platinum and gold as the inert metal electrode for this oxidation-reduction system.

A survey of the electrode preferred by various workers and a comparison of platinum, gold-plated platinum and gold of different sizes, ages and sources with air and nitrogen were given by Morgan and Lammert(84).

They used an o.l N hydrochloric acid solution with quinhydrone. They found more people preferred gold and those who found platinum and gold similar, also preferred gold or gold plate due to sharper readings. These authors preferred platinum because: (1) platinum could be sealed directly into glass, (2) gold was easily alloyed with mercury and contaminated, (3) a larger current capacity was available for platinum, and (4) gold was at times variable. They found nitrogen improved the reproducibility of platinum and gold plate but did not affect gold or graphite. This effect meant to them that possibly platinum catalyzed the reaction with oxygen better than gold. They found in addition that the method of gold plating added a variable factor. They felt that the foil or wire should be larger than one square centimeter and concluded that gold and platinum were interchangeable. Corran and Lewis(85) tried platinum foil and abandoned this metal since they obtained unreasonable values. They felt that the platinum foil acts other than as an inert metal in this system and gold foil was used. After each measurement the gold was cleaned with chromic acid, boiled in distilled water and tested in a buffer solution. This cleaning was felt to be essential for the tests. However, Grossman(86) abandoned gold in favor of platinum for the pH of organism fluids including blood. For similar solutions Mislowitzer(87) also used platinum in preference to gold.

The use of platinum was not recommended by some investigators who also did not consider gold and platinum interchangeable. Borchardt(63) found platinum wire gave erratic results in quinhydrone after trying different cleaning methods. These were: (1) nitric acid, (2) alcohol flame, (3) hot chromic and sulfuric acids, and (4) a mild abrasive such as Bon Ami. Plating the platinum with gold gave good results but the plate did not stand up with the cleaning method adopted and therefore solid gold electrodes were adopted. Dixon and Quastel(61) also found that platinum did not yield the expected accuracy in quinhydrone.

The results of the survey on the metal preferred for the quinhydrone electrode indicated either that gold was usually preferred or the metals could be used interchangeably. The preference of platinum was not a common occurrence. That there should be any difference in the behavior of gold and platinum was interesting due to the fact that quinhydrone was regarded as a well defined reversible oxidation-reduction system which could overcome the inherent characteristics of the metal(16). Therefore, the electrode should independently indicate the potential of the solution without regard to the metal used.

OXIDATION-REDUCTION POTENTIALS IN SEWAGE TREATMENT

There are many opportunities for the successful application of oxidation-reduction potentials to sewage treatment. Hood(88) has summarized the possible benefits of potential measurements in plant control as follows:

1) Detection of deposits and growths in sewers
2) Detection of industrial wastes and toxic conditions
3) Proper sludge pumping scheduling
4) Detection of primary tank stagnation
5) Determination of conditions in filters, activated sludge tanks, sludge digestion tanks, influents and effluents.

In addition to their use simply as a control device, potential measurements can also contribute to the further understanding and evaluation of sewage treatment processes.

The application of oxidation-reduction potentials in the sewage treatment field has been concentrated on the activated sludge process. The large potential changes, which occurred after aeration was stopped, provided a very fertile field for laboratory study. This was also the situation for the anaerobic aging of raw sewage. In contrast to this the anaerobic digestion of sludge received little attention.

The use of an oxidation-reduction indicator was first proposed by Spitta and Weldert(89) in 1906. They recommended the use of methylene blue as an indicator of the oxidative state of a sewage effluent. This was further developed by Phelps and Winslow(90), and called the relative stability test. Clark et al.(49) gave an excellent discussion of methylene blue and electrodes in sewage. Data was presented on the change of potential with time in buffered sewage at different pH levels using potentiometric measurements. They recommended the use of electrodes rather than dyes. This was the first case of the use of electrode measurements in sewage.

The first electrode measurement of activated sludge was by Dickinson(91), in 1940 who made a bioelectrode by growing activated sludge on a platinum foil of one square centimeter. No direct EMF measurements were taken; only deflections of a galvanometer were used. There was no quantitative agreement. Rohlich, Sarles, and Kessler(92) in 1941 were the first to obtain potential readings on activated sludge mixtures and the first to do a plant survey with potentials. This work was expanded by Rohlich(93). One platinum electrode was used in the plant survey and three electrodes in laboratory aeration studies. These usually checked within ten mv. Trouble encountered with the electrodes was believed due to a film on the metal surface and for successful cleaning, the electrode was polished with a levigated alumina paste, dipped into aqua regia or hot nitric acid, washed thoroughly, and then placed in distilled water for several hours. This recommended cleaning method was later changed by Rohlich(94) to polishing with a clean filter paper or a mild abrasive.

Moore and Ruchhoft used three platinum electrodes in activated sludge studies(95). The metal was shaped as a coil after comparison with foil and straight wire electrodes in potential studies of inoculated filtered fresh sewage(96). The maximum difference between the three electrodes in the activated sludge studies was 80 mv, but agreement was usually within five mv. Cleaning was done by alternately immersing the electrodes in hot dilute nitric acid and sodium bisulfite followed by washing and storing in distilled water.

Other potential investigations of an activated sludge media were done with a single electrode(88)(97)(98)(99) except in the case of Keefer and Meisel who usually used three electrodes(100)(101)(102). The only workers who specified a cleaning technique were Nussburger(99) who cleaned his electrodes by rubbing with Bon Ami and Hood(88) who used nitric acid followed by distilled water.

The first investigation of the potential of digester sludge and supernatant was done by Hood(88). Potentials of other plant units were also measured. The platinum electrode used was 15 to 18 cm long and although it was not specifically mentioned, it appeared as if only one electrode was used. This was cleaned by immersing in nitric acid and rinsing with distilled water for the sludge studies.

The time interval used for readings varied from 10 to 30 minutes at different plants. Readings were taken every minute until there was equilibrium or a reverse trend. No agitation was used since it was felt that this would disqualify the readings, especially in poorly poised solutions. It was stated by Hood that recent verbal advice indicated platinum might be replaced, one reason being that values were obtained which were erroneously high. Hood presented the following potential values from different plant surveys.

Digester supernatant: .... -132, -121, -67, and -139 mv.
Primary sludge: .... +44 and -75 mv.
Digested sludge: .... -54 mv.

It was concluded that the hydrogen potential for anaerobic units should be from -100 to -200 mv for maximum efficiency and that when the potential approached zero, it was no longer optimum.

The other reference pertaining to potentials of digesting sludge was by Eckenfelder and Hood(98). To obtain the potential one platinum electrode was inserted into the sludge to be tested which was agitated by a magnetic mixer. Readings were taken every few minutes for 30 minutes. They stated that the resulting time-potential curve was a measure of the dynamics of the system.

Sulfate was added to a digesting sludge with a potential of 0 to -100 mv. The potential changed to a range of -125 to -175 mv and the digestion was improved with better gas production. Other sludge potential measurements were made on a digested sludge with a potential of -75 mv and a dormant digester with a low pH, high volatile acid content, and a potential of +200 mv. Additional potential measurements were presented on other types of wastes.

From the literature survey presented above, it can be seen that the use of oxidation-reduction potentials in the field of sludge digestion has been very limited. Since only a few scattered points in the digestion period were sampled, the value of the data was restricted. The lack of information on the potential behavior in a digesting sludge seemed to underline the need for a study on the application of oxidation-reduction potentials to the process of sludge digestion.

In this thesis, the many factors affecting the potential measurement have been studied. In addition the use of potential measurements has been explored to determine whether or not changes in the condition of the digesting sludge could be detected. Methods of measuring the potential of sludge have also been investigated. This thesis, as a whole then, was an attempt to study the use of oxidation-reduction potentials as an indicator of proper digestion, and to aid in the further understanding of sludge digestion.

EXPERIMENTAL APPARATUS

The primary objective in the design of the experimental apparatus was to permit the measurement of the oxidation-reduction potential within the digestion compartment. This, in turn, governed the design of the sludge digestion equipment. This was especially true in determining the method of agitation and the size of the digester; in other respects conventional procedures in the design of sludge digesters were followed.

Sludge Digestion Apparatus

The sludge digestion apparatus consisted of three single stage digesters housed in an enclosed chamber with provisions for temperature control, sludge feeding and withdrawal, gas collection, agitation and the electrode assembly. A schematic drawing of a sludge digestion unit containing the electrodes is shown in Figure 3. The digesters were made from one gallon glass jugs.

The digesters were placed on the second level of a two level incubator containing light bulbs as a source of heat. The construction is illustrated in Figure 4. The air temperature inside the incubator was controlled at 35±1°C by means of a thermoregulator. The selection of this temperature was based on the fact that the optimum for mesophilic digestion lies between 95 and 100°F. In addition, the large amount of work done with sludge digestion at this temperature, both on a laboratory and plant scale, provided a reference for the experimental work.

The gas collection system was constructed so that digestion progressed under constant pressure. A typical gas collector consisted of two cans. The smaller can was inverted and placed inside the larger one which was filled with an acid salt solution recommended for gas retention by the AOAC(103). Each digester had two gas receivers connected in parallel. This is shown in Figure 5.

Gas sampling for carbon dioxide was done in a Burrel contact adsorption pipette containing thirty percent potassium hydroxide solution. The confining liquid used was mercury.

The desirability of continuously agitating the sludge digesters was based primarily on the work of various authors who found that agitation was helpful in the measurement of the electrode potential(65)(66)(96). In addition some form of agitation for the sludge digestion process has also been recommended(19)(26)(104)(105)(106). Preliminary potential measurements in this research with hand mixing alone also indicated that agitation would be helpful. In order to select a method of providing continuous agitation, the effect of various mixing methods on both the potential measurement and sludge digestion were considered.

Agitation of the digester contents has been done with mechanical mixers, gas recirculation, and sludge recirculation. The preferable method for this research was considered to be gas recirculation because of the resultant gentle rolling action of the digester contents with the sludge flowing upward at the center and downward at the periphery. This rolling action would allow good sludge agitation without violent mixing which would

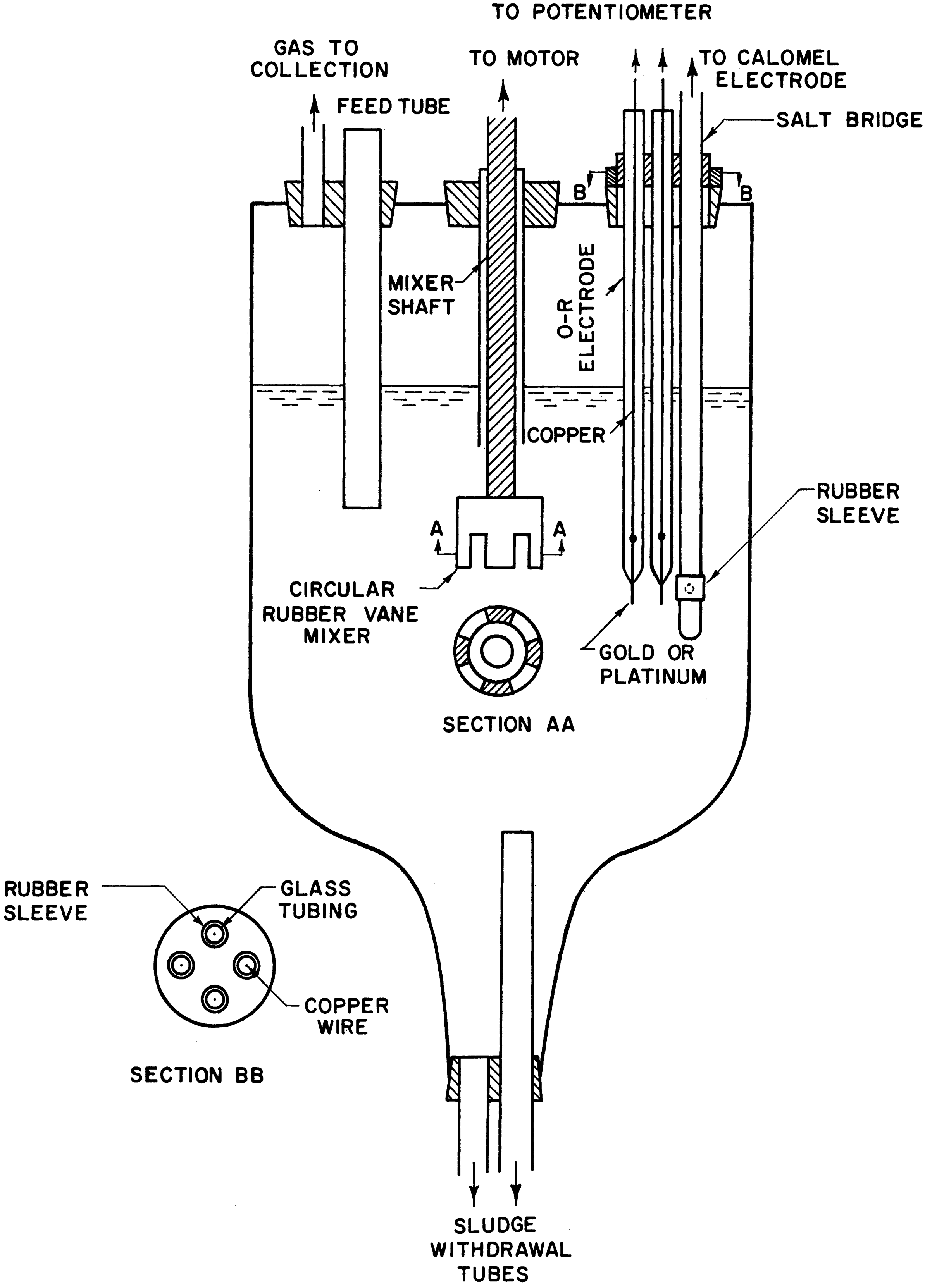


Figure 3. Schematic Drawing of a Sludge Digestion Unit Containing the Oxidation-Reduction Electrodes

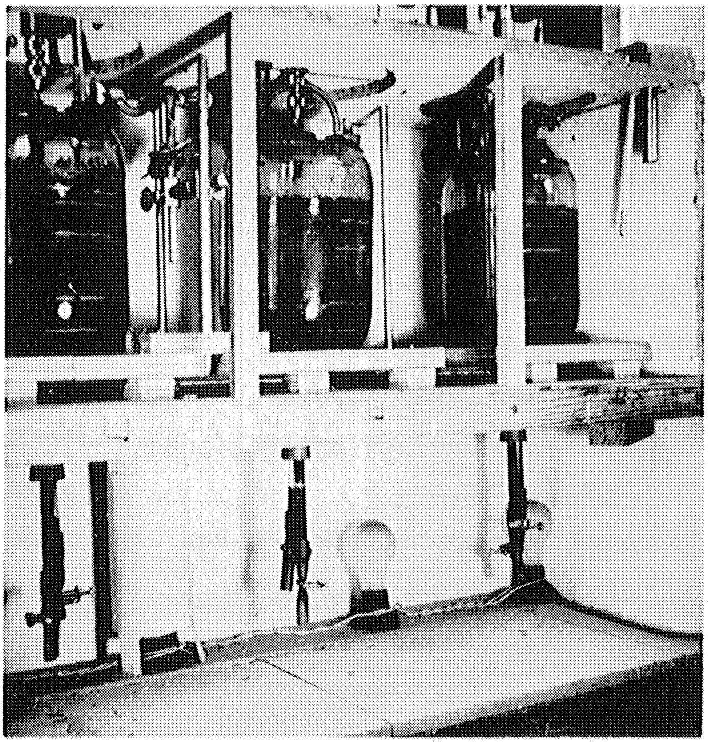


Figure 4. View of the two level incubator from the front.

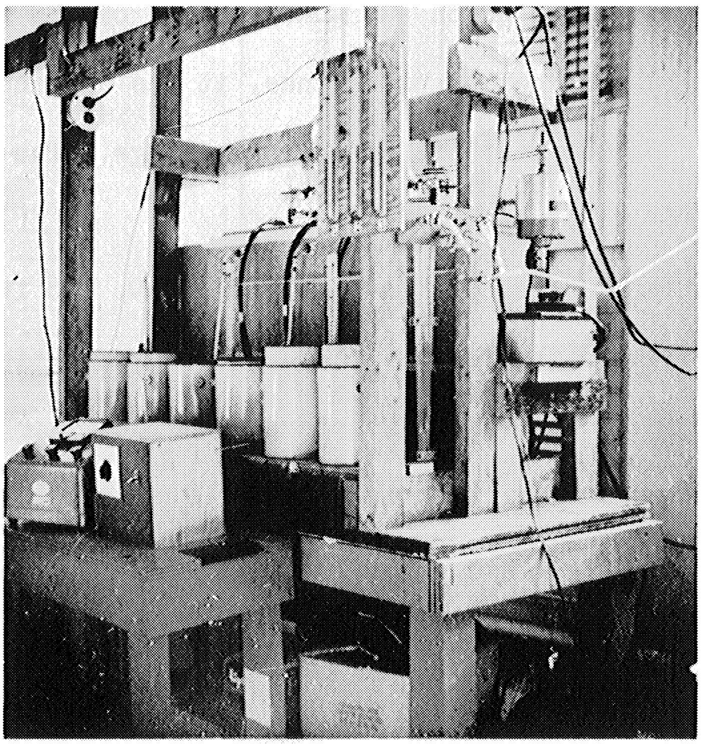


Figure 5. View of apparatus from the rear.

tend to decrease the sludge filterability. This method has been used successfully on both a laboratory and plant scale(26)(100). However, the possibility of a gas-metal effect on the electrode potential as discussed previously and the possible effect of the gas on the digestion itself led to the elimination of this method as a possible source of agitation. The effect of gases on bacteriological cultures served as a guide for the possible gas effect on the digestion process(29)(40)(54)(108)(109)(110)(111).

Some method of mechanical mixing was therefore considered. The centrifugal type mixer was given primary consideration since it would be designed to develop a lifting force in the center of the tank which seemed to be the most desirable type of agitating action. The use of vertical vanes arranged in a circle proved to have desirable characteristics. The spacing of the vanes had to be such that no plugging would occur and yet the desired action would be obtained at a reasonable speed. After trials with single and double units on one shaft, vanes on the top and bottom, and large holes in conjunction with vanes, it was decided to use one single bottom vane unit placed near the top of the sludge. The best design is illustrated in Figure 3.

The mixer consisted of a 1-3/16 inch OD, 7/8 inch ID rubber tube with four vanes cut in the tubing. The vanes were 1/2 inch long and 5/16 inch wide based on the outside circumference. The mixer shaft was inserted into a hollow spindle stirring unit with a three step pulley on top.

Dental chord was used to turn the mixers in the three digesters at the same speed. This type of belting was found satisfactory after the pulleys had black tape put on the riding surface for additional grip. The final agitation setup included two dummy pulleys, three spindle pulleys, the motor pulley and three short chords as shown in Figure 6. The motor used to drive the mixers was rated at one-tenth horsepower and continuous duty. Although it was single speed, the use of a pulley system as well as a variable transformer allowed variable speed control. The speed of the mixers under full load was near 600 RPM as measured by a stroboscope.

Oxidation-Reduction Potential Apparatus

The basic components needed for a potential measurement of a solution were the inert metal electrode, reference electrode, salt bridge and potentiometer. These components were similar to those used in the pH measuring system except for the replacement of the glass pH electrode by the metal electrode. Although the glass electrode has been universally adopted as the best method of measuring the pH, no such unanimity existed in the acceptance of the metal to be used for the oxidation-reduction electrode. Platinum has been used by the majority of experimenters with gold in a secondary position. Investigators who have considered the use of both metals did not particularly agree on which gave the best results.

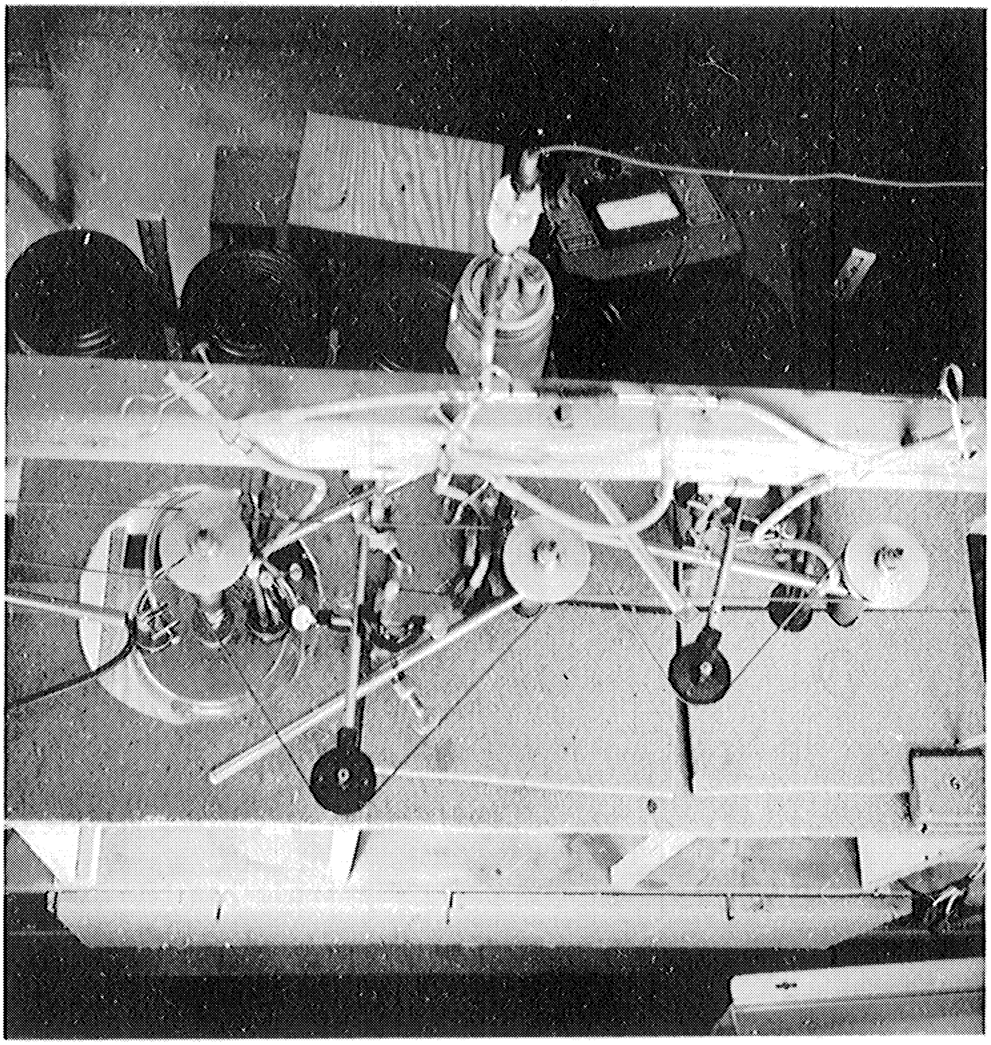


Figure 6. View of apparatus from the top.

The most thorough investigations covering the comparison of gold and platinum as an electrode were performed on the same system by two different authors(16)(61). The result produced two different opinions. Gold has been said to be more sensitive in bacteriological studies(54)(74), but another investigator did not find that the two metals differed in this respect(66). Although reference to the greater sensitivity of gold was found, the author did not find any instance where platinum was alleged to be more sensitive.

The choice of a particular metal by different investigators often seemed based on the ease of the electrode construction. In this respect platinum had a decided advantage over gold due to the fact that its coefficient of expansion was much closer to that of glass. Thus, sealing of the metal into glass was possible and the electrode metal could be fully immersed in the solution to be tested. It was of interest to note that the usual commercial gold electrodes consisted of a gold-plated platinum wire since only the platinum could be sealed into the glass.

Another possible reason for the preference of platinum might have been that so-called gold electrodes were actually gold-plated platinum. This interchanging of nomenclature was observed during the literature study. Therefore, the preference of platinum over gold might actually have been over gold-plated platinum. This distinction was important because gold and plated-gold electrodes did not always behave in the same fashion, and because of the variability introduced by the plating itself.

The investigators who used gold, constructed the electrodes by fusing the gold to platinum which was then sealed into the glass. The exposed platinum was then gold-plated. However, the development of a special glass in recent years with a similar coefficient of expansion to that of gold has made it possible to construct gold or platinum electrodes in a similar manner. Thus, the advantage of platinum described above would no longer be a factor in the choice of an electrode metal.

From the literature survey presented previously, the use of gold as the electrode appeared to have several advantages over platinum. The gas-metal effect was the most important. The production of hydrogen from digesting sludge would cause platinum, unlike gold, to assume a gas-metal potential and mask the effect of weakly poised oxidation-reduction systems. The presence of catalytic activity due to the metal was always a factor with platinum, not gold, The possibility of the greater sensitivity of gold to bacteriological solutions, and the experimental work in this research showing gold was more sensitive to quinhydrone were other factors in favor of this selection of gold.

Although the advantages of gold made it appear to be better for digesting sludge, the literature study did not provide a clear-cut answer to the definitely superior electrode. As a result, gold was selected as the standard electrode for this research with platinum being used in a supplemental manner so that the author could compare the two metals experimentally. The use of gold was the first attempt to measure the potential of the sludge digestion process with an electrode other than platinum.

The construction of either type of electrode was similar. The metal was fused to copper wire and then sealed into glass. The possibility of sealing gold into glass was made possible by a special lead glass from the Corning Glass Company with an exansion coefficient similar to that of gold. The Corning code number for this glass was 1990, and the glass ranged in OD from 6.5 to 7.0 mm. Platinum was sealed into ordinary soft glass with an OD of 6 mm.

The first step in the construction of the electrode was the joining of the copper conductor to the inert metal. One inch of the inert metal was fused over a Bunsen burner to the copper. The inert metal was then sealed over a Bunsen burner into the glass. The metal was pushed slightly forward while the glass was still hot in order to insure a water-tight seal. The electrode is shown in Figure 7. The gold and platinum wire were number 20 gage and the copper wire was number 16 gage.

The exposed length of the metal wire after sealing was about 0.25 inches giving a surface area of about 0.0259 inches or 0.162 square centimeters. The length of the exposed metal comprising the electrode was kept small to minimize the area of measurement. This length was felt to be sufficient based on the work of Vennesland and Hanke(112) who found that large platinum foil with a surface area of four square centimeters gave no better results than small wire ones in anaerobic bacteriological studies.

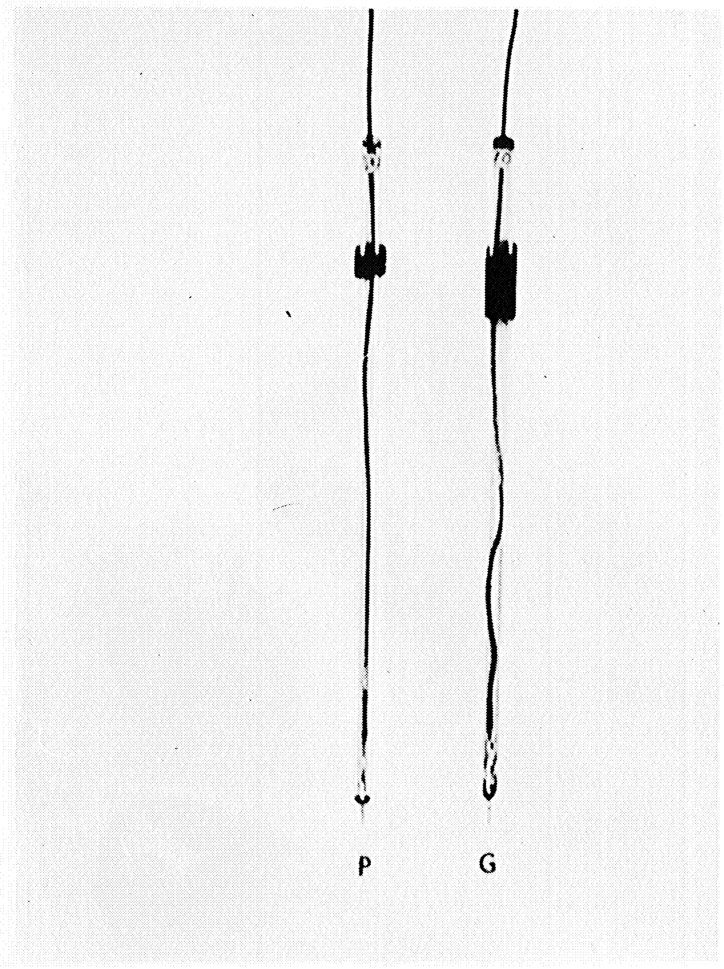


Figure 7. View of gold and platinum electrodes.

In order to determine the effect of the fusion of the metals on the potential, some platinum electrodes were constructed with a mercury seal. This provided the electrical contact instead of the fused joint. In quinhydrone solutions the difference between the two types of joints was found to be insignificant and it was concluded that the fusion method was wholly satisfactory for this work.

The reference electrode or half cell used in this research was a Beckman calomel fiber type with a salt reservoir. Since this electrode could not be used directly in the digesters, a salt bridge extension was made using glass tubing. The salt bridge solution contact point in the digesters consisted of a short rubber sleeve placed over a hole made in the glass tubing about one inch from the sealed end. This procedure proved very successful after unsuccessful trials with contact points pinched at the end as a dropper or an upturned end. Diffusion of the sludge solution into the bridge was the major problem in these open-end types. Rohlich(94) evidently experienced this with activated sludge since it was stated that the liquid junctions were a source of trouble.

Although agar-saturated potassium chloride bridges have been used widely in bacteriological work, their use was not possible here as the electrode was in the sludge over very long periods. Possible growths or other contamination would cause much difficulty. The sleeve type bridge using saturated potassium chloride worked very successfully and never needed to be removed from the sludge solution. In addition this salt bridge worked very well for potential measurements in a lake bottom mud sample. Renewal of the solution contact was very simply accomplished by squeezing the connecting rubber tube. Saturated potassium chloride solution was used as the salt bridge fluid. Although the temperature coefficient was higher than the 0.1 or 1N solutions, there was very little chance of error due to concentration changes.

The reference electrode was placed in a saturated solution of potassium chloride which was connected to the salt bridges in the digesters and the electrical connection went to the potentiometer. An air space was put on top of the salt bridge of each digester to eliminate difficulties due to air bubbles in the line. This is illustrated in Figure 6. The vacuum tube high resistence potentiometer used as the measuring instrument was the Beckman model H-2 pH meter.

A specially-made rubber stopper was used to hold the electrodes and maintain the digester pressure. This can be seen in Figure 3. The stopper was made of two sections. The base which was inserted in the digester was a rubber stopper with an opening to allow the electrodes to pass through unobstructed. The top was another rubber stopper with four holes for the three electrodes and one salt bridge. A piece of rubber tubing was placed around the electrode stem so that a gas tight seal would result when the electrodes and salt bridge were inserted into the electrode holder.

The electrodes were connected to the potentiometer through a ten point switch. This switch was placed in a box in which the inside was lined with aluminum. The wires from the electrodes to the potentiometer were shielded and the shielding part of the wire was connected to the aluminum-lined box. The shielding was used to diminish the influence of any disturbing electromotive forces outside the circuit. Stray currents from external sources such as the agitation apparatus could have caused difficulties. The aluminum lining was not grounded to any external source. This was based on two factors. White(110) in discussing shielding requirements stated that the shielding preferably should not be connected to the earth. In the initial experimental phase of this thesis it was found that a vibrating needle could be eliminated if the potentiometer was grounded to a water pipe. But it was also discovered that renewing the salt bridge produced the same result. From this it was felt that there was a possible danger in external grounding and it was not used in any further work.

Lactose Broth Feed Apparatus

The design of the apparatus used for the feeding of a lactose-peptone-beef extract mixture to a digested sludge embodied the basic requirements of electrode measurements as discussed above. The digester was a one quart wide mouth mason jar and contained about 700 ml of sludge. The salt bridge, three electrodes, a submerged feed tube, and a gas outlet were held in place by the jar cap. The electrode leads were shielded and a four point switch was used between the electrode and the potentiometer. The potentiometer used was the Beckman Model H-2 pH meter. The salt bridge system was the same as described previously.

The gas collection system was initially a water displacement type. But variable pressure caused difficulties in electrode measurements and henceforth, a constant pressure inverted can type was used. The difficulty was due to the pressure release when the gas collector was emptied. Between the digester and the gas collector a flowmeter was placed to indicate instantaneous rates of the gas flow. It consisted of a glass tube packed with glass wool yielding a linear relationship between the rate and pressure drop. This was calibrated using a wet test gas meter. The entire apparatus was placed in a vented hood in which the temperature remained at 27 ± 1.5°C.

EXPERIMENTAL PROCEDURE

Lactose Broth Feed

The feed used was Difco Bacto dehydrated lactose broth which contained a lactose-peptone-beef extract mixture. The ratios of the components were 5-5-3 for the lactose, peptone, and beef extract respectively, and the dry solid contained about 95 percent volatile matter. This was suspended in a minimum amount of water. The quantities fed varied from one to ten grams of solid. The quantities added were so small that usually no digested sludge was withdrawn.

The digested sludge at the beginning of the test was an equal mixture of two and ten month old sludge aged in the laboratory. This was obtained from the Ann Arbor Sewage Treatment Plant which used activated sludge treatment. The ten month old sludge was considered as a completely digested sludge and the two month old sludge as a digested sludge still retaining good seeding properties. It was felt that the potential changes would result only from the feeding and the digested sludge would produce no metabolic action on its own.

After the feeding, the mixture was shaken by hand to insure a complete blending of the materials. During the run, measurements were taken of the oxidation-reduction potential, gas rate and gas quantity. The gas production rate was obtained by a manometric reading and the quantity by the rise of the inverted can gas collector. The pressure of the system and temperature were checked at intervals and the action of the digestion on the volume of sludge and supernatant was followed.

Sludge Digestion

The digested and raw sludge were obtained from the Ann Arbor Sewage Treatment Plant. The raw sludge from the primary tanks was picked up at intervals and stored until used in a refrigerator at a temperature of 4°C. The temperature of the feeds was either at 10°C or 30°C.

The feed sequence usually consisted of the following steps: (1) mixer on, (2) digested sludge withdrawn, (3) mixer off, (4) feed, (5) mixer on, and (6) mixer off. The mixer was on about ten minutes before a sludge withdrawal in order to insure that a uniform sludge mixture would be withdrawn. The feeding was followed by ten more minutes of mixing to blend the raw and digested sludge.

The major measurements obtained were oxidation-reduction potential values and gas production. From the gas production, gas rates were calculated on the basis of a ten hour interval. The samples for analysis of carbon dioxide were taken from the gas collectors. Volatile acids, pH, total and volatile solids were determined according to Standard Methods(114).

Electrode Potential Measurements

For the digestion studies the electrodes were allowed to remain in the sludge for long time intervals. This allowed the continuous measurement of the potential in situ so that the metabolic activity of the digesting sludge could be followed at all times. After placing an electrode in the digester, approximately two days were allowed for the electrode to come to equilibrium with the solution potential. By this procedure the potential changes resulting from the adjustment of the electrode and the metabolic changes of the sludge would not be conflicting.

In addition to the digestion studies, electrodes were used for the potential measurement of sludge samples from plant digesters. Before reusing an electrode, an experimental procedure for cleaning the metal had to be developed. From the literature survey presented previously, it was found that there existed a large divergence on which cleaning procedure was most effective. In addition, most of these cleaning techniques could affect the metal surface and, in turn, the potential measurement. The method of using a weak abrasive appeared to be the best possibility, especially since this technique has been successfully used in sewage-activated sludge studies.

To better evaluate the effect of cleaning on the electrode to be used in digested sludge, two methods were tested. In order to provide a contrast, one method involved wiping the metal with a wet cheesecloth and the other involved soaking the electrodes in hot nitric acid. Cleaning with nitric acid was tried not only because of its ability as a powerful oxidizing agent, but also because it has been used by many workers including those who have investigated digested sludge.

Both platinum and gold electrodes were immersed in the hot acid for a period of 15 minutes. This was followed by a thorough rinsing and placing of the electrodes in distilled water for ten minutes. Upon insertion into the sludge the electrodes showed wide disagreement. The trend to the negative or reducing potential was initially much more retarded for the platinum indicating more of a residual effect from the oxidizing agent. This was also found by Kendall and Loewen(79) with the cysteine system. Since both the platinum and gold electrodes appeared to be sluggish, it was concluded that this technique would not be satisfactory.

Electrodes cleaned by wiping with a wet cheesecloth and soaking in distilled water produced good results. The agreement and reproducibility that was obtained in the sludge indicated that this method would be satisfactory. Although this technique was very mild in comparison to most cleaning methods used, a similar method was used by Dixon and Quastel(61) who found that washing the electrode in water was sufficient for tests in the cysteine system.

In the discussion of the experimental work, the changes in potential are usually referred to as rises or falls. The former signifies a change in the more positive or oxidizing direction, and the latter signifies a change in the more negative or reducing direction. The potential values are expressed in millivolts referred to the calomel electrode, E_c. If the hydrogen electrode is used as a reference, E_h, it is specifically indicated. The potential measurement is identified by various terms, all used synonomously. These are: oxidation-reduction potential, electrode potential, redox potential, and potential. Identification of a particular electrode is used when needed. This consists of a number followed by the letter by the letter G or P. The former represents gold and the latter, platinum.

BEHAVIOR OF ELECTRODES IN QUINHYDRONE

In order to check the condition of the electrode after construction and during the life of the electrode, an oxidation-reduction system was sought which has been thoroughly investigated and would provide a reference potential solution. The system had to be stable, reproducible, well-poised, result in rapid electrode equilibrium, and have a large capacity to resist change. Quinhydrone was such a solution. Because the relationship of potential, temperature and pH of this medium had been thoroughly investigated and published widely, it was thought that the use of this solution would add no unknown variable.

The solution was made by adding a small amount of quinhydrone to a buffer solution of known pH. The actual quantity added was not determined due to the supposedly small error resulting if the solution was not saturated. This would amount to less and 1 mv at 0.1 of saturation, or 0.377 grams quinhydrone per liter(115). Between tests the electrodes were wiped, washed and stored in distilled water.

Different types of gold electrodes were first tried to see whether the history or handling had any effect. One was freshly made and sealed into a special glass, another was approximately five years old and had been soaking in distilled water for at least two years, and the last was a Coleman gold-plated platinum electrode. The first and last type were fully immersible, but the second type did not allow full immersion of the metal. After wetting with water and drying with a cloth, the electrodes were inserted into the quinhydrone solution and exhibited excellent agreement.

The new type of electrode, so-called as the metal was bonded directly to the glass, was slightly cold-worked by bending. Insertion into the solution resulted in a slow adjustment. Not even in 15 minutes had it come to the correct value. This effect of physical handling has been shown by others (50)(65). This factor was considered in constructing and handling electrodes.

Comparison of the gold and platinum electrodes in quinhydrone resulted in a surprising lack of accuracy and precision by the platinum electrode. By repeating the procedure several times it was discovered that the potentials of some platinum electrodes were dependent on the concentration of the quinhydrone solution as shown in Figure 8. However, this was not the case for the gold electrodes. The first test solution, I, was made by adding a small amount of quinhydrone to the buffer solution and the potential was then determined. Another small amount of quinhydrone was then added resulting in solution II. A final addition of quinhydrone resulted in a definitely saturated solution III. The platinum potential in solution I showed a wide scatter of values which were brought closer together by increasing the solute concentration. A summary of these results is given in Table II in terms of the arithmetic mean, $\overline{X}$, standard deviation, S.D., and high and low potential values. The sample consisted of twelve platinum and nine gold electrodes. The only solution in which these electrodes were previously used was quinhydrone.

Table II

COMPARISON OF GOLD AND PLATINUM ELECTRODES IN QUINHYDRONE SOLUTIONS WITH VARYING SOLUTE CONCENTRATIONS

Electrode	Quinhydrone Solution Number	$\overline{X}$ (mv)	S.D. (mv)	High Reading (mv)	Low Reading (mv)
Platinum	I	86.33	12.6	107	65
	II	81.33	5.6	91	72
	III	77.67	1.6	81	75
Gold	I	75.67	1.14	77	74
	III	75.33	0.84	76	74

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 were of low capacity and often behaved in a sluggish manner. If platinum was less sensitive in quinhydrone, perhaps, but not necessarily, it would be the same in biological solutions.

No reference was found in the literature concerning the relative sensitivity of gold and platinum in quinhydrone. However, platinum was found to be more sensitive than gold-plated platinum(115). Investigations of the potassium ferri-ferro-cyanide system by various authors also indicated a difference in electrode sensitivity. Lewis and Sargent(116) first tried plain platinum foil. Later the platinum was platinized, iridized or gold plated. They stated, "The gold gave by far the most consistent and accurate results." Comparison of the work of two other authors clearly demonstrated the difference in electrode sensitivity. Michaelis(16) stated that a gold electrode yielded a potential at a concentration of 0.0001 M while Shaffer and Williams(117) found with platinum that the potential was indefinite at 0.001 M.

The general effect of the solute content on the potential was discussed by Clark et al.(49). They found that electrodes of different or the same metal agreed perfectly when appreciable amounts of oxidant and reductant of an active reversible O-R system were present. But if extremely dilute solutions were used or the ratio of oxidant to reductant approached zero or infinity, the electrodes would disagree.

A very practical result of the solute concentration on the potential was seen in a statement by Hewitt(48), "The concentration of quinhydrone has little effect on the potential...". The results of this research indicated that by following this procedure, supposedly erratic platinum electrodes would be discarded even though they might be perfectly satisfactory.

However, the correct potential reading in quinhydrone by an electrode did not insure that the electrode was not poisoned. It has been found that an electrode which appeared erratic in a sludge solution, acted satisfactorily in quinhydrone. The main value of the quinhydrone was in detecting distinct malfunctioning of the electrode metal before use in biological solutions.

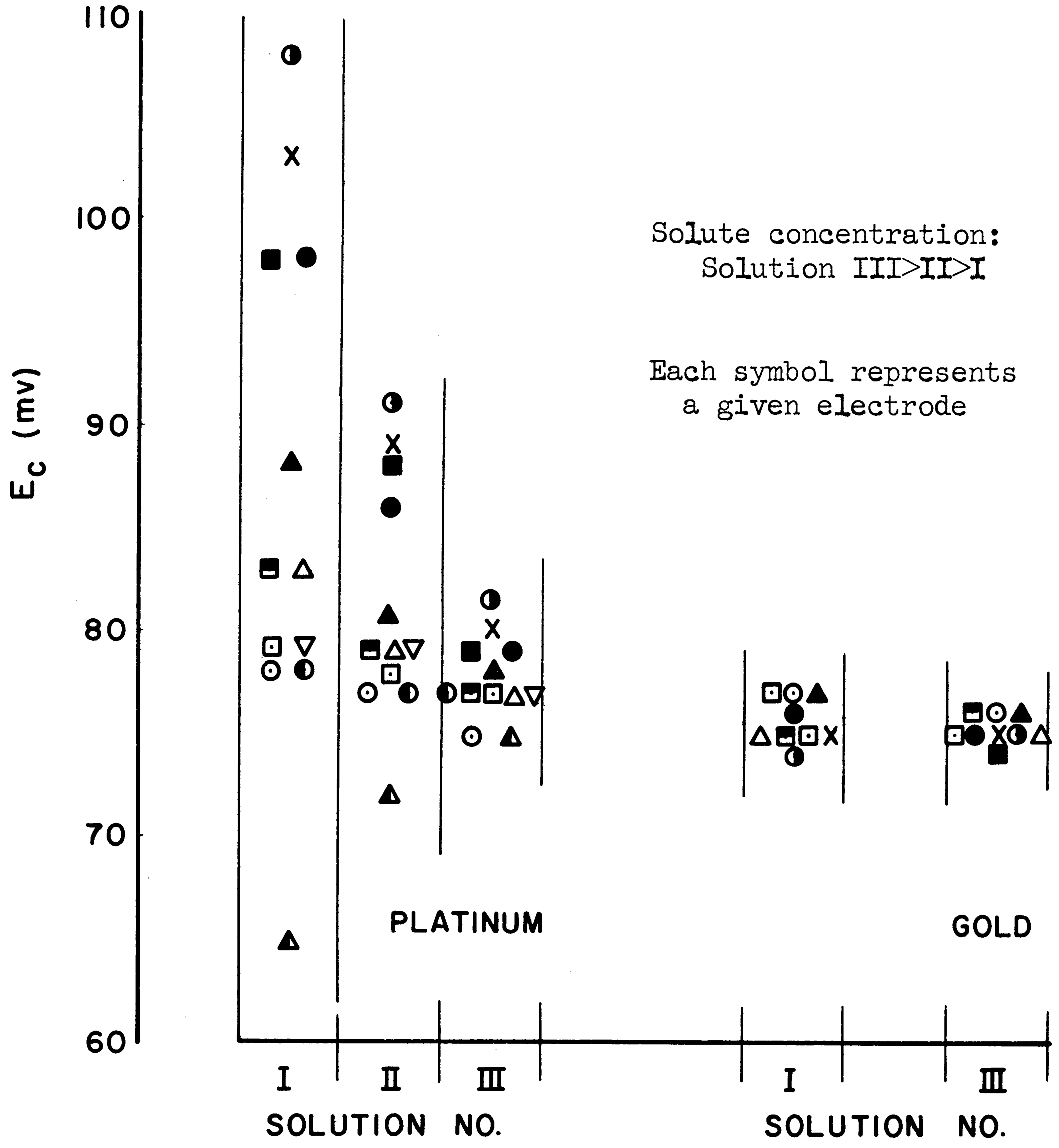


Figure 8. Comparison of Platinum and Gold Electrodes in Varying Concentrations of Quinhydrone Solution

ADJUSTMENT OF THE METAL ELECTRODE TO THE SLUDGE POTENTIAL

The determination of the oxidation-reduction potential of a digested sludge did not appear initially to be a complex technique. Although previous work on this subject was very limited, the recommended procedures consisted of short time electrode immersion. Hood(88) found that 10 to 30 minutes was sufficient with readings taken every minute until equilibrium or a reverse trend occurred. It was recommended that no agitation be used as he considered the readings might not be valid, especially for a poorly poised solution. However, agitation with a magnetic stirrer was recommended by Eckenfelder and Hood(98). They stated that readings should be taken with one platinum electrode every few minutes for a total of 30 minutes.

Initial experiments using a 30 minute time period appeared to substantiate the recommended short time immersion. However, further work disclosed that this procedure was greatly in error since the time needed to fully stabilize the potential reading was at least ten hours or more. Because the determination of the correct potential of a sludge was considered to be of utmost importance, a considerable amount of time was spent on this subject. The fact that the only published technique for obtaining sludge potentials was erroneous added to the importance of this study.

A study of the literature of the bacteriological and biochemical fields disclosed that the electrode adjustment period, or time necessary for the electrode to come to equilibrium with the solution, used by various workers was much longer than 30 minutes. Six to eight hours were used by Knight(62) with freshly gold-plated electrodes; Lepper and Martin(57) with special gold-plated and iridium electrodes autoclaved a meat media after inserting the electrodes and let the mixture equilibrate overnight; Reed and Orr(78) found a few hours were needed with platinum for a reducing agar with sodium thioglycollate; and Michaelis(16) used four to six hours in a cysteine solution for platinum and a slightly longer time for gold-plated platinum.

A very important characteristic of practically all the adjustment times reported was that nitrogen or autoclaving was used to deaerate the media to create anaerobic conditions after the electrode was in the media. Although the work of Reed and Orr(78) was an exception, unfortunately the anaerobic conditions were created by chemical means. Thus, no quantitative information on the potential measurement of an already existing anaerobic bacteriological or biochemical system was available. However, the adjustment periods listed above did indicate that a longer time than 30 minutes would be necessary.

It was of interest to note that the adjustment period was practically always reported as a time interval and not a fixed time. From this it would appear that a variable factor existed either in the solution or the electrode or both simultaneously. The work of investigators who have used more than one electrode in a solution indicated that the major variable in the testing procedure was the electrode although the solution effect could also be appreciable.

On examination of one of the many adjustment curves obtained in this research, some very significant observations were made. This potential-time relationship shown in Figure 9 was representative of the results obtained in a digested sludge under quiescent conditions. The platinum electrode, one of six used, was inserted into a sludge which had been removed two hours previously from a plant digester.

By plotting the abscissa in minutes, the curve appeared to approach a constant potential value near 60 minutes. However, by following the potential over a longer period and expressing the abscissa in hours, it became apparent that the potential adjustment actually took a considerable length of time. The short time abscissa in minutes yielded a pseudo-equilibrium which evidently was what caused Eckenfelder and Hood(88)(98) to recommend that 30 minutes was sufficient for a digested sludge potential measurement. Although the curve was still dropping at 30 minutes, the slope had decreased substantially to about 0.5 mv/minute and this could possibly have been assumed by them to be indicative of the approach of equilibrium.

The reading at 30 minutes was -388 mv and at equilibrium it was -488. This indicated an error of 100 mv would be made if the short time adjustment period were used in this example. If these potential readings were expressed as E_h, the 30 minute and equilibrium readings would be -142 and -242 mv respectively. Therefore, these values could be compared to those published by these authors. For the digester supernatant the following values were given: -132, -121, -139, and -67 mv. Three values were given for digester sludge: -75, -54, and -125 to -175 mv. Since practically all 30 minute readings obtained in this thesis were within the E_h range of -60 to -160 mv, it could be seen that most of the values cited above fell within this potential range.

An adjustment trial was made with a magnetic stirrer to follow the recommended procedure of these authors(98). The results in the short time interval were not significantly different from the quiescent condition. This was also shown by other trials with agitation. From these results it must be concluded that the potential values given by these authors were not valid for the potential of digested sludge.

After it had been established that no valid sludge potentials had been published, this section of the experimental work was directed towards the factors in the single potential determination of a digested sludge. This type of measurement basically consisted of inserting a metal electrode in a sludge solution and following the potential change with time until equilibrium was reached. However, there existed two variables in this measurement, the electrode and the sludge. This investigation was concerned primarily with the electrode and methods to obtain the sludge potential.

Adjustment trials were done with various sludges ranging from a freshly drawn plant digester sludge to a sludge remaining dormant for a three year period in a laboratory digester. A major portion of the testing program was done in the laboratory digesters where the metabolic activity level could be approximated from the history of the digestion. The work outside the digesters was mainly concerned with plant digester sludge. Both platinum and gold electrodes were used and the number of electrodes at one time in a sludge ranged from one to twelve. Tests were run with both quiescent and agitated sludges.

The agitation tests were done in the laboratory digesters under a slight gas pressure. In this manner it was assured that there would be no oxygen diffusion into the sludge which could affect the potential(16)(66)(77)(112). An example of the effect of oxygen adsorption on the electrode potential in sludge is shown in Figure 10. The sludge had been taken from a plant digester and placed in a two liter beaker which was open to the air. Twelve electrodes, six platinum and six gold, were then placed in the sludge. Five days later the sludge was gently stirred with a glass rod. This is indicated in Figure 10 as "hand mix". The second mixing was done 23 hours later for 22 minutes with a vane type mixer similar to that used in the laboratory digesters. The degree of mixing was much more thorough as can be seen by the much larger potential rise.

The potential values were averaged from six electrodes. With this number of electrodes it was possible to discard erratic values and still be reasonably assured that the average value was representative. Electrode agreement was better for gold after the first mix and better for platinum after the second mix.

During the second mixing the platinum started to drop after the initial rise of about 100 mv. The potential reduced its change rate near -455 mv which approximately corresponded to a similar situation for the gold electrodes. However, the gold rose 58 mv, much less than the platinum. The potential rise after the first mix was also much less for gold, 3mv, than for platinum, 22 mv. This clearly indicated the greater susceptibility of platinum to oxygen.

The cause of the potential change to a more positive value was oxygen since it had been established during agitation trials in the laboratory digesters that mixing caused a trend toward a more negative potential. However, the mechanism of the effect was not as clearly known. The electrodes were over three inches from the surface and therefore could not have had any direct contact with the atmosphere. Thus, it must have been adsorbed oxygen which created a gas-metal electrode effect.

The apparatus used by Eckenfelder and Hood(98) was of interest in this connection. The electrode was placed in a rubber stopper which in turn was placed in an Erlenmeyer flask containing a magnetic bar for agitation. Although it was mentioned that air must be kept from entering the flask, no provision was made for the air in the gap between the sample and the stopper. This would definitely cause erroneous readings as seen from the previous discussion. A solution to this problem would be to fill the flask to the top and replace the stopper so that no oxygen would be entrained.

The quiescent tests were done both in the laboratory digesters and in beakers open to the air. The two liter beaker was filled with about 1500 ml of sludge and the electrode metal was about three inches below the surface. The exposure of the sludge surface to the air did not affect the potential results when quiescent. It appeared as if the sludge formed a protective zone at the surface against oxygen diffusion. Tests with quiescent sludge were emphasized in this research in order to contribute towards the goal of the simplest possible method for potential determinations in the field. In addition, insertion of an electrode into a digester would be under conditions of a relatively quiscent sludge. Without agitation, the only apparatus necessary would be a portable pH meter and the electrodes.

However, the length of time necessary to reach the equilibrium potential under quiescent conditions would be a disadvantage for routine process control. Any reduction in this time would be a valuable goal. One method of achieving a more rapid electrode response was by the use of agitation(14)(75). Although the experimental results indicated that this technique greatly reduced the adjustment time, erratic behavior in both the gold and platinum electrodes was a disadvantage. It was not usually possible to determine the potential with any accuracy due to sudden changes in the electrode reading.

One of the more successful tests is shown in Figure 11. Agitation was started two minutes after the platinum electrode was inserted into the sludge which had a potential of -505 mv. When the potential reached -528 mv, the agitation was stopped. This occurred near 4.5 hours. The potential then rose and in a short time leveled off near -502 mv. This value was maintained for the next 20 hours. Unsuccessful trials differed in that the potential rose much more after agitation was stopped before dropping again to the correct potential. It appeared in these cases as if the electrodes were indicating a temporary potential due to the agitation. The potential that the electrode rose to was near a value corresponding to a quiescent sludge adjustment trial. Since only one speed was used for the agitation tests, it was possible that an optimum stirring rate existed which would eliminate the erratic electrode behavior.

In all agitation trials the first 20 to 30 minutes of adjustment did not differ from the results of quiescent adjustment. The erratic behavior took place after this period. Although agitation did not affect the early adjustment phase, it did improve the adjustment after the potential-time slope began to decrease. It was not the initial potential drop to between -300 to -400 mv that created the long adjustment phase, but rather the subsequent drop over the last potential interval. It appeared as if the driving force became less as the potential indicated by the electrode approached the equilibrium potential.

Although agitation had decreased the adjustment time to about three to five hours, it was felt that the time could be shortened by another technique, pre-conditioning the electrode in an anaerobic media. In this manner it might be possible to overcome the existing lag in the latter phase of the adjustment period. By removing the electrodes from the sludge and reinserting them after different exposure periods to air, it would be possible to determine the effect of pre-conditioning the electrodes in the digested sludge to be tested. The exposure times used for both gold and platinum were 0.25, 1, 3, and 5 minutes. The results are shown in Figure 12. The electrodes had been in the sludge for seven days before being removed and no agitation was used.

The gold electrodes differentiated the effect of these different pretreatments very clearly. The electrodes with the 0.25 and one minute exposure resulted in a more rapid potential drop than the electrodes with the three and five minute exposure. There appeared to be a critical exposure time between the one and three minute values since the potentials of the two electrodes with the low exposure were similar as was the case for the more exposed electrodes. The time required to reach within ten mv of the equilibrium potential was three to 3.5 hours for the 0.25 and one minute exposed electrodes. The other two electrodes required a longer time of eight to nine hours.

Although the platinum electrodes did not reflect the various pretreatments as clearly as gold, the overall effects were similar. The longer exposure times did not appear to change the adjustment for about the first hour. However, after this time the electrodes began to shown differences. Since the platinum equilibrium potential was about ten mv more negative than gold, a longer time of about 12 hours was required to reach within ten mv of this potential. If the equilibrium potential indicated by gold was used, then the platinum approached within ten mv in about three to five hours for the 0.25 and one minute exposures.

The various exposures to air resulted in a greater differentiation in the gold than in the platinum. Although platinum was more susceptible to oxygen effects, it usually had a more rapid adjustment than gold. However, the adjustment times were very close for the gold and platinum electrodes exposed for 0.25 and one minute. The three and five minute exposures provided the difference. From this it would appear that the gold lost the residual effect of the sludge more easily than platinum when exposed to air for more than approximately two minutes. This result was similar to the data obtained in gas-metal studies where it was found that by changing the gas from hydrogen to oxygen, platinum changed slowly while gold changed rapidly(141). Conversely, the changing from oxygen to hydrogen produced a rapid change in platinum and a slow change in gold.

The use of a short exposure to air seemed to affect the platinum electrodes by creating temporary potential rises. This occurred during the first ten minute period for the electrodes exposed for 0.25 and one minute. This was again repeated near six hours for the former time exposure and near 3.5 hours for the latter time exposure. The gold electrodes exposed for one minute also exhibited a temporary rise starting near four hours. Although the temporary changes did not appear to affect the overall adjustment curve of any electrode, it did indicate a certain degree of instability was possible after very short exposures to air. This was especially true for the platinum.

This technique of sludge conditioning reduced the adjustment time under quiescent conditions. But it did not offer a method which could be done within a short time interval such as 30 minutes. To do this the electrode would probably have to be conditioned with a more negative solution so as to make the initial potential more negative than the sludge and thus adjust from the more negative to the less negative sludge potential.

A trial was made by conditioning a platinum electrode in a strongly basic sodium thiosulfate solution with a potential around -610 mv. The electrode was transferred as rapidly as possible to the sludge and the potential changes were followed. The potential did not retain its negative value and at 2.5 minutes was at -412 mv. At 21 minutes the potential had dropped linearly to -478 mv, and then continued to drop at a lower rate but still in a linear manner. The potential finally leveled off at six hours at a potential of -578 mv. Four days later the potential has risen to -510 mv.

The change in slope at -478 mv and 21 minutes was very distinct and the indicated potential approximated that of the sludge. Thus, this method might enable rapid sludge potential determinations to be made, There were many possible highly negative solutions which could be used as an electrode conditioner and this approach would warrant further study of the technique.

The conditioning of the electrode in an anaerobic solution before use in a digested sludge was opposed to the accepted practice of cleaning the metal by techniques such as acids, oxidizing agents, abrasives and heat. As was demonstrated previously, the history of the metal which includes cleaning was an important factor in the adjustment time of the electrode. In addition, the metal history could also play an important role in determining the shape of the adjustment curve, especially in the early phases of the adjustment. However, the final equilibrium potential was usually dependent on the sludge and not on the electrode.

It was this initial period after the electrode was immersed that could possibly be developed into a means of determining the metabolic activity level of the sludge. No method was available for determining the sludge activity and therefore, this would provide a valuable supplement to the existing tests for sludge. However, certain important factors must first be considered.

It has been found in this research that the electrode could be more important than the sludge in determining the potential-time relationship. With apparently identical electrodes with identical backgrounds, a more dormant sludge could appear more dynamic than an active sludge. A survey of the literature also disclosed many instances of the lack of electrode agreement after the initial insertion(16)(49)(66)(73)(75). In addition it has been found that metal surfaces could not be considered the same even though apparently treated identically(138)(41). On the basis of the above information, it should be stressed that the electrode must be in a reproducible condition before being placed in the sludge if the adjustment period is to be used as an indicator of sludge activity.

The use of a controlled oxygen electrode(131)(132) would appear to be an excellent method to determine the dynamics of the sludge. The metal would contain a predetermined amount of an oxidizing agent and in this way provide the same initial electrode characteristics. Thus, the removal of these oxidizing materials on the electrode would provide a potential measurement reflecting the activity level of the sludge.

The treatment of the electrode metal before use has been shown to affect the adjustment curve. In addition the inherent characteristics of the metal could also be a factor as shown previously in Figures 10 and 12. Another example of a distinct difference in the behavior of gold and platinum was found when the electrodes were immersed into a sludge freshly drawn from a plant digester. The adjustment of the gold was responsible for the difference since it appeared to form a temporary plateau between

-350 and -400 mv before finally reaching the equilibrium potential. One of the more distinct examples of this is shown in Figure 13. Platinum exhibited a slight tendency towards this behavior, but it was not nearly as distinct a phenomenon. Rather, the adjustment followed more closely the usual situation where the potential-time relationship tended to be a continuously decreasing slope without any interruption in the continuity.

The cause of this unusual behavior became more clear when the electrodes were reinserted into the sludge 12 days after the initial trial. The usual type of continuous curve resulted with practically no trend towards a plateau. Tests in other fresh sludges showed some tendency towards the formation of a plateau, but never as distinctly as shown in Figure 13.

The reason for this behavior could have been due to both the sludge and the electrode. The use of six electrodes ruled out any possibility of an erratic electrode being the cause. It appeared as if a weak oxidation-reduction system in the sludge was affecting the gold more than the platinum. This possibility existed since platinum has been shown to be less sensitive than gold in this research and by other workers(16, 54, 74).

Another possible reason for the difference in the metals is that platinum may have been more reactive to the equilibrium potential than gold. Thus, weakly poised systems would not interfere with its adjustment. The work of Lepper and Martin(15) with cooked meat media in a buffer solution produced similar results. It was found that the special gold-plated electrodes were not affected by the hydrogen gas present and remained poised by the feeble redox system. However, iridium rapidly converted to a hydrogen electrode reaching a more negative potential.

The fact that this plateau effect with the gold electrodes was not as noticeable 12 days after the initial trial and that other sludges did not produce as distinct an effect could be explained by the sludge itself. The volatile solids content was at a high level of 65 percent which was not present in any other sludge tested. Therefore, it was possible that the sludge possessed a redox system which disappeared when the sludge was further along in the digestion period.

In contrast to the experiments with fresh digested sludge described above, adjustment trials were conducted with an extremely well-digested sludge which could be classified as dormant because of a three year storage period. Before insertion of three gold electrodes, the sludge was mixed to blend the supernatant with the settled sludge. Since the sludge was three years old and had been exposed to the atmosphere during this period, it was anticipated that the solution would be more aerobic than the other sludges used in adjustment studies. In addition, it was considered possible that the potential might reflect the oxidative state of a fully digested sludge.

Although no characteristic potential could be determined due to the very large disagreement of up to 250 mv between the electrodes, the adjustment time and potential reached was very surprising. One of the electrodes reached -715 mv and another reached -650 mv. These values were much more negative than any potential obtained in digestion studies. The value of -715 mv closely approximated the potential of a hydrogen electrode. However, it should be mentioned that these values could not be considered reproducible.

Another large difference with normal sludges was indicated by the shortness of the adjustment periods. One electrode fell from -320 mv to a constant potential at -680 mv in one hour. Another fell from -340 mv to -690 mv in about the same period. The electrodes had been exposed to the air for 15 minutes between their removal and reinsertion into the sludge. The rapid adjustment could indicate a well-poised solution, but the poor reproducibility of the potential and lack of agreement between electrodes did not make this assumption valid. Therefore, it appeared that this three year old sludge differed from a normal digested sludge in its ability to produce a residual effect on the electrode.

This sludge seemed to possess the dynamic property of establishing a rapid potential even though it was completely dormant. Therefore, it must be placed in a special category for the use of the adjustment period as an indicator of the metabolic activity level of a sludge. The highly negative potential indicated by the electrodes also placed this sludge in a special category.

Although the cause of this low potential was not known, the electrodes were not considered to be faulty since they exhibited normal behavior in all other sludges in which they were used.

In addition to the adjustment trials with various digested sludges, the author had an opportunity to follow an adjustment curve in a lake bottom mud sample. The results were included here because of the surprising similarity to the sludge adjustment curves. The sample was obtained from the bottom of Ford Lake, an artificial lake near Ypsilanti, Michigan. The first similarity to sludge was in the adjustment period. The platinum electrode took about ten hours to come to a constant potential which remained at this level until 25 hours when the test was completed. The shape of the adjustment curve was also similar to that resulting from sludge. Furthermore, the potential reached was -465 mv which also fit into the results of sludge trials.

A brief survey of the literature disclosed that Mortimer, who worked extensively with lake muds, used a two hour adjustment period(119). It was not known whether this shorter time was correct or not for lake mud potentials since this experiment was the only trial made. But, the results did indicate that both anaerobic solutions, lake mud and digested sludge, could exhibit very similar potential characteristics.

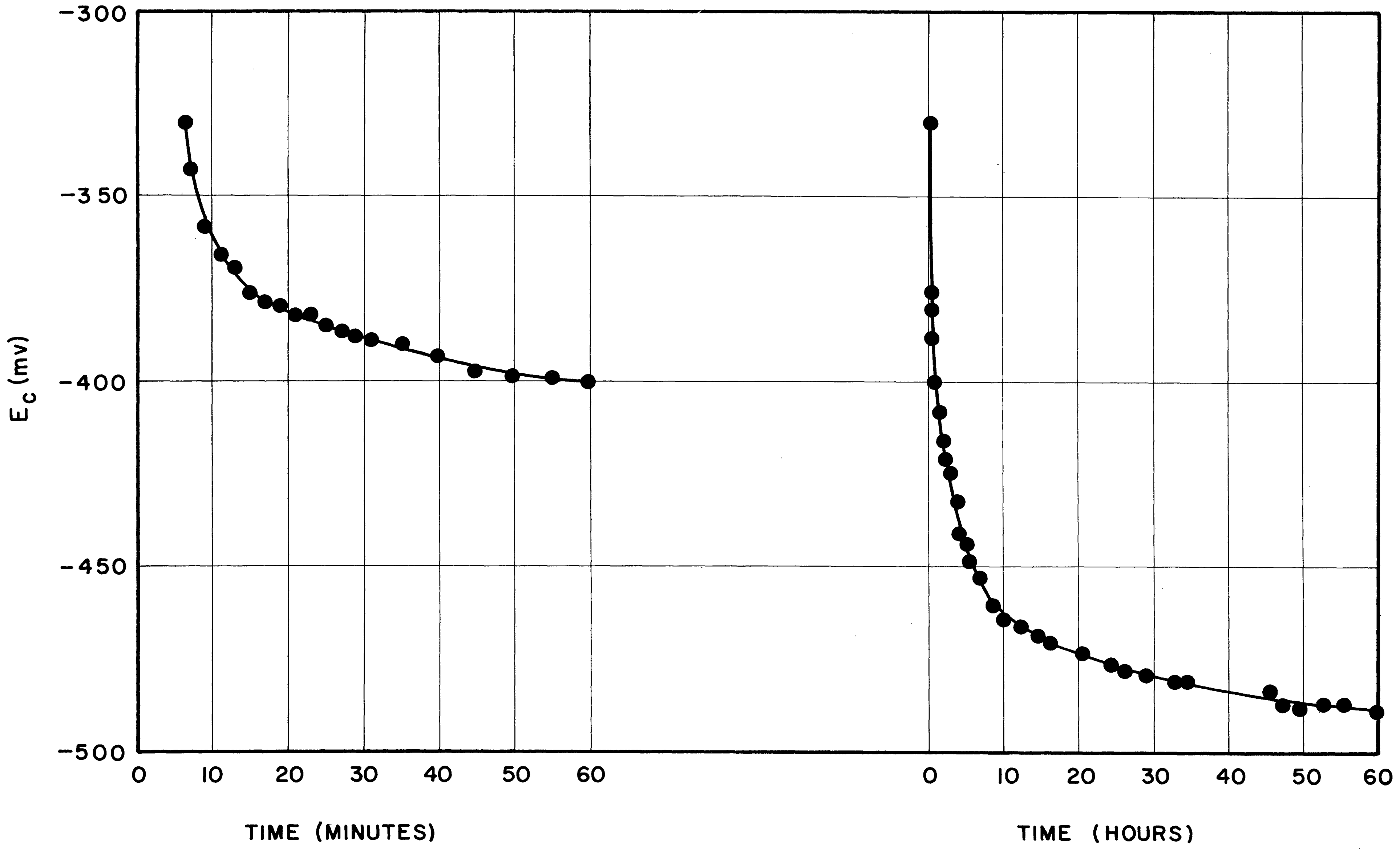


Figure 9. Adjustment of a Platinum Electrode in a Digested Sludge

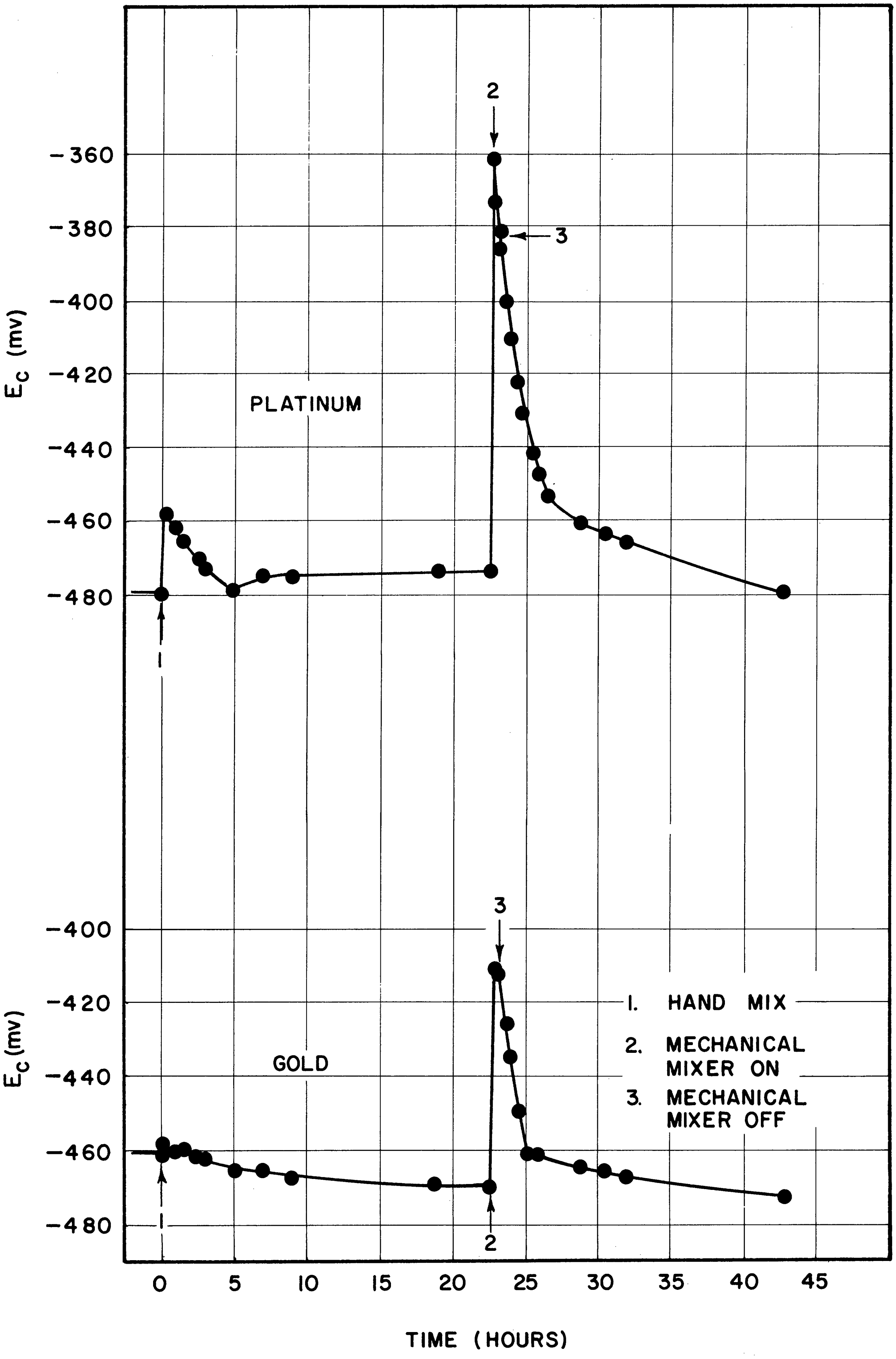


Figure 10. Comparison of the Potential Changes of Platinum and Gold Electrodes due to Stirring a Digested Sludge Exposed to Air

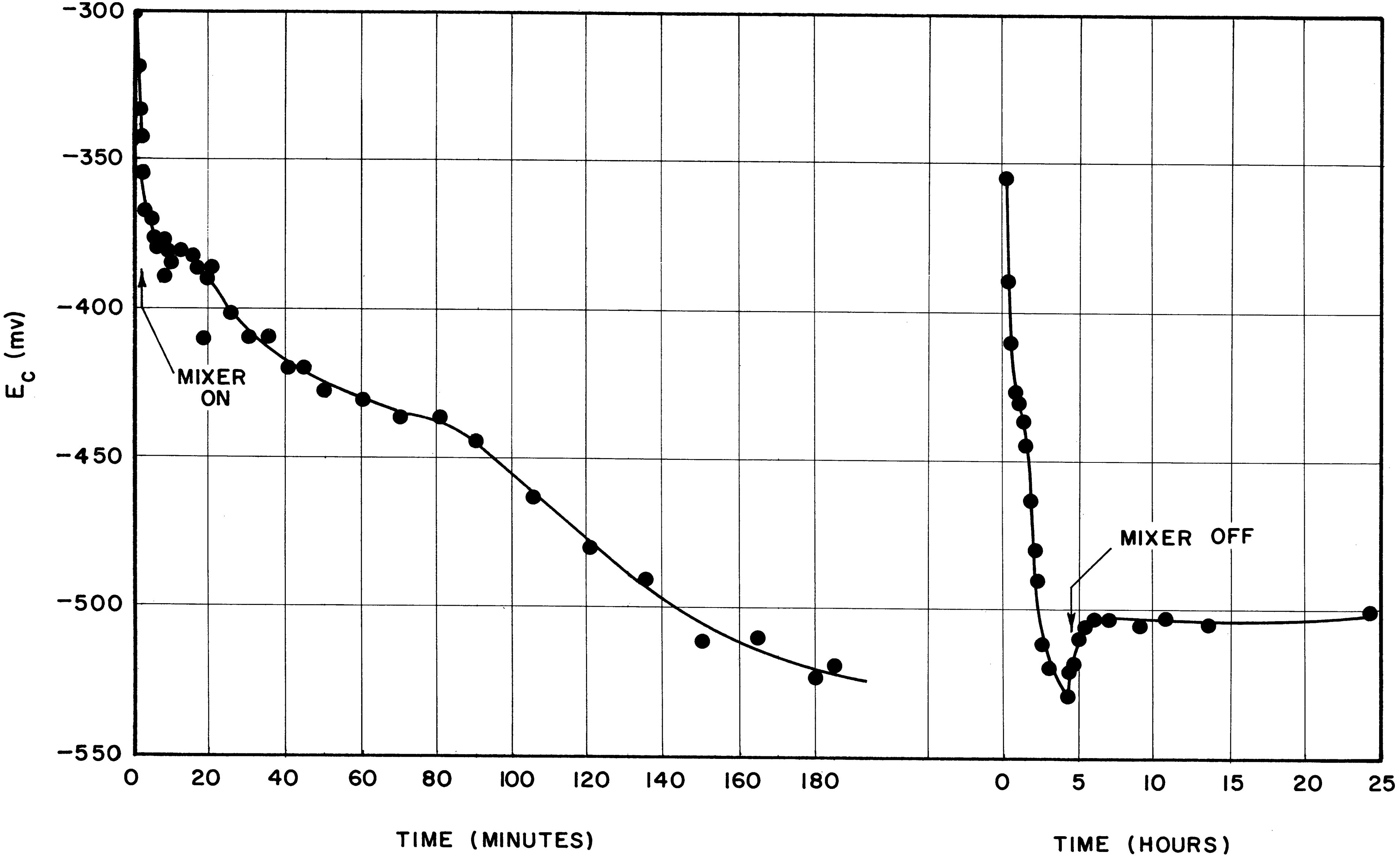


Figure 11. Effect of Agitation on the Adjustment of A Platinum Electrode in Digested Sludge

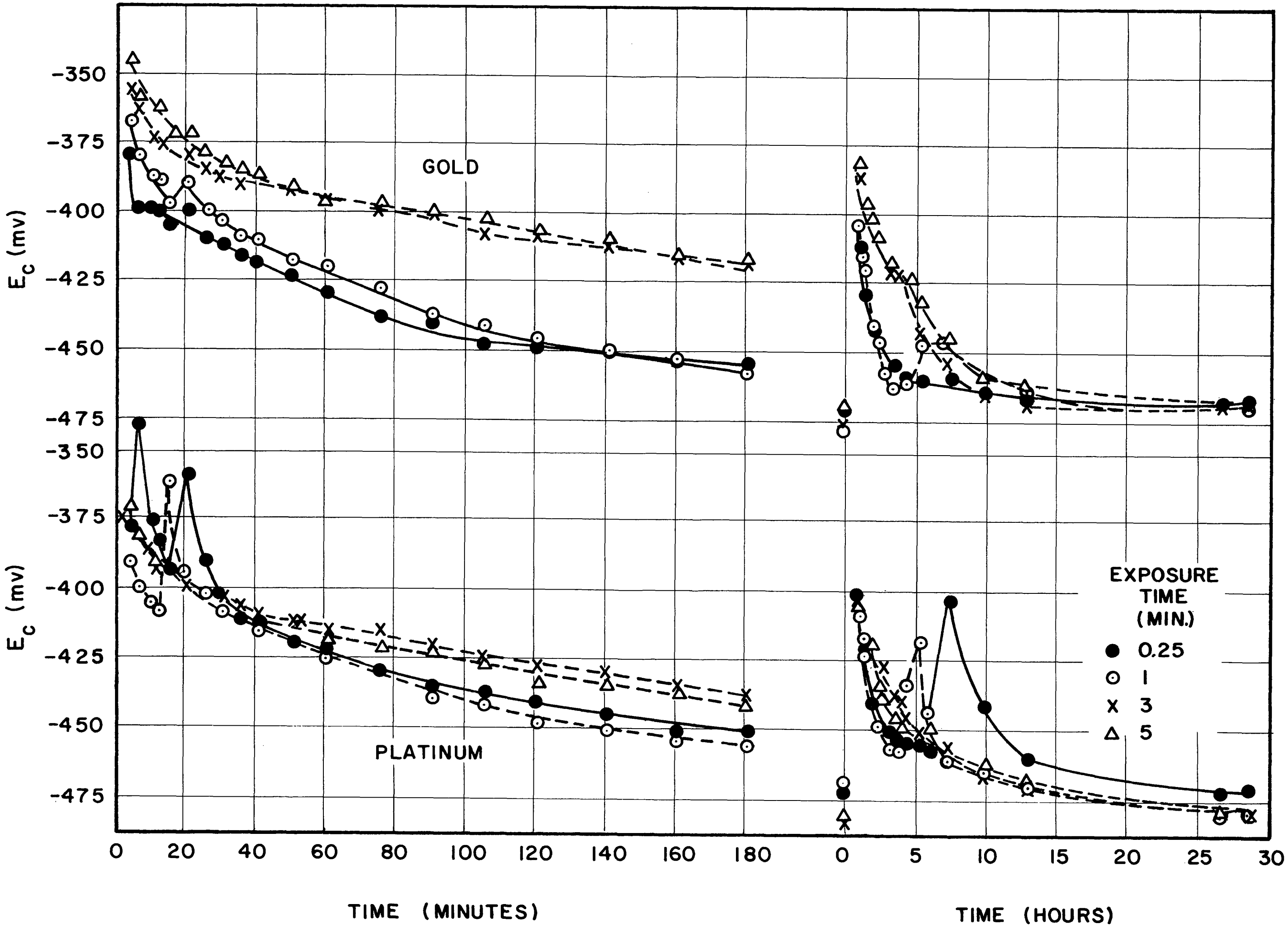


Figure 12. Comparison of the Adjustment of Gold and Platinum Electrodes in Digested Sludge after Being Conditioned in the Sludge and Exposed to Air

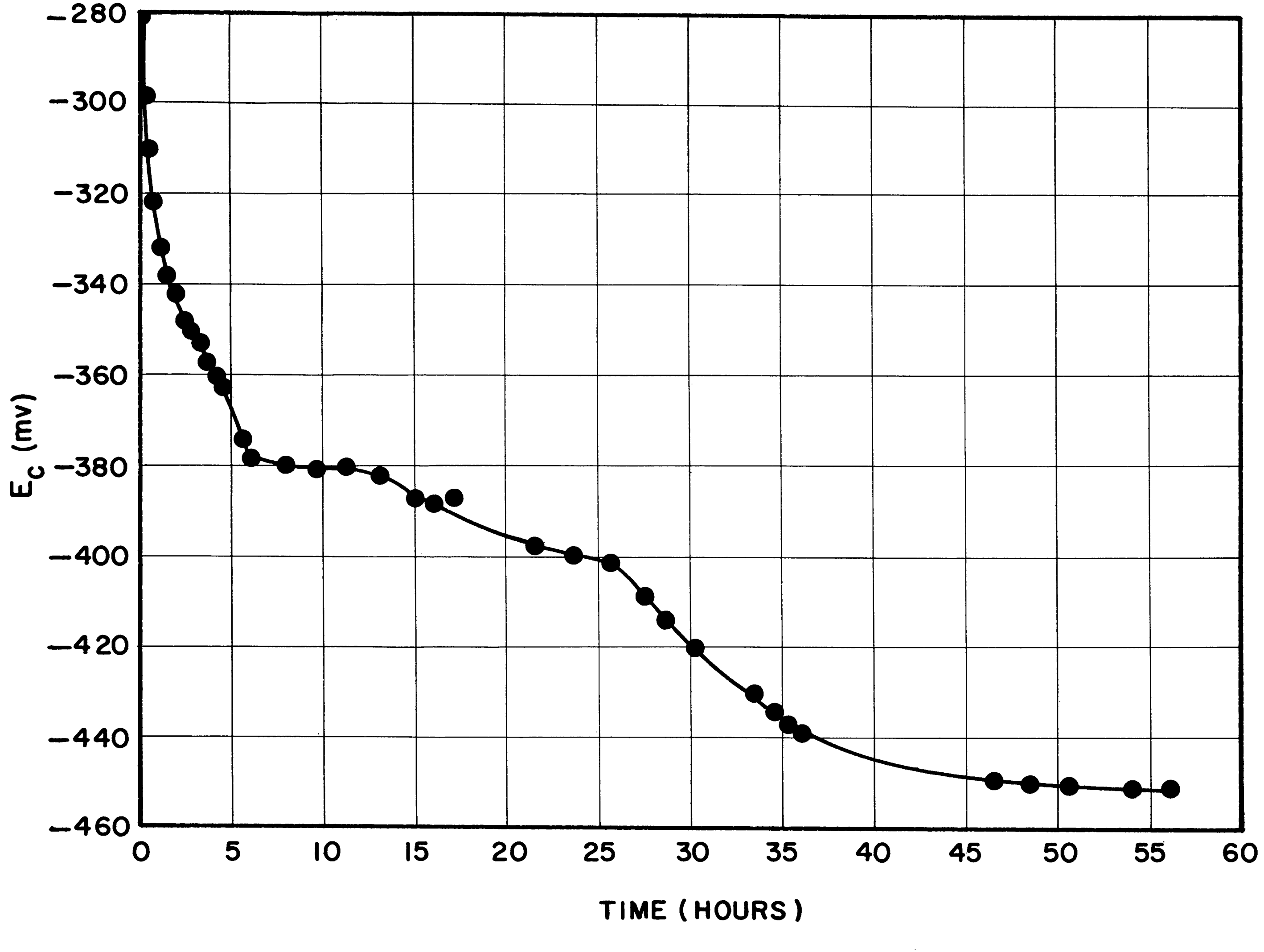


Figure 13. Adjustment of a Gold Electrode in a Digested Sludge with a High Volatile Solids Content

LACTOSE BROTH FEEDING OF A DIGESTED SLUDGE

The composition of the raw sludge fed to a digester is very difficult or impossible to reproduce exactly. Therefore, to aid in the evaluation of the potential changes produced by the natural feed, it was decided to use a synthetic constant composition solution as a feed to a digested sewage sludge. This would provide controlled loadings as well as reproducibility.

The use of a sugar in an inoculated bacterial media would result in rapid and large potential changes. Since much work on this subject has been done, a comparison would be possible by using a synthetic feed containing a sugar. In addition, this type of feed would provide an indication of the magnitude of the potential changes possible in a digested sludge media.

The feed selected was Bacto Lactose Broth (hereafter called LPB) in which one gram contained 0.385 grams of lactose and peptone, and 0.230 grams of beef extract. This particular feed was selected primarily because of its sugar and peptone content. Furthermore, a similar feed was used in sludge digestion studies by Morgan(13).

Three gold electrodes were placed in 700 ml of a well digested sludge which consisted of equal quantities of two and ten month old sludge. Additions of the LPB mixture were started after the electrodes had reached equilibrium. The feedings were primarily on a batch basis although the results could be placed together so that it could be regarded as a semi-continuous basis. The initial digested sludge was used throughout as the media. An addition of digested sludge and removal of supernatant was made when the mixture had become too dilute due to the water used to suspend the solid feed.

Feedings of two and three grams of LPB were spaced twenty hours apart and corresponded to a loading of 0.17 and 0.28 pounds of volatile solids per cubic foot per day. The potential exhibited an instantaneous rise after the feeding followed by a fall, a rise and another fall. This same general pattern was followed with a ten gram feed (0.96 pounds of volatile solids per cubic foot per day) as seen in Figure 14.

After the feed, the potential became more negative, leveled off, and then continued to its maximum negative value. The leveling off period appeared to be related to the lag phase as indicated by the gas production. This level period ended as the gas rate approached its maximum value and the beginning of the potential rise corresponded to the drop in the gas production.

The gas collection system was not a constant pressure type and the high gas production with the ten gram feed necessitated a release of the pressure at 7.7 and 9.1 hours after the feeding. Although the latter time corresponded to the beginning of a rapid potential rise, it was not felt that this was responsible for the potential change, since the gas production had become very low at this point. To avoid the release of pressure, a constant pressure gas collection system was adopted.

A feeding of four grams of LPB gave similar results in a constant gas pressure system. This is shown in Figure 15. Since a relationship between the potential and gas production was shown by various feeds, it could be concluded that the potential was a sensitive indicator of the metabolic changes occurring in this batch-type system.

Gas rates were measured by a glass tube packed with glass wool in which the pressure drop was a linear function of the gas rate. The gas rate meter was used to establish the rate of gas production since calculation of the rate from total production was not as accurate because of the rapid gas changes. However, the gas rates yielded the same conclusion as total gas production; namely, the relationship of gas flow and potential. The rates also confirmed the work of Morgan(13) as to the rapid change in gas production with a synthetic type feed. In addition to this, he has shown that a dextrose-peptone-beef extract mixture fed to a digested sludge resulted in an increase followed by a decrease in the volatile acid content, and that the acid content was proportional to the rate of gas production. From this finding and the results of this research, it could be said that the potential changes also reflected the volatile acid changes.

The previous results have shown that the lag phase was reflected by the potential. Therefore, it would be anticipated that if the lag in gas production were small, the potential should reflect this difference by reaching the maximum negative potential without first exhibiting a plateau. Examples of this result are shown in Figures 16 and 17 for which the feed was four grams of LPB for each case. This was equivalent to loading of 0.38 pounds of volatile solids per cubic foot per day. The decrease in the lag time was probably due to the effect of previous feeds in stimulating the bacterial activity.

The potential in Figure 16 fell to a constant maximum negative level and then rose slowly. The rise started soon after the maximum gas rate was reached. Figure 17 exhibited a more distinct rise in potential after falling to a short constant maximum negative potential period. This rise started near the beginning of the maximum gas rate period which extended over several hours and did not exhibit a distinct maximum rate. In all cases studied the potential reflected the end of the rapid gas production by rising to a more positive potential.

The immediate effect of the feed upon the potential was in a positive direction in all cases but one. The one exception was due to erratic electrode behavior and therefore could be discounted. The solid feed was suspended in small amounts of distilled water and because of its more positive potential, should have caused a positive change in the potential as was the result.

A factor which could not be overlooked when discussing the immediate feed effect on the potential was the effect of mixing on the electrode. After the feeding the sludge solution was mixed by hand. The results of mixing when no feed was added indicated that the potential in most cases became more negative. Thus, the overall positive effect of feeding included the opposing negative tendency of the electrode due to mixing.

The potential resulting from any feeding exhibited one general pattern. After the feeding, the potential fell and then reversed itself within a twelve hour period. This potential fall was expected as the metabolic activities of the anaerobe initially created a more negative potential. The work of many authors using pure cultures of bacteria indicated that after the maximum negative potential was reached, a more positive potential resulted. Using synthetic sewage, Moore, Rucchoft and Wattie(96) found that after the maximum negative potential was reached, a positive trend followed. With E. coli a stabilized condition soon resulted due to their inability to utilize the end products. In contrast, A. aerogenes being able to utilize the end products continued to show a positive rise in the potential.

Certain bacteriological methods of anaerobiosis often allowed air to enter the system which could partially explain positive potential changes. However, in this research anaerobic conditions were maintained by the sludge itself in a sealed system under pressure. Therefore, no access of air was possible which could cause a positive potential trend. It would appear that this potential change was due to metabolic action alone. The first rise and fall in potential could be referred to as a primary rise and fall for comparison with the other potential changes.

The behavior of the potential after the gas production had practically ceased exhibited a definite pattern. After the primary potential rise, it was noticed that a secondary fall in potential developed without an appreciable increase in gas production as was the case for the primary fall. This can be seen in Figure 14. The mixing of the solution near 24 hours was not responsible for this fall. It has already been demonstrated in several instances that the fall would occur without mixing. This is shown in Figure 17. The effect of the mixing was in creating a more negative potential instantaneously which did not begin to fall in a continuous manner until at least two hours after the mix.

Further potential measurements over longer time intervals revealed that there existed both a primary and secondary fall and rise followed by a third fall which appeared to level off. This is shown most clearly in Figure 16 in which the time period covered about 75 hours. The primary fall and rise occurred in the 0 - 24 hour period, the secondary fall and rise in the 24 - 48 hour period, and the tertiary fall and plateau after 48 hours.

The similarity in the potential curves after various feeds led to the conclusion that an LPB type of synthetic feed resulted in three zones of falling and two zones of rising potential in the first 72 hours. The fact that this feed brought into play different bacterial and enzymatic systems than a raw sludge feed was shown clearly by the resulting potential-time curves. Raw sludge feeds produced a very level potential curve without periodic ups and downs.

These reversals of potential could not be attributed to any one bacterial system due to the complex flora that existed. Possibly these reversals were a reflection of the changes in acid production as well as different bacterial systems.

The potential was followed beyond 75 hours for one of the feedings. This is shown in Figure 17. The potential started to fall at 95 hours reaching a plateau of about -519 mv near 145 hours. This fall to a new low level probably indicated a more highly reducing system was created as the bacterial systems became dormant. The potential did not vary widely until at 195 hours a rise began which reached a maximum near 245 hours of -405 mv. The potential started to fall at 260 hours until it leveled off near 295 hours at -500 mv. It then started to fall slowly at 325 hours to -520 mv. This level was maintained from about 430 hours to 480 hours at which time readings were terminated.

It should be noted that the potential returned to the same level as before the last rise and fall. The potential changes were probably due to the metabolic activities of certain bacterial systems. The rise at 195 hours could have been influenced by a temporary release of the pressure to -6 mm at 175 hours and a mix of the solution at 193 hours. The mixing would have made possible the renewal of the activity by exposing new food sources and removing localized waste products.

The potential before the feed was -467 mv and the primary fall reached -481 mv. The fall to -519 mv at 145 hours represented a change of 38 mv based on the maximum primary fall potential. This could be compared to the ten gram feed shown in Figure 14. The maximum of the primary fall at eight hours was -496 mv and at 145 hours the potential was -539 mv. This resultant difference of 43 mv exhibited a remarkable agreemdnt which seemed to indicate that there existed a certain overall reproducibility for this type of synthetic feed.

The first potential fall was probably due to the increase in metabolic action shown by an increased gas production which resulted in more negative potentials. The following rise after the peak gas production was reached was probably due to more oxidized materials accumulating in the solution.

The second fall was not as easy to explain. Possibly a new bacterial system was brought into action by the waste products created initially, or the same initial system after adjusting to the waste products created this change. The two systems could operate in series with the new system changing the waste into new food or destroying the toxic effects so the original system could continue to metabolize.

Gas production was not large enough to show any relationship to the second fall and rise although gas production did not cease. However, rapid gasification was not apparent after 12 hours. In Figure 17 there was more gasification than usually was the case up to about 40 hours, but this was an exception. This would indicate the sugar must be nearly completely used in the first 12 hours and the peptones must be the source of the additional gas. This would indicate a new bacterial system was in operation after the initial phase.

The third fall at about 50 hours was not followed by a rise in potential which could indicate the food supply was consumed. The maintaining of a constant potential level could be attributed to the fact that the oxidized substances which had altered the potential were decomposed into substances which poised the sludge at a certain potential level.

There have been other workers who have observed potential changes after the primary fall and rise. A double reversal was found by Vennesland and Hanke(112) for a synthetic media containing one percent glucose inoculated with Alcaligenes fecalis, a non-fermenting obligate aerobe, and Bacterordes vulgatus, a non-spore forming anaerobe. Hewitt(48) also observed this phenomenon with E. coli in a one percent glucose broth. With a media of two percent neopeptone and eight percent galactose, Longworth and MacInnes(54) found that Lactobacillus acidophilus also yielded a secondary fall and rise in the potential. Although the digested sludge provided a mixed culture and a different media base, it was of interest that a potential reversal also occurred under these conditions.

All of the above authors concluded that the potential reversal was not due to the pH, but to the production of acid. Checks on the pH during the experimental work revealed that the sludge was a good buffer since the pH was not found below seven. Thus, the potential reversals were probably due to acid production based on the work of the above authors.

In order to establish a characteristic potential for this system, the variation in potential after feeding should be considered. For the ten gram feed in Figure 14 the variation was 84 mv. Four gram feeds in Figures 15, 16, and 17 yielded differences of 66, 42, and 32 mv respectively. These variations were for the time period from the feeding to 35 hours. By considering the midpoint of the variations in the potential for the above and other feedings, the characteristic potential zone of this system ranged from -440 to -470 mv or an E_h of -194 to -224 mv.

Upon extension of the time to 150 hours after the feeding, the variations for the ten and four gram feeds in Figures 14 and 16 were 128 and 71 mv respectively. The resulting potential due to the ten gram feed was at -540 mv after 150 hours. Subsequent feedings resulted in a normal primary fall and rise but the secondary fall and rise caused the potential to become more positive. The time between feedings did not exceed 55 hours. There appeared to be a strong tendency for the potential to return by steps to the characteristic potential zone. This return substantiated the location of the characteristic potential zone.

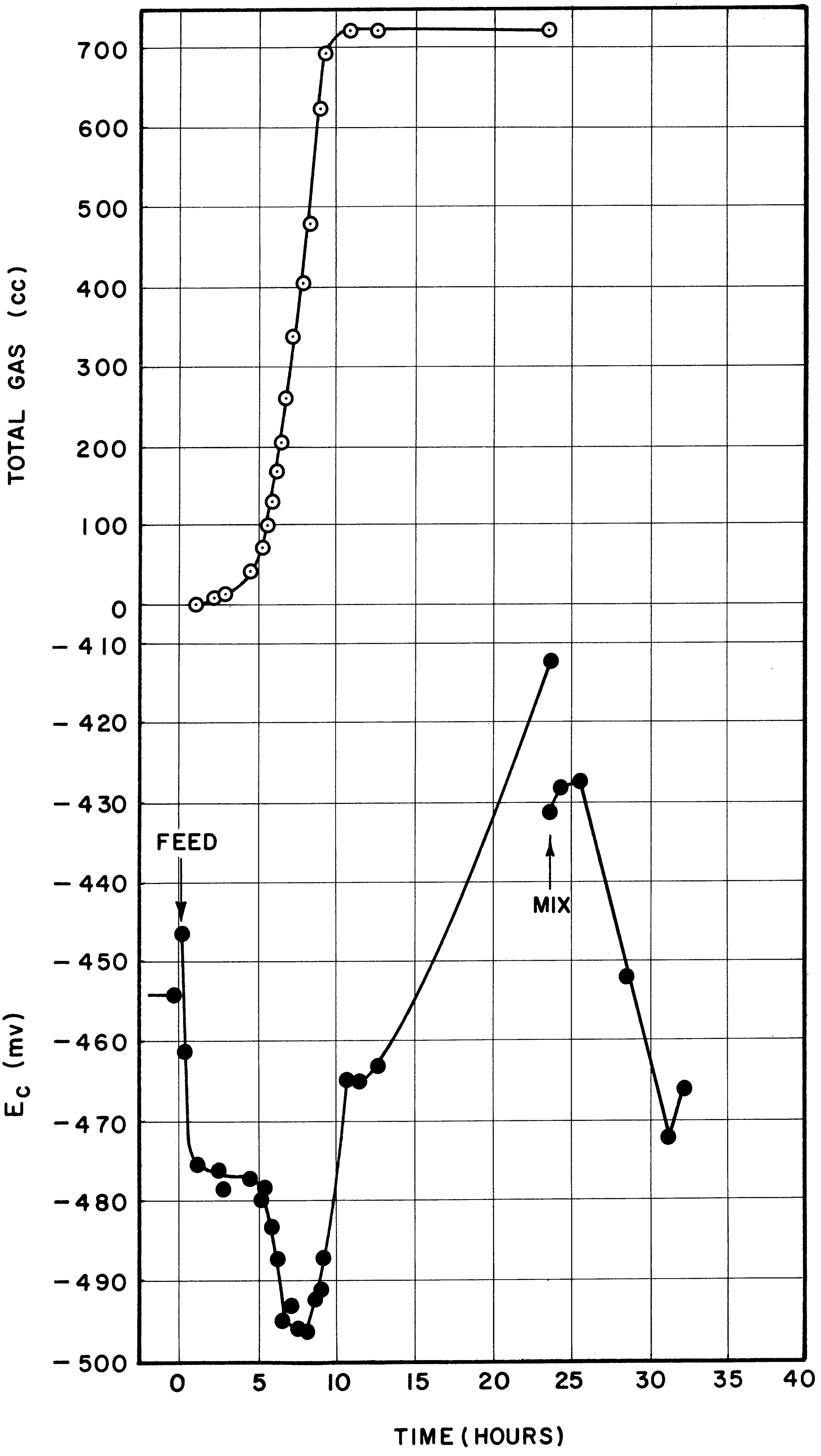


Figure 14. Electrode Potentials and Gas Production after the Addition of Ten Grams of Lactose Broth Concentrate to a Digested Sludge Media

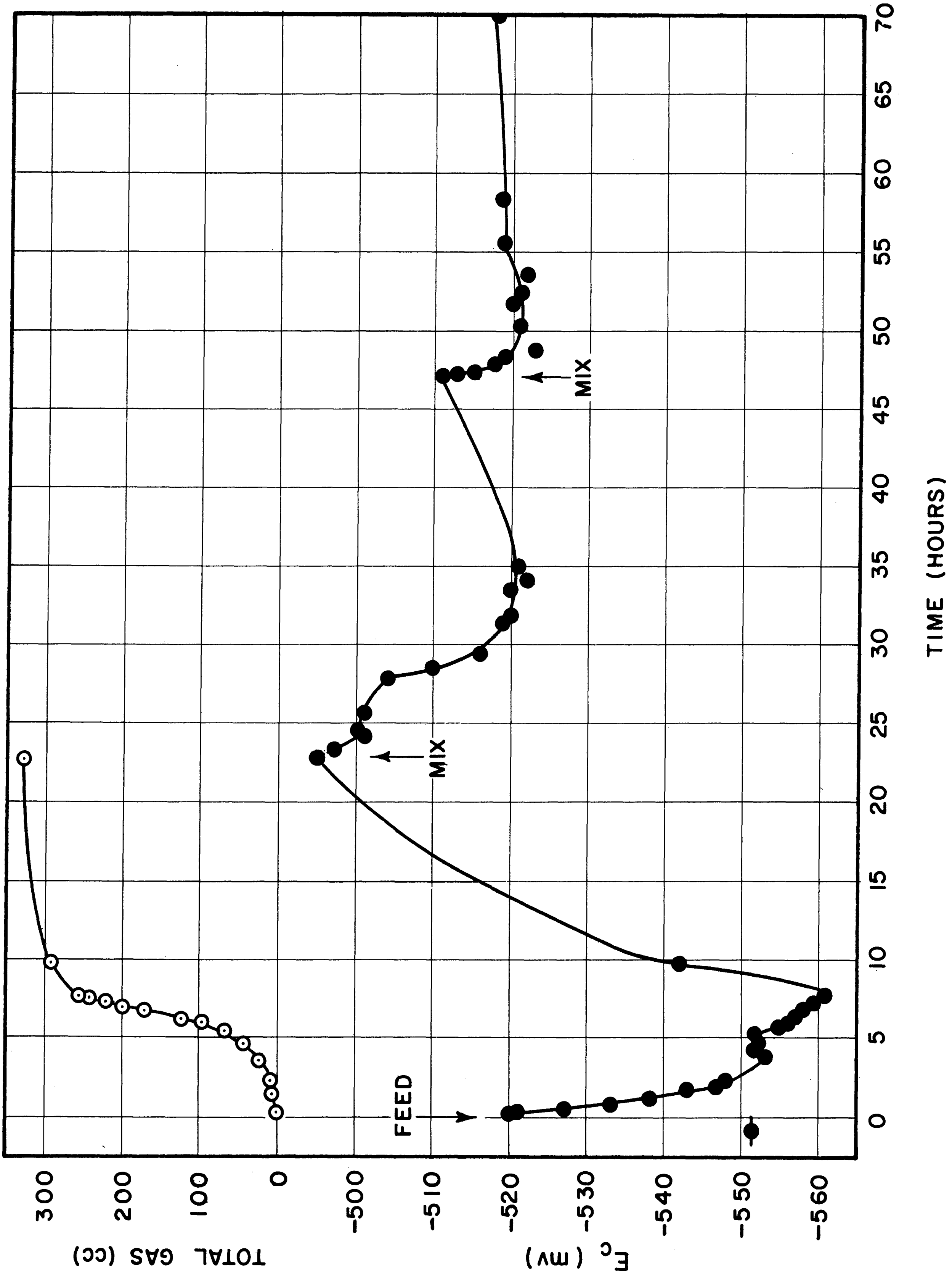


Figure 15. Electrode Potentials and Gas Production after the Addition of Four Grams of Lactose Broth Concentrate to a Digested Sludge Media

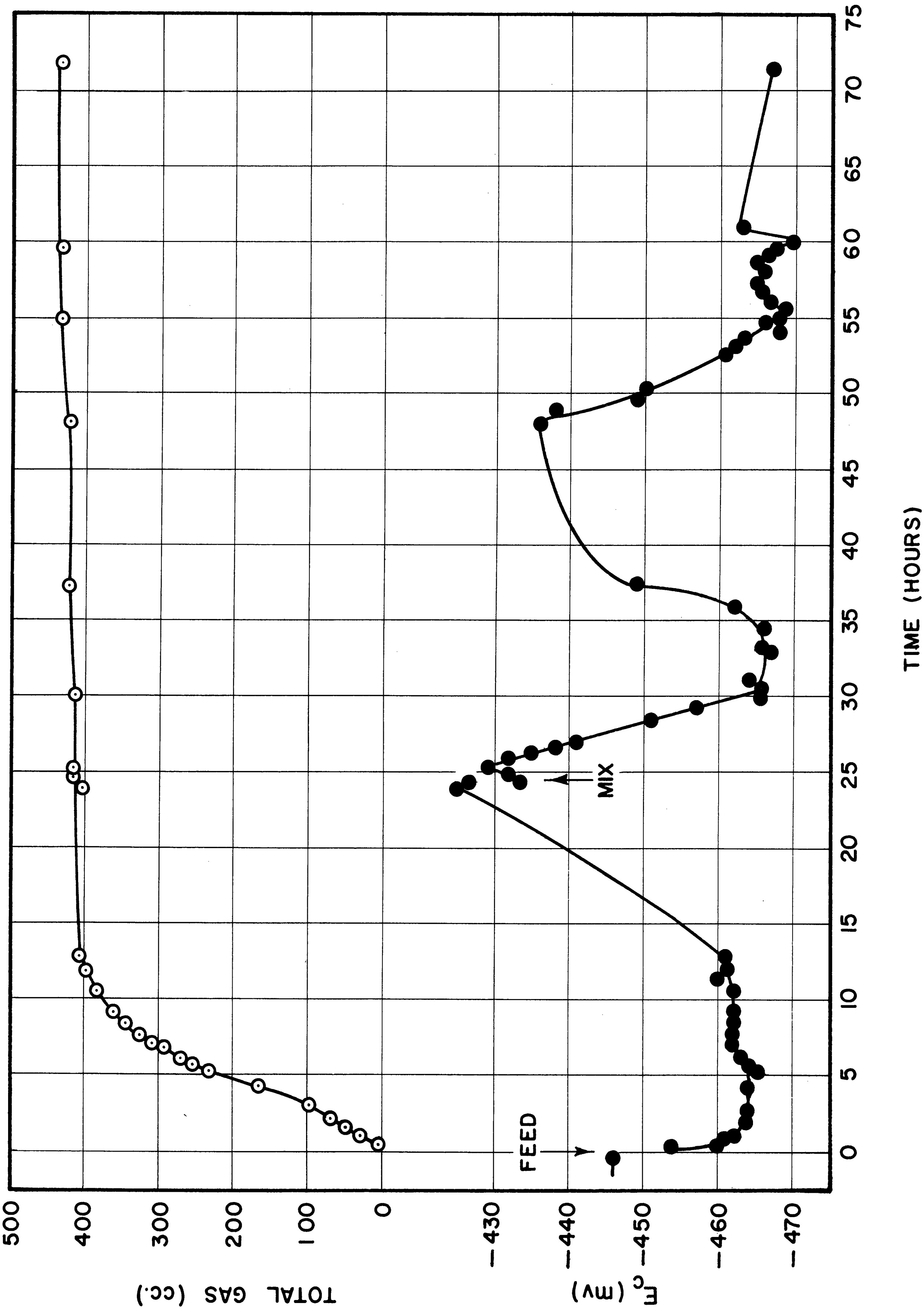


Figure 16. Electrode Potential and Gas Production Resulting from a Short Lag Period Digestion after the Addition of Four Grams of Lactose Broth Concentrate to a Digested Sludge Media

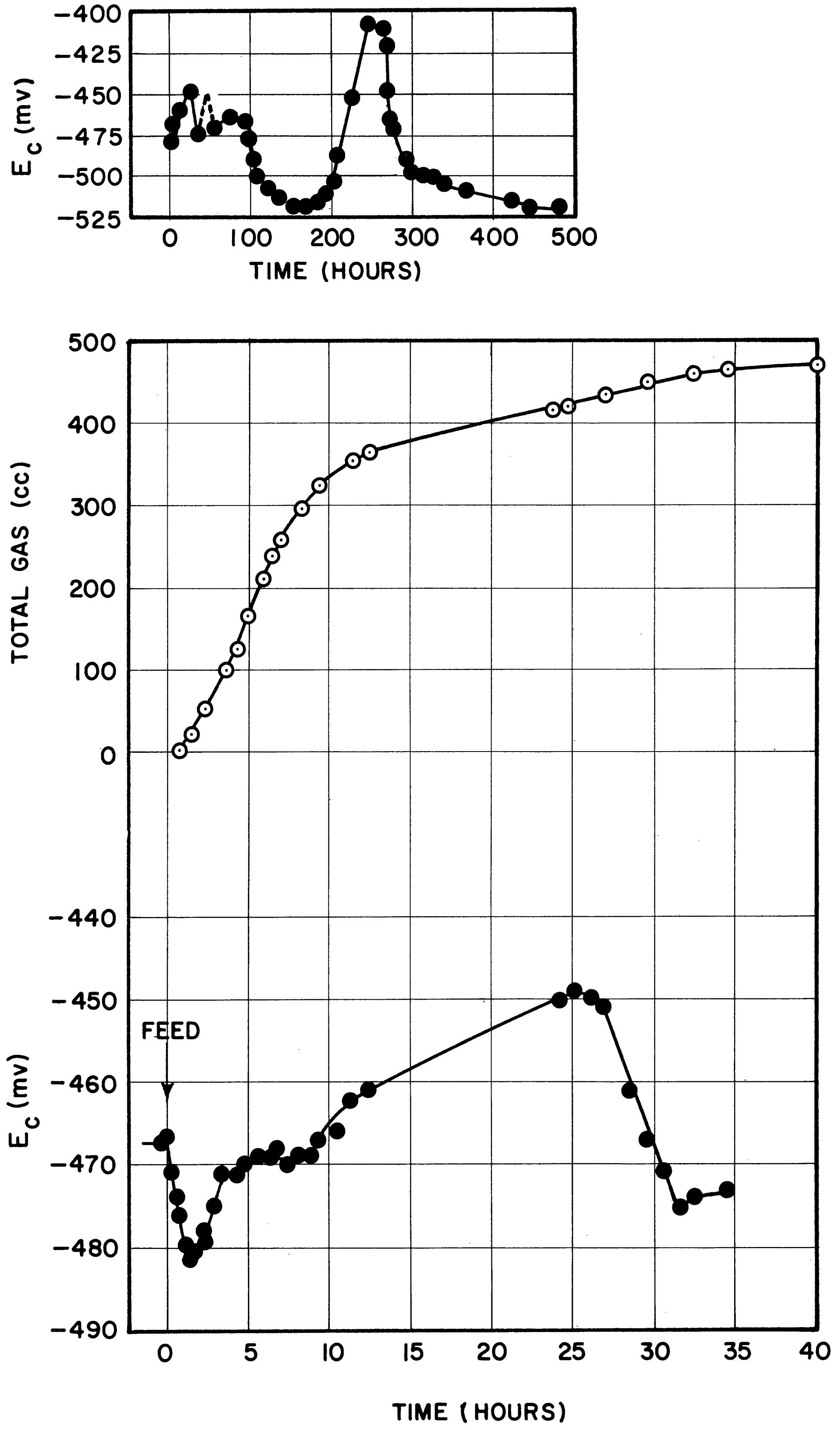


Figure 17. Electrode Potentials over a Long Time Period and the Gas Production Resulting from a Short Lag Digestion after the Addition of Four Grams of **Lactose Broth Concentrate** to a Digested Sludge

INITIAL POTENTIAL STUDIES ON SLUDGE DIGESTION

The lactose broth experiments have shown that potential measurements in a digested sludge media could provide information on the mechanism and control of this type of biological process. This was primarily due to the magnitude and rate of the potential changes, which were large enough to: (1) overcome the media poise or resistance to change and (2) minimize any variability introduced by the metal electrode per se. Although the potential changes produced by a digesting sludge with raw sludge feedings would not be as distinct as those with lactose broth feedings, it nevertheless appeared that an evaluation of the former system would be possible.

The lactose broth data also indicated the reproducibility of electrode potential measurements was possible in an active digested sludge. In addition, these experiments helped to define the best means of measuring the potential. This resulted in the use of three digesters, each with three electrodes, and provision for continuous agitation of the sludge.

Three electrodes in each digester eliminated any reliance on a malfunctioning electrode which would not be possible if only one electrode was available. Three digesters allowed comparison of the behavior of electrodes in different digesters under identical conditions as well as the electrodes within one digester. By establishing this variability under identical conditions, it would then be possible to evaluate the results when the feeds were not the same in each digester.

The importance of understanding the behavior of the metal electrode in digesting sludge was considered to be an essential component in the evaluation of any potential data. Much valuable data had been obtained from previously presented studies on electrodes in quinhydrone, digested sludge, and digested sludge with lactose broth additions. However, since the digestion of sewage sludge had never been followed by potential measurements, the initial studies on sludge digestion were primarily to observe and establish the general characteristics of the metal electrode in this system.

The feedings were begun on a daily basis to provide a 25 day detention period by feeding 100 ml of raw sludge corresponding to a loading of 0.091 pounds of volatile solids per cubic foot per day. The digesters were continuously agitated. The digested sludge had been removed from a plant digester about two weeks before and was placed in the laboratory digesters at 25°C. There was no noticeable gas production at this temperature.

The first feeding was set at 50 ml after which the 100 ml feeds were started. However, unusual behavior of the electrodes led to the cessation of daily feeding after the third addition in order to follow the subsequent potential changes. It was felt that in this way more valuable data on electrode behavior would be gained.

The first instance of unusual potential behavior occurred prior to feeding when the temperature of the sludge was raised from 25°C to 35°C in continuously agitated digesters. The electrodes had been inserted into the sludge five days previously and the electrode adjustment followed.

The temperature was raised in order to bring the digesters to the proposed operating level of 35°C. This procedure allowed the opportunity of following the potential changes resulting from an increase in sludge activity by a temperature change, not an addition of raw sludge. The three digesters did not yield the same potential changes as can be seen in Figure 18. The gas production yielded an "S" type gas curve simulating the results of a batch-type digestion. The maximum gas rate occurred on the second day after the temperature was raised.

Before the temperature rise, the electrodes averages -496, -498 and -488 mv in Digesters 1, 2 and 3 respectively. Digester three first showed a rise in the potential followed by a falling potential until at about two days, a temporary leveling occurred. This was followed by a further drop until seven days when the average potential was about -519 mv. The initial potential rise was probably caused by the entrance of air into the digester due to a leak which was fixed after the first day. Digester one showed a dropping potential which became constant in six days at a value near -515 mv.

In contrast to the above behavior was the action of Digester two since the potential in this case did not drop to the lower potential of the other two digesters. In six days the potential averaged about -472 mv after becoming essentially constant after only one day. The cause of the initial rapid rise from -498 to -479 mv was unknown. There was also no apparent reason for the potential rising instead of dropping and being about 40 mv more positive than the other two digesters. The difficulty in finding an explanation arose from the identical experimental conditions of the digesters and the good agreement of the electrodes. This is discussed further at the end of this chapter.

Raw Sludge Feedings

Raw sludge feedings were begun after the potentials had become approximately constant and the gas production was at a very low level. This occurred about seven days after the temperature was raised. At zero hours 50 ml of raw sludge at 8°C were fed to each digester. This was followed by 100 ml feeds at 24.5 and 51.75 hours. The resulting potential change and gas production are shown in Figure 19 and Table III. The potentials rose after each feeding and there was always a subsequent trend to the more negative prefeed value. The potential values used were the average of either two or three electrodes. At times one electrode acted erratically which, if it were included, would not give an accurate picture of the changes.

Table III

SUMMARY OF ELECTRODE POTENTIALS AND GAS PRODUCTION
DURING THE PERIOD OF CONTINUOUS AGITATION

Time (hours)	Feed	Potential (E_c) Before Time Indicated (mv)			Change In Potential from Before Feed One (mv)			Total Gas Production (cc)		
		Digester			Digester			Digester		
		1	2	3	1	2	3	1	2	3
0	1	-512	-472	-518	-	-	-	-	-	-
24.5	2	-509	-469	-522	+ 3	+3	- 4	380	520	380
48.5	3S[a]	-505	-469	-500	+ 7	0	+18	1190	1340	1020
51.8	3	-500	-471	-470	+12	+1	+48	-	-	-
72.5	-	-497	-468	-489	+15	+4	+29	1910	2030	1490
196.0	-	-511	-481	-516	+ 1	-9	+ 2	4830	5300	5300

a: - Sludge withdrawal before feed 3

The second feed of 100 ml yielded similar potential changes and gas yields for Digesters one and two. The behavior of Digester three differed by an immediate rise to a new potential level followed by changes similar to the other two digesters. There was no tendency toward recovery of the prefeed potential, only toward the displaced potential level. The gas production appeared to reflect this rapid initial displacement as it was about 18 percent lower than the other digesters for the 23 hour period after the feeding.

After the third feed digesters one and two exhibited similar electrode behavior with the potential rise due to feeding higher for Digester one. The gas production was also slightly higher for this digester. A leak and pressure loss in Digester three, which was caused by the sludge withdrawal before the feed, resulted in a large potential rise. The pressure was restored at the time of the feeding. The potential then began to drop toward the potential existing prior to the pressure loss. The gas production corrected for the loss was less by about 33 percent than the other digesters for the 20 hour period after the feeding.

The reason for the potential rise in Digester three was probably due to the gas-metal effect since air had entered the digester. But the large difference in the gas production and gas rate indicated that the air affected more than just the behavior of the metal electrode. Since the gas necessary for the pressure restoration was taken into account, there could have been a residual effect on the digester process itself. That this was a lag in the gas production was shown by the total gas production at 150 hours where the yields for all three digesters were about equal.

The evaluation of the potential measurements could be done on the basis of potential changes, as had been done above, or on the basis of the potential level. Digester two in the 72.5 hour period with continuous agitation remained largely in the -460 to -470 mv range. Digester one varied from around -475 to -510 mv with about -500 mv being the most representative level. The largest variation was -470 to -520 mv for Digester three. The most representative level was difficult to determine due to the large variations but it could be approximated as the same as Digester one, -500 mv.

Similar gas yields for Digesters one and two respectively at 72.5 hours indicated that the potential level did not necessarily indicate the production efficiency. Digester three with a lower yield did not bear comparison due to adverse experimental occurrences.

The gas production at 145 hours indicated the digesters were still producing gas comparable to the rate obtained several hours after the third feeding. The potentials of Digesters one and two had fallen slightly since 72.5 hours. Digester three had become more negative exceeding the potential after the second feed by falling from the more positive potential caused by the pressure loss. The potentials appeared to be approximately constant until a trend to a more negative level occurred near 170 hours. This potential drop for Digesters one and two corresponded to the beginning of the rapid drop in the gas production rate. The correlation for Digester three was not as apparent since the gas rate did not begin the rapid drop until ten hours after the new potential level had been reached.

After the fall of the gas rate was nearly completed, the continuous agitation was stopped at 200 hours. Divergence of at least one electrode in a digester and certain erratic electrode behavior prompted this action to determine if the agitation was in any way responsible. Since the results after stopping the mixer were very favorable, agitation was henceforth used only to mix the sludge before a sludge withdrawal and after a feeding. Separate experimental work on the effect of agitation on the electrode is discussed later in this thesis.

Small potential rises followed by a constant potential resulted from the cessation of the agitation. The beginning of the constant potential could be related to the beginning of a secondary rise in the gas rate. However, the constant potential gave no indication of the fall of the gas rate.

Before the agitation was stopped at 200 hours, the potentials were very close to the values before the first feed. Digester two had not varied widely from this prefeed potential of -472 mv and at 200 hours was near -480 mv. Digester one with a variation of nearly 40 mv was at -510 mv very close to the prefeed potential of -512 mv. The widest variation by Digester three of almost 55 mv found the potential at -515 mv, slightly higher than the prefeed value of -519 mv. These results indicated the prefeed potentials could be called base levels which the potentials sought after an addition of a solution with a different potential.

Ninety hours after the cessation of agitation and 291 hours after the first feeding when the potentials appeared to be constant, another feed of 100 ml was given to the digesters. The previous feeding had taken place ten days before and gas was still being produced. The only difference from previous feedings was that mixing was done only for a total of 45 minutes during which time the digesters were fed. Included in this time period was 30 minutes of agitation after the feed to insure good mixing. The potential results are shown in Figure 20.

The potentials before this fourth feeding were at -506 for Digesters one and three and at -464 mv for Digester two. After 170 hours the potential of each digester returned to within a few millivolts of the original potential before the feeding.

The behavior of Digester two differed from the others by dropping to a potential more negative than the prefeed value and rising, instead of leveling off, after this potential was reached. The cause of this behavior could have been the prefeed potential which was 40 mv more positive than the other digesters. This would indicate a tendency to the more negative potential level.

Although the potential changes were not large, the relationship between the production of gas and potential could be compared. The constant potential zone for Digester one and three reached near 50 hours corresponded closely to the peak gas rate and start of the rapid gas rate drop. The rapid change in the rate was reflected by a slight drop in the potential to a new constant level in Digester one. The potential of

Digester two leveled off near 35 hours, and did not reflect the maximum gas rate. The peak gas rate of Digester two near 45 hours fell between the constant potential zone starting at 30 hours and the rising potential zone starting at 60 hours. The sharp change in the gas rate starting near 70 hours did show a relationship to the potential which exhibited a drop starting at 60 hours.

The total gas production could not be considered wholly on a pure batch basis as there was a residual condition from the previous feed. This was particularly true for Digester one which exhibited a spurt in gas production at 35 hours unmatched by the other digesters. In the 460 hour period after the first of the four feeds the total gas production was about 9550, 9050 and 9800 cc for Digesters one, two and three respectively.

Electrode Check

The potential at 460 hours after the initial feed was at -501, -462, and -502 mv for Digesters one, two and three respectively. The more positive potential of Digester two had persisted for over a month beginning with the raising of the incubator temperature to 35°C and continued during subsequent feedings. Since the three digesters had been treated identically, the cause of this was not apparent. In order to investigate this potential difference of 40 mv between Digester two and the other two digesters, the electrodes in Digester three were switched with those in Digester two to discover if the electrodes were at fault. The potentials of the digesters were known from previous experiments and this provided a reference for the electrode readings. The digesters had not been fed for seven days;

the potentials were constant and agreed well; and the gas production was practically nil. Before the transfer electrodes 10, 11 and 12 G in Digester two averaged -462 mv and 13, 14 and 15 G in Digester three averaged -502 mv.

Electrodes 10, 11 and 12G were put in Digester three after being exposed to the atmosphere for about eight minutes. The normal adjustment curve leveled off at about 30 hours. The average was at -499 mv which agreed well with the previously determined digester potential of -502 mv. Thus, it was shown that inherent characteristics of the electrodes were not causing the lower negative potential in Digester two.

The behavior of electrodes 13, 14 and 15 G when placed in Digester two did not help explain the potential difference. The potential first leveled off near -492 mv at 60 hours. This was followed by a slight drop near 90 hours to a potential of -497 which closely paralleled the potential of the other two digesters. The previously determined sludge potential of -462 mv was not reproduced or even approached closely.

The potential changes exhibited by Digester two had been similar to the changes of the other two digesters even though at a different potential level. The gas production did not indicate any distinct reflection of this difference. It thus appeared that the more positive potential level was a temporary, although persistent, condition that had been set up by some unknown action during the temperature increase period.

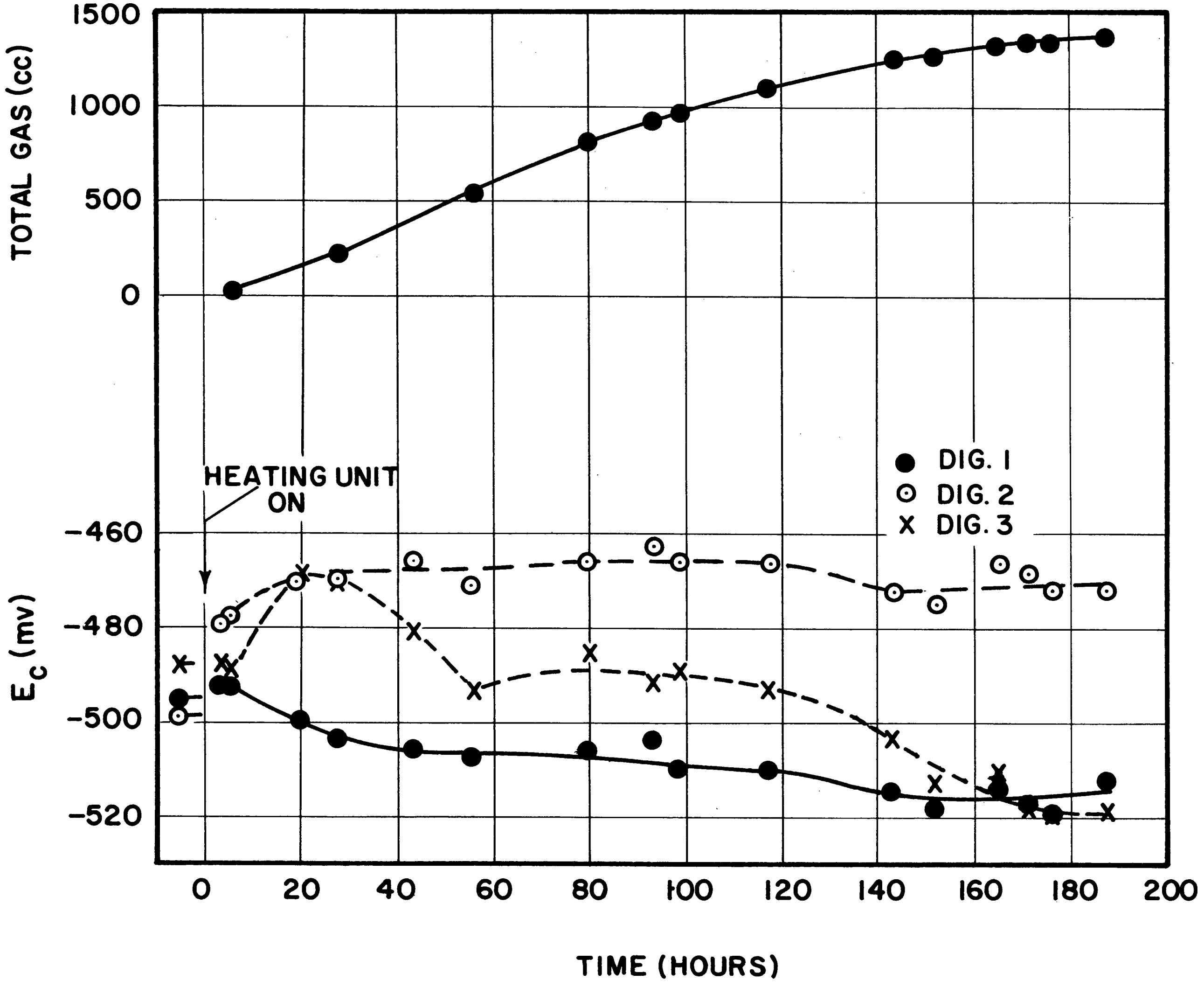


Figure 18. Electrode Potential and Gas Production Resulting from an Increase in the Temperature of the Sludge from 25 to 35°C.

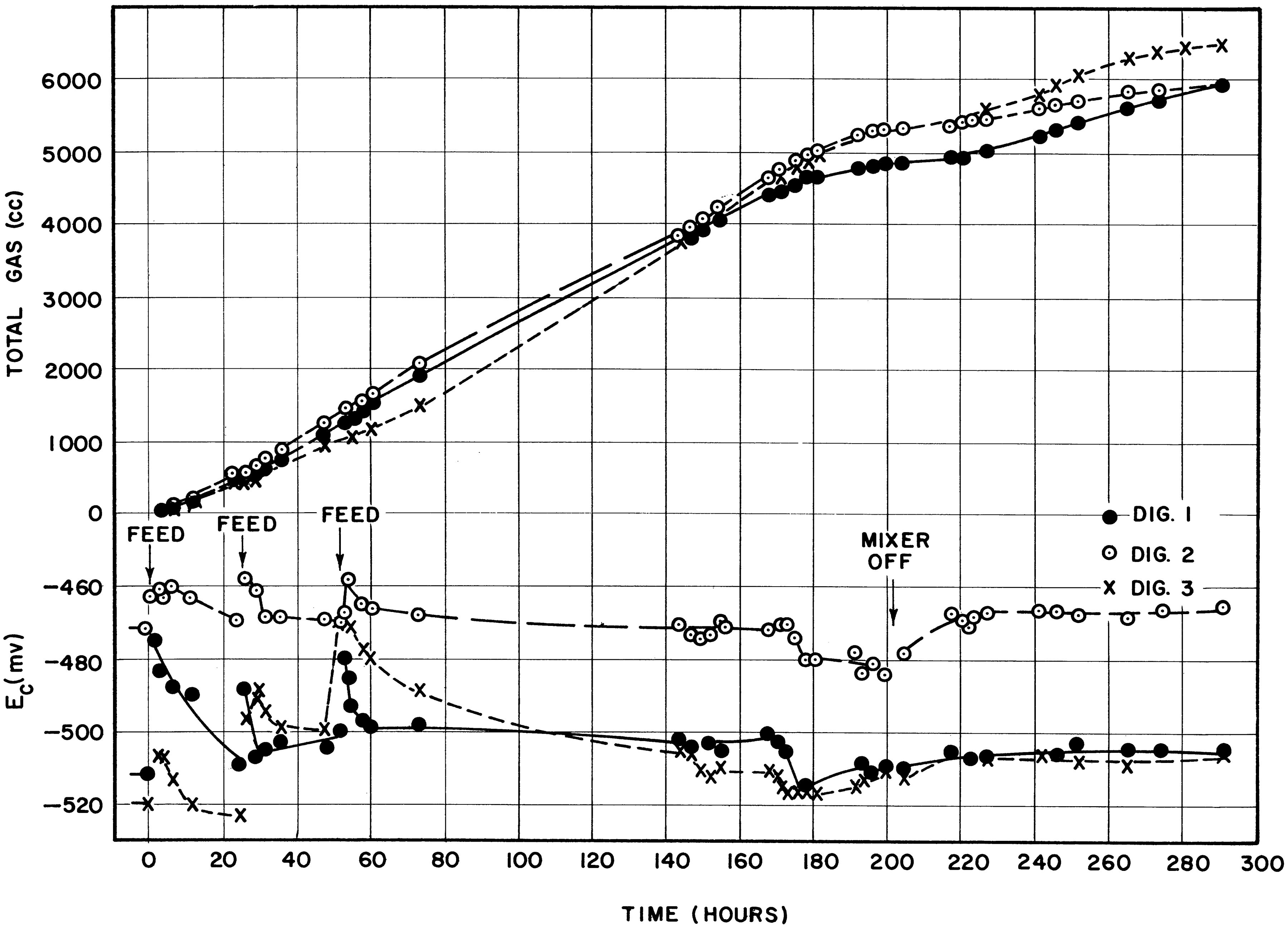


Figure 19. Electrode Potentials and Gas Production Resulting from Digester Feeding with Continuous Agitation

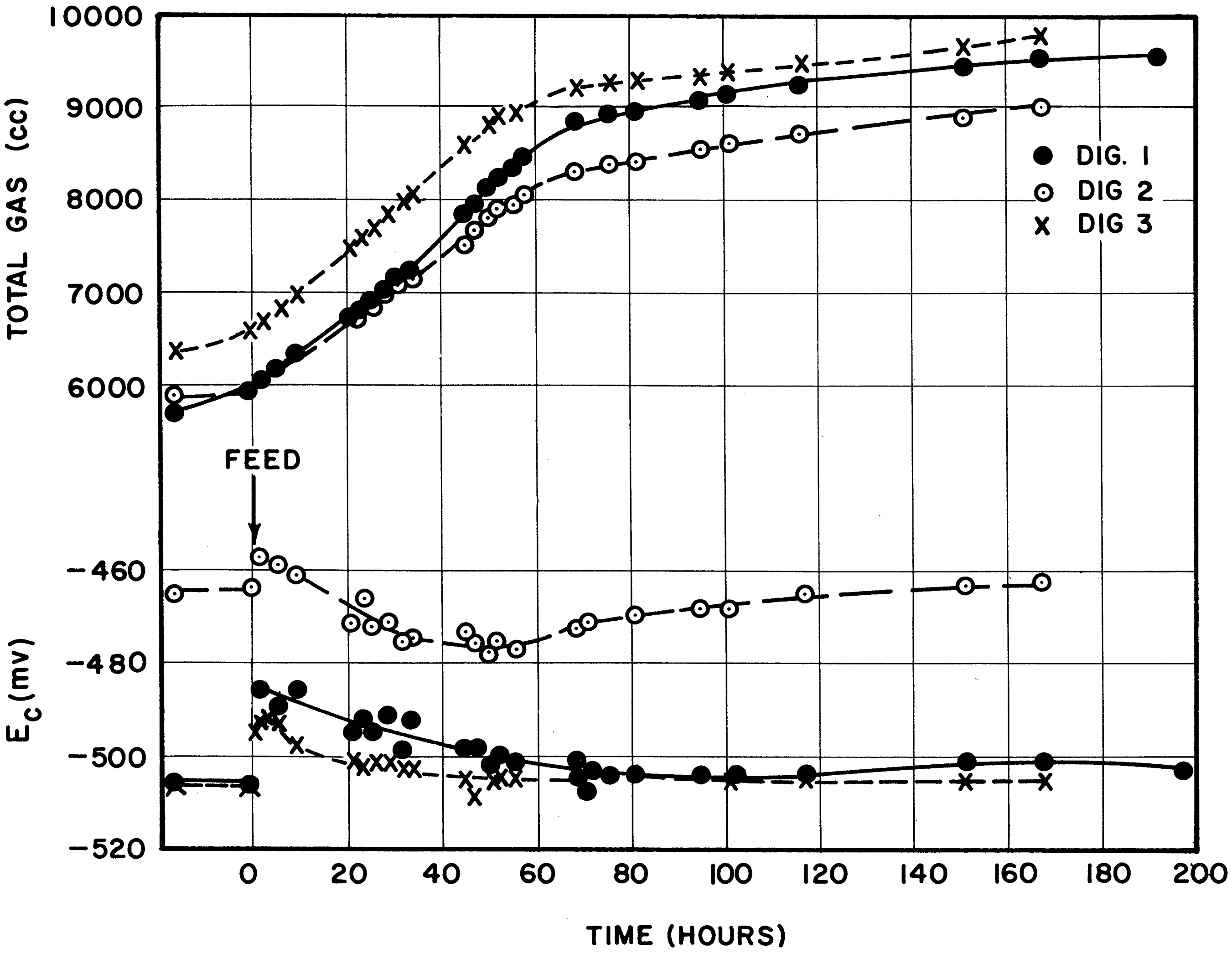


Figure 20. Electrode Potentials and Gas Production Resulting from Digester Feeding after the Continuous Agitation was Stopped.

BATCH TYPE FEEDING

The results of the lactose broth feedings have shown that the potential would reflect a lag in the gas production after feeding. Since the last raw sludge feeding in Figure 20 yielded a very short lag period, it was decided to attempt to lengthen the lag period and observe whether the potential would reflect this with raw sludge feedings. By using a sludge not fed for 30 days, a ripe but non-gassifying sludge, a lag period should be observed.

By employing a single feed and creating a batch type digestion, it was also felt that the potential changes would be more distinct than in a continuous system. This was important since the previous experimental work had shown that the variability in the metal electrodes could mask the actual potential change if the magnitude of the change was small.

The 100 ml feed simulated a batch condition wherein a ripe sludge received a feed equivalent to 0.091 pounds volatile solids per cubic foot per day or to a 25 day displacement without any direct influence of previous feedings. On a batch basis the ratio of fresh to digested sludge was one to ten based on the volatile solids content. The prefeed potentials were at -499, -493 and -501 for Digesters one, two and three respectively.

The expected rise in potential after feeding took place followed by a rapid recovery to the prefeed potential as seen in Figure 21. In this case the feed made the potential more positive while the five minute mixing about 20 minutes later started the trend toward more negative values. At 165 hours the potentials did not differ from the prefeed values by more than two millivolts.

The increase of the gas rate occurred in two stages. The first plateau reflected the lag phase and the second reflected the maximum rate. This is shown in Figure 21. The average rate based on the first ten hour period was at eight cc/hour which increased from a negligible gas production before the feeding.

There was some relationship between the potential and the gas rate. After the feeding the potential dropped and the gas rate rose but the potential did not reflect the leveling off of the gas rate near 20 hours. The potential drop ceased at 30 hours and the gas rate started to increase to its maximum at 40 hours.

It could be observed that the midway point between the beginning of the initial gas rate plateau and the rapid rise correlated with the start of the potential plateau. The cessation of the rising gas rate at 70 hours was only reflected by a rising potential in Digester two which started at 50 hours and ended at 68 hours. The start of the rapid drop at 120 hours was not reflected by the potential.

The next significant change in the potential was the beginning of the potential rise toward a new constant level, the potential before before the feeding. The end of the rapid gas rate drop preceded this potential rise by about ten hours. This was opposite to the relationship of potential and gas rate before the start of the rapid gas rise. In this case the gas rise followed the beginning of the potential plateau by about 15 hours.

From these results it appeared that it was necessary for the potential to reach a certain level before the gas production could approach its maximum rate. Before this potential level was reached, the sludge exhibited a lag period with a constant gas rate equal to about one-half the maximum rate. After the gas rate dropped to a low level, the potential returned to its original value representing a ripe sludge with a very low gas production.

A significant result of this experiment was the small potential changes. This was rather surprising as the conditions were similar to a batch feed condition with a definite lag phase where it would be expected that large changes would result. Excluding the immediate potential changes due to the feed, the change from 2 to 200 hours was 10, 14 and 11 mv for Digesters one, two and three respectively. It was during this period that all the gas rate changes occurred. It would appear that the digested sludge was very well poised to resist the potential changes resulting from the feed.

Even though the potential change was not large, the excellent agreement of the electrodes within a digester as well as between digesters indicated that the results shown in Figure 21 were an accurate representation of the potential changes. The electrode agreement indicated that potential measurements could be a reproducible tool for sludge digestion studies. However, it should be mentioned that the initial studies previously presented as well as other studies did not exhibit the fine electrode agreement shown here. Thus, it was considered desirable to produce larger potential changes in order to overcome any electrode variability as discussed in the next experiment.

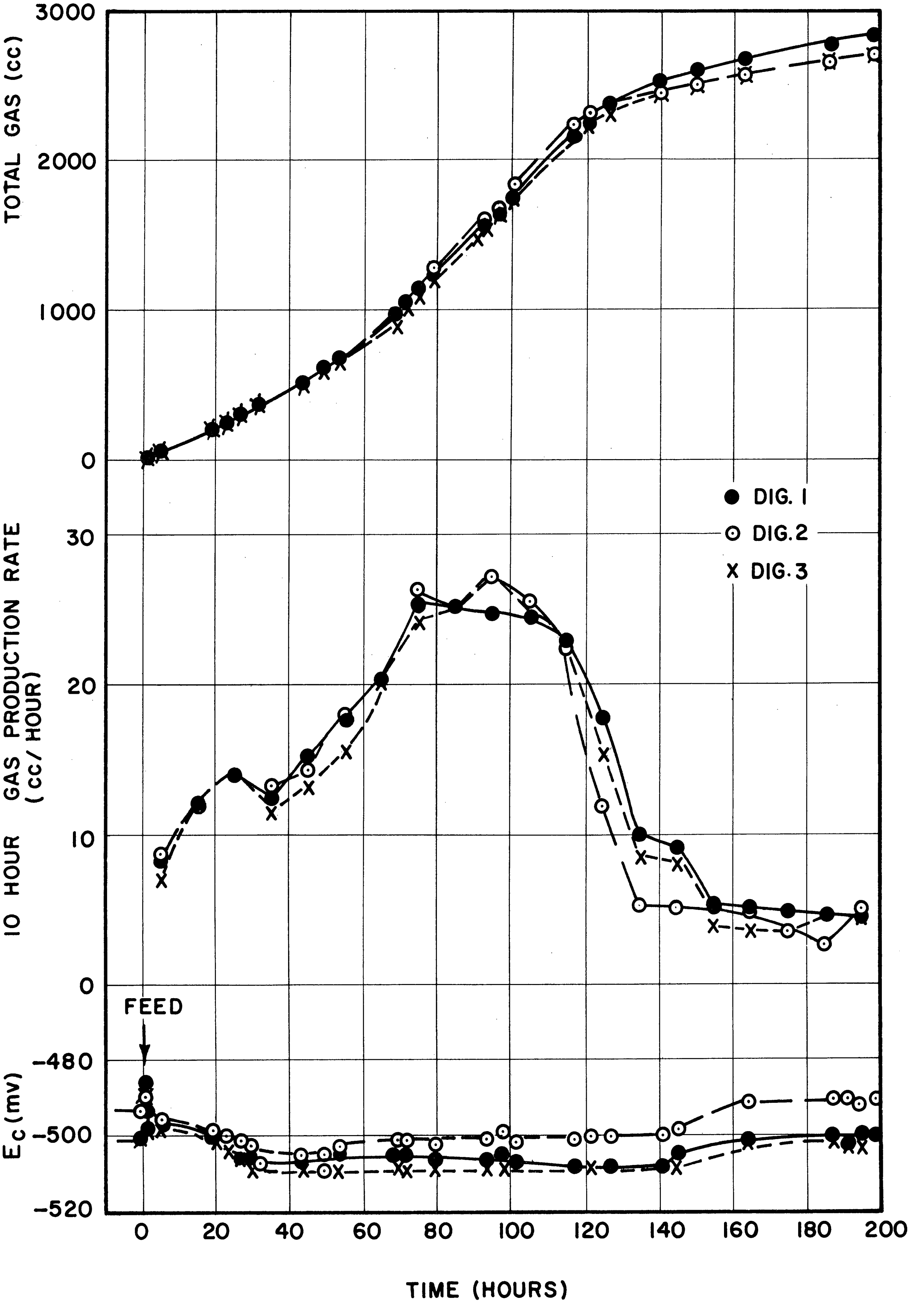


Figure 21. Electrode Potentials and Gas Production Resulting from a Batch-Type Feed

ACTIVATION OF A DORMANT SLUDGE

The ability of a ripe sludge to poise the potential after additions of raw sludge resulted in small changes in the potential. Because of the variability in the metal electrodes, these small potential changes were difficult to evaluate accurately.

The lack of a wide potential range in the batch type feeding previously discussed with a sludge aged for one month led to the use of a sludge media aged for four months. It was thought that this aging period would produce a dormant sludge (lack good seeding characteristics) which would yield larger potential changes after additions of raw sludge.

The aging time to classify a digested sludge as dormant was based on the work of Heukelekian(120) who found that after three months at 20°C the seeding value of the sludge was lost rapidly based on gas production. He felt the optimum time was after the decomposition of the digesting mixture was completed and up to one month after. In addition, Heukelekian and Heinemann(33) found that the maximum number of methane bacteria were present at the peak of gasification and that the organisms maintained their values for at least 90 days with a decrease after gasification stopped.

The use of a dormant sludge also offered an opportunity to study a long lag period digestion and the resulting relationship between the potential and gas production. In this manner the results could be compared to the shorter lag periods where an active digested sludge was used and to the lactose broth experiments.

After several widely spaced feedings, the identical feed quantity to each digester was varied. This was done to study the potential differences arising from different feed quantities. The varied or non-parallel feedings were initially begun on a daily basis. However, the potential exhibited unusual trends resulting in the discontinuance of the feedings. The digestion was then followed without any further sludge additions since it was felt the results would be more meaningful than if further additions were made. There was a total of six feedings given to each digester with the first four being equal and spaced about 90 hours apart. The two non-parallel feedings were given 24 hours apart with one digester receiving the same quantity as in the previous parallel feeding sequence. The feed was preheated to 30°C before being added to the digesters. The digesters were agitated before and after each feed for five minutes. The potentials during the feeding period are summarized in Table IV.

Parallel Feeding

The first feed of 50 ml of raw sludge produced very little gas as seen in Figure 22. The first few hours after feeding showed a negligible gas production which was contrary to the effect of feeding an active sludge. The second feed of 100 ml at 91.5 hours also yielded negligible gas production for the first eight hours. However, 71 hours after this feed there was production of gas which, compared to an equal time period after the first feed, was over five times as great. This indicated the methane bacteria were becoming active. This was also shown by a rise in the gas rate after

TABLE IV

SUMMARY OF ELECTRODE POTENTIALS DURING THE FEEDING PERIOD STARTING WITH A DORMANT SLUDGE

Time (hours)	Time Interval (hours)	Feed No.	Feed Quantity (ml)			Potential (E_c) Before Feed (mv)			Resulting Potential Change (mv)			Potential Change Based on Value Before Feed One (mv)		
			Digester			Digester			Digester			Digester		
			1	2	3	1	2	3	1	2	3	1	2	3
0	--	1	50	50	50	-496	-481	-478	-	-	-	--	--	--
91.42	91.42	2	100	100	100	-519	-495	-526	- 23	- 14	- 48	- 23	- 14	- 48
163.25	71.9	3	100	100	100	-506	-491	-519	+ 13	+ 4	+ 7	- 10	- 10	- 41
258.9	95.6	4	100	100	100	-492	-475	-500	+ 14	+ 16	+ 19	+ 4	+ 6	- 22
355.25	96.6	5	300	100	200	-484	-468	-500	+ 8	+ 7	0	+ 12	+ 13	- 22
379.92	24.6	6	300	100	200	-477	-470	-500	+ 7	- 2	0	+ 19	+ 11	- 22
404.2	24.3	-	---	---	---	-469	-470	-491	+ 8	0	+ 9	+ 27	+ 11	- 13

the third feed of 100 ml at 163 hours. This was the first time the rate had increased soon after the feeding. The fourth feeding of 100 ml at 259 hours also exhibited this rise.

The first feed produced a rapid negative potential change which was most severe for Digester three. This is shown in Figure 22. The pattern of this fall to a more negative potential after feeding was not exhibited in other experiments where the usual result was a rapid positive trend followed by a recovery to the more negative prefeed level. This difference was probably due to the condition of the dormant sludge. The large change to a more negative potential could have been due principally to the hydrolytic enzyme systems since the gas production was so small. However, the changes were not distinct enough from other potential measurements to warrant any breakdown concerning the system causing this potential change.

Mixing of the sludge at 79 hours for seven minutes produced a sudden positive change in Digester one, a gradual positive change in Digester two and practically no change in Digester three. Since the usual effect of agitation was in creating a more negative potential, the results here appeared to be due to the sludge and not due to the electrodes.

The potential changes after the second feed at 91 hours were not as rapid as were those after the first feed. There was a slow trend toward a more positive potential. This was the period in which the gas production began to increase. There was no direct indication by the potential of this increase.

The third feed at 163 hours produced more rapid potential changes than the second feed as well as an immediate increase in the gas rate. The potentials became more positive. A distinct change in the gas rate at 210 hours was not reflected by the potential.

The potential changes after the fourth feed were not large and showed fairly constant behavior during the 96 hour period following the feed.

The potential, 96 hours after feed four, was at -484, -468 and -500 mv for the Digesters one, two and three respectively.

The activity of the sludge had reached a level where the gas was produced at an approximately constant rate. Although this rate was not as high as obtained on the other runs, it appeared that the sludge was functioning normally. On the basis of the gas production as well as the similarity of the potential curves after feed four, it was felt that the parallel operation could be abandoned and non-parallel feedings started.

Non-Parallel Feeding

The loadings for Digesters one, two and three were set at 300, 100 and 200 ml of sludge. These were equivalent to a displacement of 8.33, 25 and 12.5 days and a loading of 0.25, 0.083 and 0.166 pounds volatile solids per cubic foot per day. The feed to Digester two was kept the same as in the parallel feeding section in order to use this digester as a reference.

Although the potential after feeds five and six reflected the different loading levels, the results when compared to the previous feeds were following a different pattern. It was therefore decided to postpone the next feeding 24 hours to see if a longer time after feeding would throw more light on this situation. By the end of this period the potentials had exhibited a potential drop for all the digesters. Since this had not occurred with any of the previous feedings, it was decided to follow the resulting trend without any additional feedings.

The beginning of this dropping potential occurred 35 hours after the sixth feed. By reference to the time of the first non-parallel feed, number five, as zero, then the drop for all three digesters began near 60 hours. These potential changes are summarized in Table V.

The potential of Digester two remained essentially constant from the time the negative trend ended near 102 hours until the completion of the run at 310 hours. All the major changes in the gas rate of this digester occurred before 102 hours. The potential of Digester three varied little after 145 hours and near 280 hours rose slightly to a potential of -511 mv. The potential of Digester one started to drop near 220 hours until reaching a new low near 290 hours of -509 mv. This drop was probably a reflection of higher metabolic activity due to the larger feed quantities.

The agreement of Digesters one and three within two mv was of special interest since they had not been that close since after feed one which took place 675 hours previously. After four parallel and two non-parallel feedings which provided differences up to 30 mv, the agreement provided a basis for the determination of the potential level of ripe suldge.

According to Figure 24 it was possible to relate the gas rate and potential in many instances. However, the data also indicated that neither the potential nor the gas rate changes could be used to predict the behavior of each other. But it was found that the relative production of gas and the relative feed quantities could be predicted from the change in the potential. By considering the negative trend or recovery period starting at 60 hours, the differences in potentials at the first point where all the digesters exhibited constant potentials would yield this result.

TABLE V

SUMMARY OF THE POTENTIAL CHANGES FOLLOWING THE MAXIMUM POSITIVE POTENTIAL

Time (hours)	Time Interval (hours)	Potential (E_c) (mv)			Potential Change (mv)			Potential Change from 61 hours (mv)		
		Digester			Digester			Digester		
		1	2	3	1	2	3	1	2	3
61	--	-468	-469	-492	--	--	--	--	--	--
78	17	-478	-478	-502	-10	-9	-10	-10	-9	-10
102	24	-488	-481	-511	-10	-3	-9	-20	-12	-19
126	24	-492	-480	-511	-4	+1	0	-24	-11	-19
145	19	-500	-480	-514	-8	0	-3	-32	-11	-22
310	165	-509	-480	-511	-9	0	+3	-41	-11	-19

The first time this occurred was at 145 hours. Previously at 110 hours two of the three digesters were constant but the comparison appeared to be more valid when all digesters exhibited constant potential zones. This could be compared to the gas production in Figure 23 where the relative production could not be accurately measured until all three digesters exhibited relative flat curves. Before this time the results would be misleading. At 350 hours after feed five the production was approximately

10,000, 4,000 and 7,000 cc for the three digesters. The ratios were not even multiples of the feeding ratios, but by correcting these figures for the gas contributed by the previous parallel feedings, the ratios became 3.05/1, 1/1 and 2.08/1 for Digesters one, two and three respectively. The corresponding feed ratios were 3/1, 1/1 and 2/1 and this indicated equal efficiency for each digester at a different feeding level.

The negative potential changes in the 60-145 hour period were 32, 11 and 22 mv for Digesters one, two and three respectively. If the lowest change were used as a basis, the ratios would be 2.91/1, 1/1 and 2.0/1. This corresponded very closely to the non-parallel feeding ratios as did the relative production of gas. These ratios were only approximate as the potential changes were not sufficiently large enough to decrease the sensitivity of this ratio to small errors in the potential. But the approximate trend gave results that proved very enlightening as these ratios were indicative of the three different feed quantities.

Overall Results of the Feedings

The two methods of feeding the digesters have been considered separately in order to better present the experimental data. However, the overall results which included both the parallel and non-parallel feedings also provided some significant results as seen in Figure 24. The feed of Digester two was kept at the same constant feed level so that the overall result could be considered without the effect of a varying loading complicating the results. In addition, this digester could be used as a reference for the other digesters which were at different feeding levels for the last two feedings. The potential in the dormant sludge before the first feed was at -481 mv for Digester two. After six feedings and 680 hours later the potential had dropped to -504 mv, risen to -468 mv and dropped again to -479 mv.

Although Digesters two and three showed similar patterns, the resulting potential of Digester three was not nearly as close to the initial value as was Digester two. This possibly was due to the last two feedings being higher. But it was more probably due to temporary readings in the dormant sludge as evidenced by the larger changes upon feeding than that exhibited by Digester two. Digester three began at -479 mv, dropped to -530 mv, rose to -491 mv and dropped again to -511 mv. Digester one started at -496 mv, dropped to -527 mv, rose to -467 mv and dropped again to -509 mv.

In the case of Digester two where all six feedings were at the same level, an unexpected drop in the potential occurred after feed five at 355 hours. The drop was followed by a rising potential which after 25 hours was two mv lower than the prefeed potential. The potential had also dropped after feed one, and continued to drop whereas after feed five the potential rose. Feed six followed feed five by 25 hours and produced practically no change.

At 420 hours or 35 hours after feed six the potential began to drop and continued dropping until near 460 hours. This potential varied very slightly until the end of the run at 670 hours.

The dropping of the potential 35 hours after feed six was not observed after the first four feeds which had time intervals following them of more than 60 hours. The potentials after feeds three and four were taken in an actively gasifying sludge while feeds one and two were given to the sludge when in the beginning stages of activation. The fairly constant gas rates after feed four and the rising rates after feed five indicated full activity was being developed during this interval.

It was possible to explain this potential drop by means of the gas rate since the rate was always rising or remaining essentially constant after the first five feeds. However, about 20 hours after feed six the gas rate began to drop near 400 hours. This could be related to the potential drop at 420 hours by stating that the start of the dropping gas rate resulted in the starting of the potential drop.

However, the heavier feedings in Digesters one and three did not follow this pattern. The drop in potential of all three digesters began near 420 hours but the drop in gas rate began near 425 hours for Digester three and near 455 hours for Digester one. Although the magnitude of the potential change varied proportionately to the feed as previously discussed, the time of the start of the potential drop did not reflect the feeding loads. This indicated that the beginning of the rapid drop in the gas rate was not responsible for the potential drop in Digester two. This could possibly be part of the reason, but the consistency of the time of the potential drop for the three differently fed digesters must lead to a different conclusion.

By considering the surprising immediate potential drop after feed five in Digester two, the condition of the digested sludge before feed one, and the potential drop at 420 hours, it was concluded that the overall potential pattern was a reflection of the process of activating a dormant sludge. The natural tendency of the potential to go towards the characteristic value of a ripe sludge after becoming actively digesting occurred at 60 hours after feed five or 420 hours after feed one. Therefore, the buildup of the sludge activity was reflected by a cyclic potential pattern consisting of a drop, a rise and a final drop to the characteristic potential of ripe sludge.

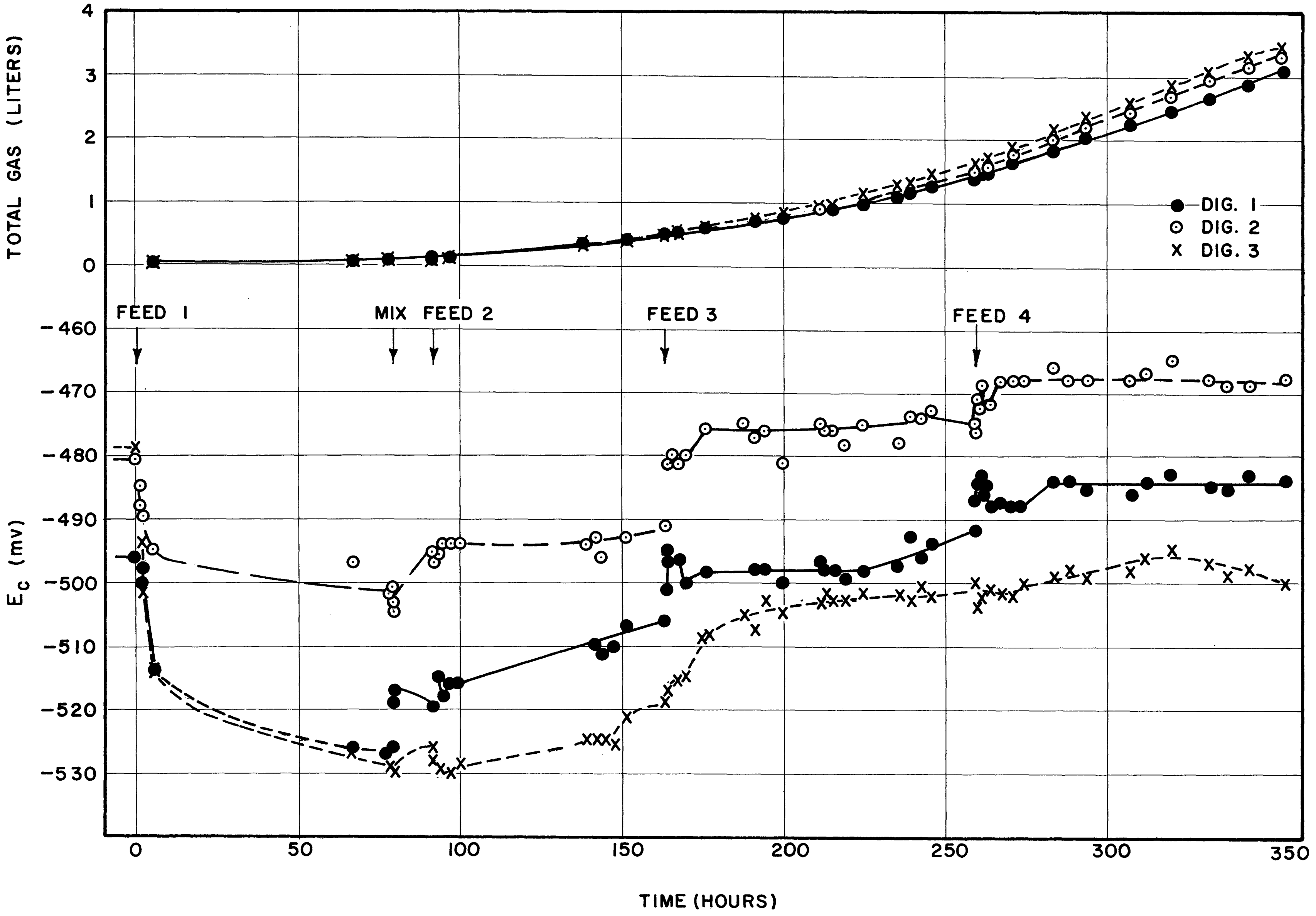


Figure 22. Electrode Potentials and Gas Production Resulting from Feeding a Dormant Digested Sludge

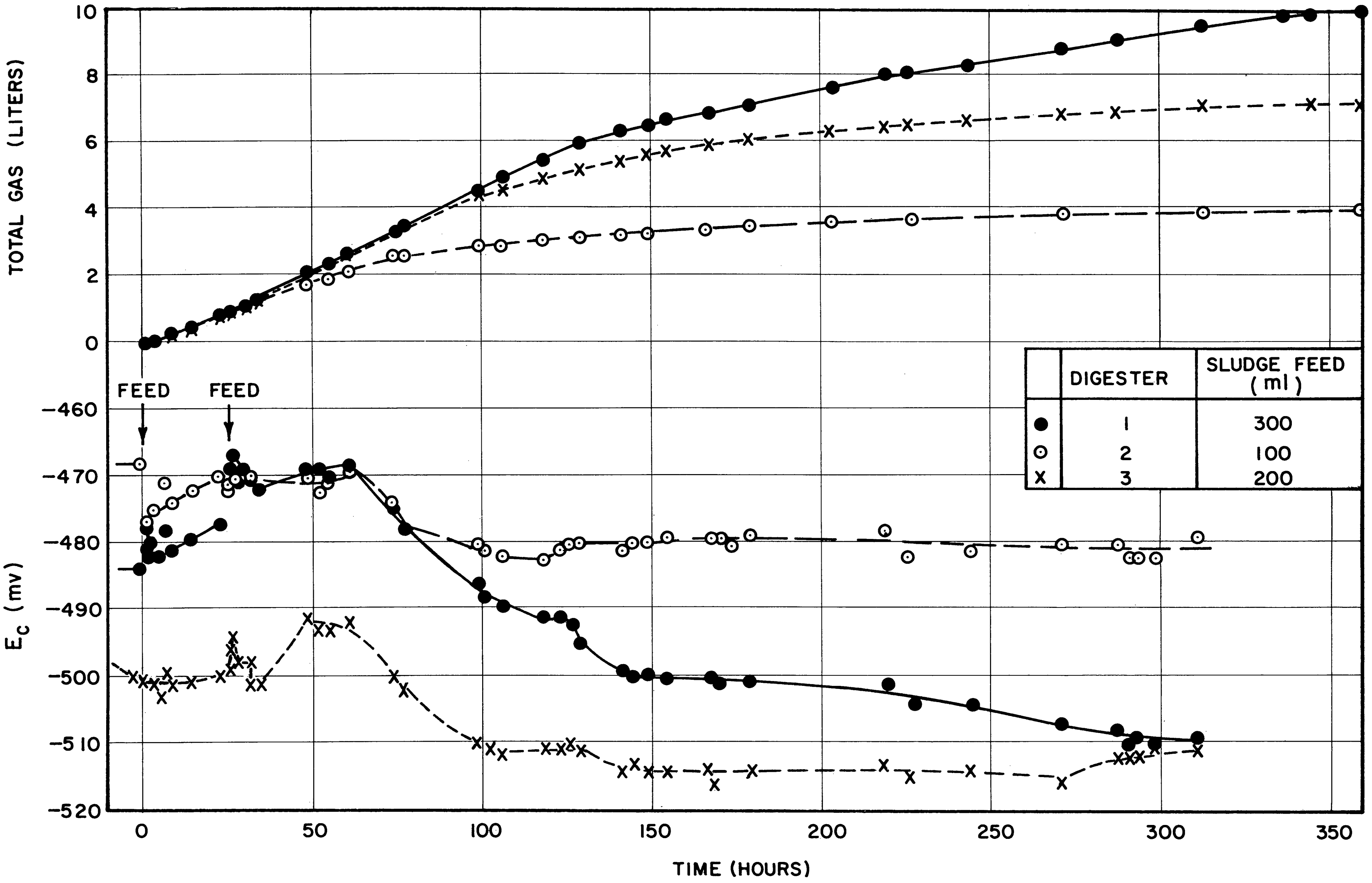


Figure 23. Electrode Potentials and Gas Production Resulting from Different Feeding Levels

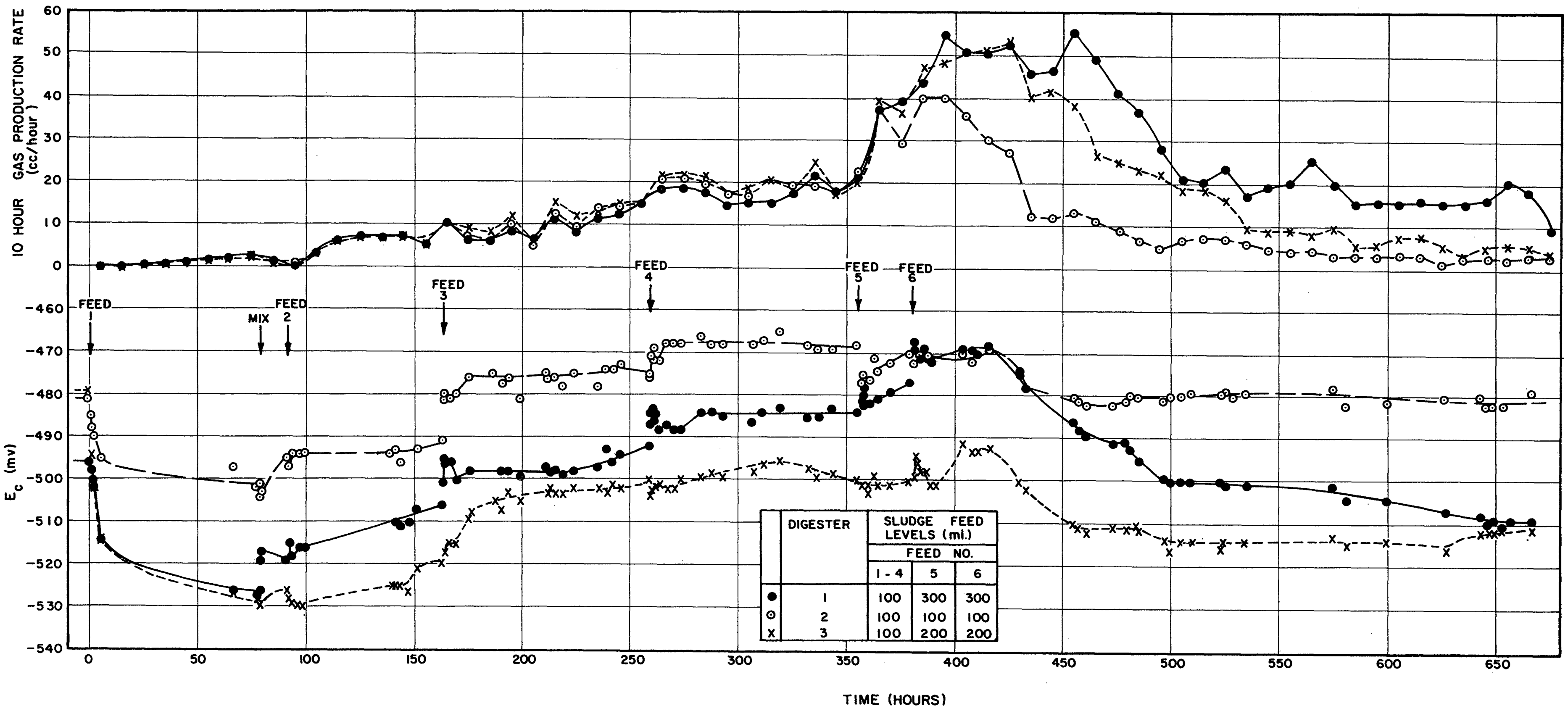


Figure 24. Electrode Potentials and Rates of Gas Production Resulting from Activating a Dormant Sludge by Feeding

LOADING TO A TEMPORARY DIGESTION FAILURE

The main objective of this experiment was to evaluate the behavior of the oxidation-reduction potential in a sludge undergoing some type of digestion failure. The failure of a sludge digester could be detected by various parameters such as a rise in the volatile acid content, cessation of gas production or a rise in the carbon dioxide content of the gas. Volatile acids have been generally considered the best indication but the time necessary to perform the test would detract from its value in control operations. The use of oxidation-reduction potentials offered the possiblity of a more rapid method for the detection of failure. Another objective of this experiment was to observe the relative effectiveness of platinum and gold electrodes in detecting failure conditions. Since these metals could exhibit differences in their potential behavior, this was considered to be an important phase of the experiment.

The experimental conditions were determined according to these objectives. Feed levels of 300 ml of raw sludge were given to Digesters one and two to create a failure condition. The former contained one gold and two platinum electrodes and the latter contained one platinum and two gold electrodes. Digester three with three gold electrodes was used as the reference digester with a feeding level of 100 ml. This low feeding was used in all other experiments and thus provided a reference point.

The digested sludge had stopped producing gas eight weeks before the run. Although it could not be strictly considered a dormant sludge, it was desired to use a sludge that would not be as able to resist failure conditions as well as a riper sludge. It was felt that a more rapid approach to failure conditions would yield greater potential changes in a shorter time and set an extreme condition to test the use of potential measurements.

The feeding sequence consisted of eight additions of raw sludge. The feedings were stopped when it appeared that the digestion was in a failure condition. This was done in order to follow the potential of the sludge recovery from the temporary failure condition.

The purpose of the first feed at 10°C was to check potential changes immediately after adding a cold raw sludge. The subsequent feeds were preheated to about 35°C in order to achieve failure not by temperature causes, but by loading per se. The feeding schedule is shown in Table VI. Mixing, instead of feeding, was done at two points for ten minutes after the first and second feedings in addition to allowing large time intervals after feeds one and two in order to assist in the buildup of the digester activity. The mixing was done at 23.5 and 59.4 hours. The resulting potential changes during the feeding period are given in Table VI and the overall potential trends are given in Figure 25.

This first feed at 10°C produced little immediate change in Digester three. However, Digesters one and two at the higher loadings showed a considerable effect from the feed by an immediate rise in potential followed by a recovery and then a positive trend. This immediate effect was influenced largely by the low temperature of the feed. The gas production rate which is shown in Figure 25 lagged for the first few hours and then began to fall off 30 hours after the feeding. The gas production curves shown in Figure 26 were similar except that Digester three produced less gas.

The gas rate after feed three was higher initially and began to drop off about seven hours after the feed for all three digesters. The total gas produced before feed four at 107 hours was 1236, 1130 and 758 cc for Digesters one, two and three respectively and the gas rates were approximately 19, 17 and 8 cc/hour. These figures indicated that the methane bacteria were not fully developed.

TABLE VI

SUMMARY OF THE ELECTRODE POTENTIALS DURING THE FEEDING PERIOD BEFORE DIGESTION FAILURE

Time (hours)	Time Interval (hours)	Feed No.	Potential (E_c) Before Feed (mv)			Potential Changes (mv)			Potential Change Based on Potential Before Feed One (mv)		
			Digester			Digester			Digester		
			1	2	3	1	2	3	1	2	3
0	----	1	-501	-488	-528	--	--	--	--	--	--
47.5	47.5	2	-495	-478	-529	+ 6	+10	- 1	+ 6	+10	- 1
96.1	48.6	3	-494	-476	-529	+ 1	+ 2	+ 0	+ 7	+12	- 1
107.1	11	4	-493	-467	-523	+ 1	+ 9	+ 6	+ 8	+21	+ 5
119.7	12.6	5	-475	-466	-521	+18	+ 1	+ 2	+26	+22	+ 7
125.2	5.5	6	-471	-464	-516	+ 4	+ 2	+ 5	+30	+24	+12
145.5	20.2	7	-455	-455	-506	+16	+ 8	+10	+46	+32	+22
148.3	2.9	8	-453	-455	-513	+ 2	+ 1	- 7	+48	+33	+15
195	46.7	-	-442	-433	-504	+11	+22	+ 9	+59	+55	+24

After the fourth feed, Digesters two and three yielded little change in the potential level. However, Digester one showed a large immediate rise of 14 mv. The immediate potential rise could possibly be better described as a displacement of the potential level by the feed. This was followed by a slight drop and then a rise to a potential 18 mv positive than before feed four. This was the largest overall potential change and initial displacement caused by any of the feedings.

After the seventh feed, Digester two for the first time exhibited a drop after the feed instead of a more positive potential. The gas rates after feed seven for Digesters one and two approximated those shortly before the feed. Digester three exhibited a decline in the rate.

Three hours later at 148 hours the eighth feed was given to the digesters. The pH of the withdrawn sludge indicated that the digesters were not operating properly. The pH for the more heavily fed Digesters one and two was 6.5 and 6.58 while the lighter fed Digester three yielded 7.1. It was felt that the lower pH of the sludge was indicative of an impending cessation of the rising gas rate and the feedings were suspended temporarily. The gas rate for the three digesters exhibited an initial short rise followed by a slight decrease. The rate then increased to the highest values obtained up to that time before falling sharply near 170 hours indicating a temporary failure of the digestion.

Because of the drop in the gas rate, no more sludge was added to the digesters. The second phase of the experiment involved the potential changes after the discontinuing of the feed and up to the cessation of the gas production which occurred 625 hours later. However, since the potential changes practically ceased 300 hours after the feed stoppage, the following discussion will be largely concerned with this period.

After the eighth feed at 148 hours, there was 36 percent by volume of raw sludge in Digesters one and two not over 28 hours digested. Forty-nine percent was not over 51 hours in the digesters. Twenty percent of the digester volume was fed within the last three hours. For the two days preceding the last feed there were six feeds of 300 ml each. This corresponded to a three day displacement time. There was only 40.4 percent of the original seed sludge left.

Digester three was not nearly as heavily loaded. At 148 hours there was 13.5 percent by volume of raw sludge not over 28 hours digested. The amount of sludge not over 51 hours in the digester was 19.6 percent. Seven percent of the digester volume was fed within the last three hours. Nearly 75 percent of the original seed sludge was left.

Based on the ultimate gas production and the gas produced up to the time of the final feed at 148 hours, the percentage of digestion that occurred was about nine percent for the more heavily fed digesters. From the volatile solid content of the raw and digested sludge, the volatile solids of the raw sludge comprised 75 percent of the total volatile solids in Digesters one and two. This was equivalent to a batch digestion with a ratio of three parts of volatile solids from the raw sludge to one part volatile solids from the ripe sludge. The lighter feeding to Digester three resulted in a ratio of one part from the raw sludge to two parts from the ripe sludge at 148 hours.

After the final feed, the potential of Digester two rose until reaching its maximum positive potential of -432 mv near 200 hours, 52 hours after the feed. At 250 hours the potential started to drop slowly. At 270 hours the slope became greater and the potential fell linearly to near -495 mv at 335 hours. After a ten hour steady period the potential continued to drop until becoming constant again at 360 hours and at -508 mv. This was 20 mv more negative than the potential before the initial feeding which was -488 mv.

The potential in Digester one exhibited a slight rising trend after an initial sharp drop and rise until reaching a maximum of -441 mv at 190 hours. The potential began to drop slowly after this and at 250 hours and -452 mv the slope became greater and followed a linear path. The potential began to level off at 315 hours and -495 mv until reaching a constant zone of -500 mv at 330 hours. This potential corresponded very closely to the original potential before feeding of -501 mv.

The potential of Digester three rose very slowly to its maximum positive potential of -504 mv near 195 hours. This was followed by a slow drop to 224 hours and -507 mv where the potential began a linear drop at a more rapid rate of change. At 300 hours the potential leveled off near -528 mv and this level did not change appreciably up to 365 hours. This potential was practically the same as the value before the first feed.

The digesters were mixed for 20 minutes after the potentials had leveled off at 365 hours. At 455 hours electrode adjustment experiments were run in Digesters one and two. This lasted through to 490 hours. Digester three adjustment runs were from 480 to 525 hours. These experiments interrupted the normal potential readings due to changes in electrodes and agitation. Even though normal readings were not possible during the adjustment period, the results indicated no other changes occurred in addition to those due to the adjustment procedure.

The gas rate changes after the last feed at 148 hours and corresponding potential levels are summarized in Table VII. From this table and Figure 25 the relationship of changes in the gas rate and potential could be evaluated.

TABLE VII

GAS RATE CHANGES AND CORRESPONDING ELECTRODE POTENTIALS

	Time (hours)			Potential (E_c) at Time t (mv)		
	Digester			Digester		
	1	2	3	1	2	3
End of rising gas rate and point of gas failure	172	175	170	-447	-440	-508
End of falling rate one	194	198	180	-441	-432	-506
Beginning of rising rate one	215	229	190*	-446	-433	-505*
End of rising rate one	263	276	260	-459	-446	-515
Beginning of falling rate two	286	313	286	-464	-475	-523
End of falling rate two	---	---	390	---	---	-528
Beginning of rising rate two	313*	348	---	-495*	-500	---
Beginning of dropping rate three .	438	375	---	-504	-507	---
Beginning of rising rate three....	---	420*	---	---	-510*	---
Maximum rate	440	498	275	-504	-509	-520
Beginning of dropping rate four ..	---	548	---	---	-511	---
End of dropping rate four	507	586	---	-506	-508	---

* Beginning of rise to maximum gas rate

The gas rate in Digester two began to drop before the maximum positive potential was reached near 200 hours. This latter time coincided with the end of the dropping gas rate. The renewal of the rate occurred about 30 hours after the maximum potential where the potential was only one mv more negative. The above gas rate changes occurred within an eight mv potential range which was larger than that for Digester one but could still be considered small in relation to the overall potential change.

The first gas rate rise ended shortly after the start of the linear potential drop and the subsequent drop occurred in this zone. After the potential leveled off and then dropped, the gas rate began to rise again. This rate dropped and finally at 420 hours began to rise to a maximum. This rise occurred shortly after a small drop in the potential to a new constant level.

The beginning of the gas rate drop for Digester one occurred about 20 hours before the maximum positive potential was reached. At this point the rate drop ended. The renewal of the rising rate occurred about 20 hours after the time of maximum positive potential and 40 hours before the start of the linear drop. The potential range in which these three rate changes occurred was six mv. This small range was slightly larger than that of Digester three.

The end of the rising gas rate and subsequent falling rate as well as the renewal of the rising rate for Digester three were spaced in the period where the potential changes were very small. The beginning and end of the drop in the gas rate occurred before the maximum positive potential was reached as did the beginning of the gas rate rise to a maximum. The maximum difference in potential during this period was four mv.

There were further changes after 410 hours in the gas rates of Digesters one and two although the potential showed little variation. At 790 hours where the gas rates were approximately constant and less than five cc/hour, the potentials were -502, -512 and -513 mv for Digesters one, two and three respectively. These values would seem to indicate the potential range of a ripe sludge. The corresponding E_h values would be -256, -266 and -267 mv.

Before 410 hours the changes in the potential pattern usually reflected a gas rate change although the reverse did not yield as good a correlation. After 410 hours the potential varied little even though the gas rate was still undergoing changes. The initial period resembled more a batch type of digestion where the potential and gas rate were changing. The latter period partly resembled a continuous type of system in which the potential changes were small. In a true continuous system both the gas rate and potential would be relatively constant. Therefore, a relationship between the gas rate and potential could only be expected in a batch type of feeding in which the metabolic bacterial systems went through all phases of their growth pattern. This was shown earlier in this thesis where a synthetic feed containing sugar was fed on a batch basis. This also was exhibited by the sludge feeds on a batch basis.

An interesting relationship was shown by the potential and the beginning of the gas rate rise to its maximum value. The beginning of the rate rise to the maximum was at a potential of -495 and -510 mv for Digesters one and two. For Digester three this occurred at -505 mv. From this it could be concluded that there existed a characteristic potential level necessary for the gas rate to reach its maximum.

However, the inverse did not seem to apply as seen from the results of Digester two. The -508 mv mark was reached about 60 hours before the rate began its rise to the maximum. This would indicate that the potential can define a necessary, but not a sufficient experimental condition. This could be referred to the results found by Kaplovsky(43) that high volatile acids hindered digestion but a low content did not insure good digestion.

Another significant relationship was exhibited between the potential and gas rate. The linear potential drop for Digester one preceded that of Digester two even though they were fed identically. This would appear to indicate that the activity of Digester two lagged behind that of Digester one. By observing the gas rate curves for the initial rise after failure, it could be seen that the same conditions were described. The similarity in the potential and gas rate curves which both indicated an activity lag for Digester two provided an excellent example of a relationship between the potential and sludge activity.

Another instance where the potential could be used to indicate certain characteristics of the digestion was by the use of potential changes. Since the digester loading was different, this difference, as well as the relative gas production, could possibly be reflected by the potential as demonstrated in previous experimental work.

After the potential recovery from the minimum negative value had started, the first sample of all three digesters yielding a constant potential levels at the same time occurred near 335 hours. The potentials were at -500, -494 and -528 mv for Digesters one, two and three respectively. The difference between these potentials and the maximum positive values were 59, 62 and 24 mv. The highest positive potential was shown by Digester two which reached -432 mv. Digester one rose to -441 mv and Digester three rose to -504 mv. The ratio of the changes would then be 2.46 and 2.58 to one for Digesters one and two based on Digester three. These ratios did not reflect the feeding ratios of three to one for Digesters one and two to three.

The corresponding ratios for the total gas production over the complete digestion period yielded values of 2.47 and 2.5 to one for Digesters one and two compared to Digester three. This corresponded very well to the potential change ratios.

The gas production ratio indicated that the more heavily loaded digesters were not as efficient in the breakdown of the organic substances in the feed as the normally loaded digester. Since the potential directly reflected the gas production ratios, the potential also indicated the less efficient digestion. This same technique yielded similar results for another potential recovery curve presented previously. In that instance both the feeding and gas production ratios were similar and were directly reflected by the potential ratio calculated on the same basis as above. The ratios indicated the differently loaded digesters were operating at efficiency equal to the lowest loading.

The gas ratios were also reflected by the potential change between the potential before feeding and the maximum positive level. The changes were 60, 56 and 24 mv for the three digesters respectively. These yielded ratios of 2.29 and 2.5 to one for Digesters one and two compared to Digester three. These results were similar to the ratios based on the recovery potentials which reflected the lower efficiency of the more heavily loaded digesters.

The linear portion of the potential recovery curve was also evaluated for indications of the digester operation. The duration of this straight line zone and the corresponding potential levels are given in Table VIII.

The slope ratio indicated a possible relationship to the different feeding levels of three times as much for Digester one and two than for three. The potential change ratio indicated only that the loading was different.

TABLE VIII

POTENTIAL-TIME RELATIONSHIP DURING THE LINEAR POTENTIAL DROP

Dig.	Time (Hours)			Potential (E_c) (mv)			Slope (mv/hr.)	Slope Ratio	Pot. Change Ratio
	Begin	End	Diff.	Begin	End	Diff.			
1	253	313	60	-452	-495	-43	-0.725	2.75	2.15
2	271	334	63	-441	-494	-53	-0.831	3.14	2.65
3	224	300	76	-507	-527	-20	-0.264	1.0	1.0

The carbon dioxide of the gas was determined at several points in the experiment. The samples tested were taken from the gas holders after a certain amount had accumulated. By calculation an average carbon dioxide content of the gas was determined for the accumulation period. Although certain assumptions were used for the calculations, it was felt that the resulting values would yield a fairly representative picture of the situation. These results are given in Table IX as the average for a definite time interval.

The cause of the failure condition indicated by the pH, carbon dioxide production and sharp drop in the gas production was due to overloading the digesters by feeding. In order to determine if the potential gave an indication of this digestion failure, a time of failure needed to be defined. The low pH at 148 hours possibly indicated an impending failure condition. By use of the gas production as the basis, the time of the digestion failure occurred near 170 hours. The actual time of the failure must have been before the drop in the gas production. This was based on the work of Morgan(26) who found that a sudden drop in gas production followed a sudden rise of the volatile acids to 1000 ppm. He defined failure as the time the volatile acids reached 1000 ppm for two days or more since it was found that the drop in gas production and a further rise in volatile acids followed.

TABLE IX

AVERAGE CARBON DIOXIDE CONCENTRATIONS FOR VARIOUS TIME INTERVALS

Time Interval (hours)	Calculated Average CO_2 in Gas (percent)		
	Digester 1	Digester 2	Digester 3
144-178	57.9	56.7	35.8
178-219	66.2	62.2	47.3
219-246	57.9	72.5	39.0
246-299	43.3	51.0	27.5
299-340	29.7	38.8	27.0
340-399	26.2	29.0	22.5
399-420	26.2	----	----

A volatile acid determination on Digester two at 148 hours yielded 1900 ppm as acetic acid. If the definition of failure as defined by Morgan were used, there would be a lag of about two days to reach this acid content, or to reach the drop in gas production. This would place the time of failure between 100 and 120 hours.

The potential changes after feed three at 96 hours exhibited possible indications of the failure. In normal digestion the potential exhibited a rise due to the feed followed by a drop toward the prefeed potential and then remained essentially constant. It had been thought that an abnormal feed condition would result in some deviation from this normal procedure. Digester one after this feed did not change but Digester two rose, fell and then rose again. The second rise by Digester two possibly indicated an abnormal condition.

However, the potential for Digester two did not exhibit this second rise after feed four at 107 hours. The potential of Digester one was displaced by the feed to a more positive level which then dropped slightly and then rose by six mv.

Feed five at 120 hours was followed by feed six at 125 hours. During the five hour period the potential level rose but no definite trends were apparent. Feed six produced a very large secondary rise in the potential for Digester one. Digester two also rose but not as much. The difference between the maximum and minimum potential during the 21 hour period after the feed was 16 and nine mv for Digesters one and two respectively and the potentials were at -455 and -456 mv.

The type of potential curve after feed six at 125 hours in conjunction with the potential level reached appeared to be the best indication of the digestion failure. This time was near the previously assumed failure time range of 100 to 120 hours. Although Digester two after feed three exhibited an abnormal curve and Digester one after feed four did likewise, a time was sought when both digesters would react abnormally since their feeding loads were identical and the failure times were the same. The continued rising potential after the eighth feed at 148 hours could also have indicated the impending failure.

It was of interest to note the maximum positive potentials were -441 mv at 190 hours and -432 at 198 hours for Digesters one and two respectively. These relatively positive potential levels were not reached in any other digestion experiment.

Since other analytical data beside the potential and gas measurements were not taken regularly due to the experimental objectives, the time of failure was not definitely known. The potential measurements did not definitely indicate the failure time. But the results were sufficiently promising to indicate that the oxidation-reduction potential could be a valuable tool for process control in sludge digestion.

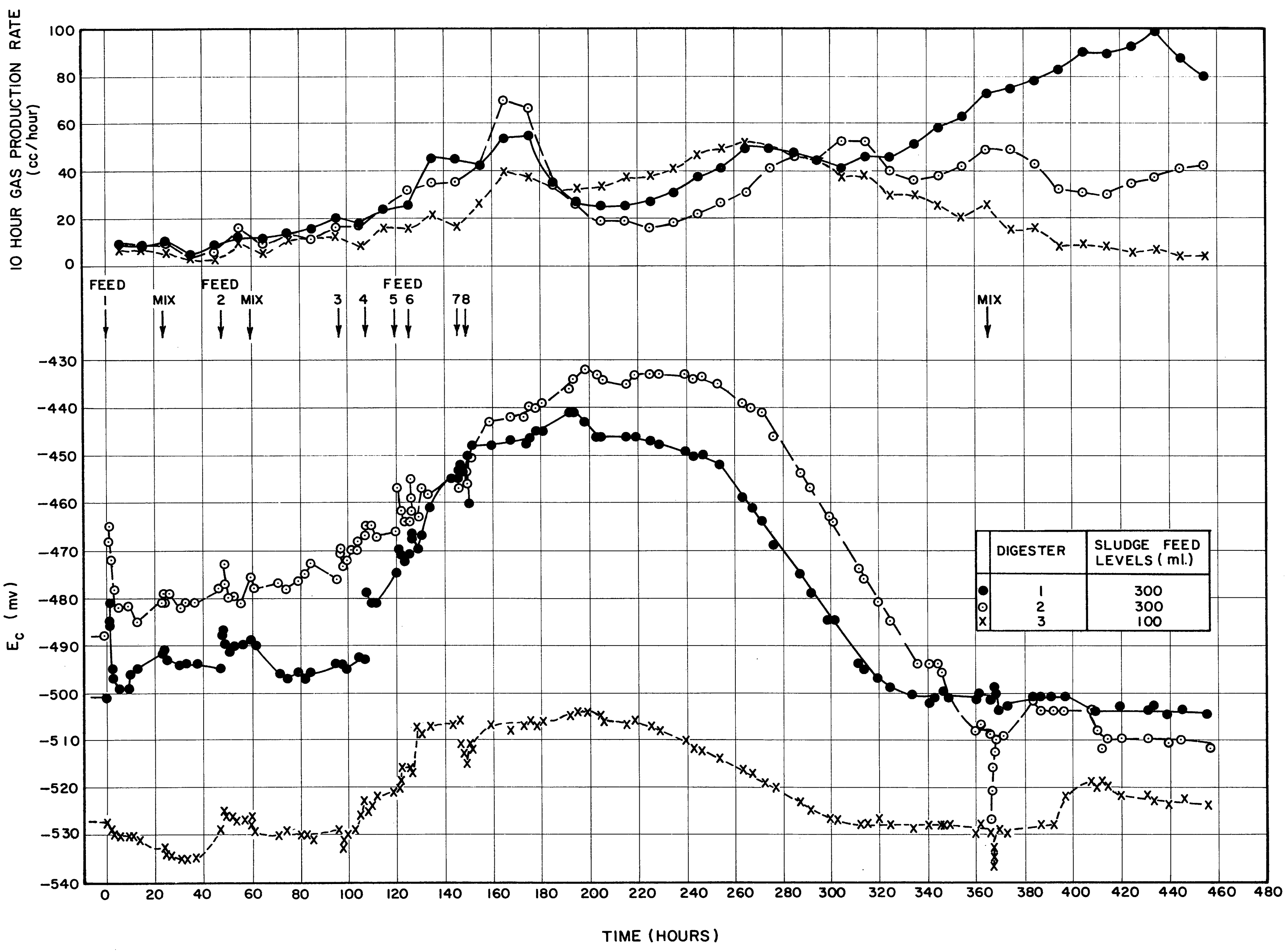


Figure 25. Electrode Potentials and Rates of Gas Production Resulting from Overloading a Digester

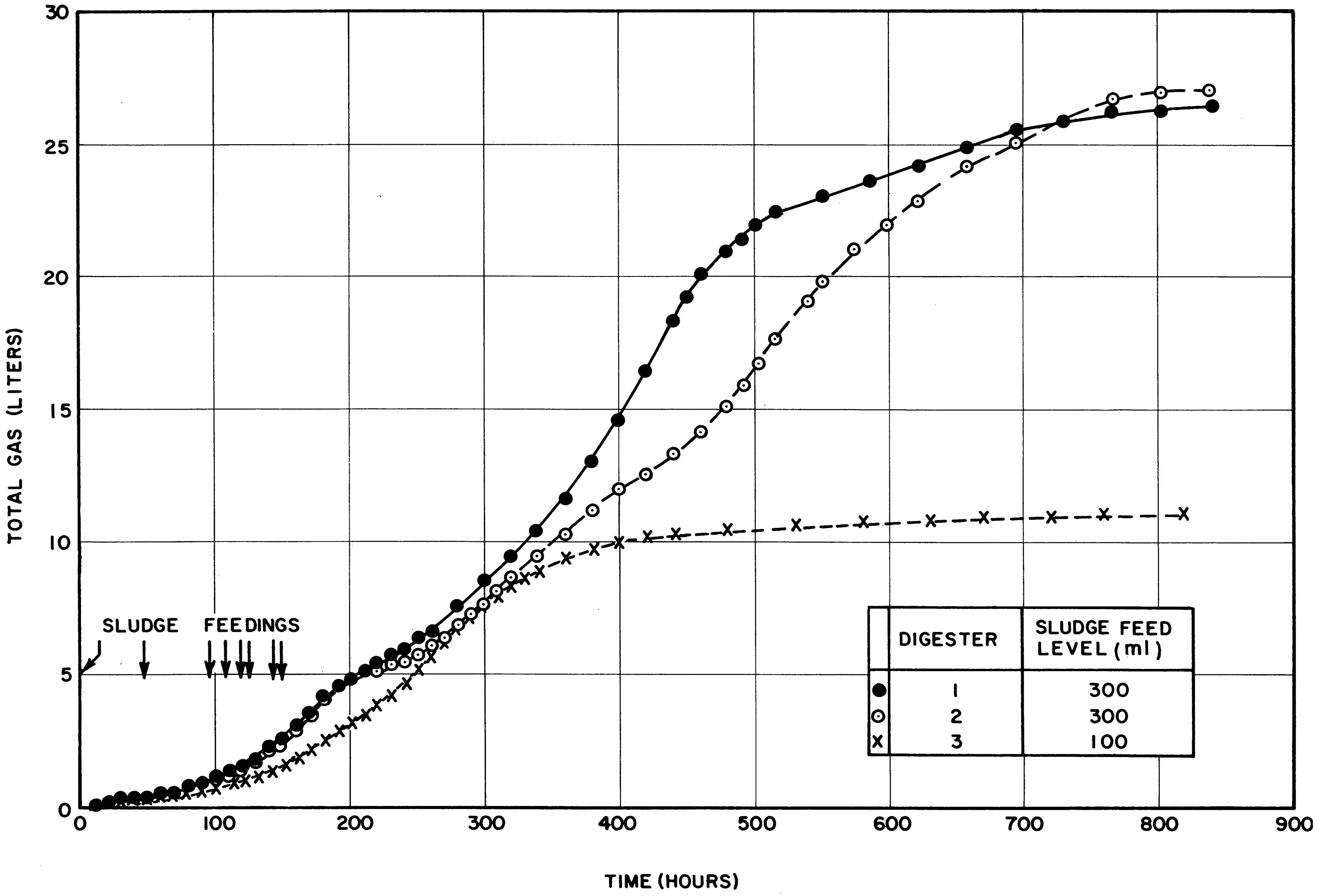


Figure 26. Total Gas Production Resulting From Overloading a Digester

THE EFFECT OF AGITATION ON THE ELECTRODE POTENTIAL

Agitation of the solution in which oxidation-reduction electrodes were immersed introduced a new variable due to the effect of the agitation on the potential measurement. French and Kahlenberg(17) found that stirring resulted in potential changes in a potassium chloride-gas solution. They concluded that this was due to a condensation film on the electrode surface. They also stated that the film was a variable quantity and was affected by stirring, dirt on the surface, etc. This reference was the only one found to present quantitative data on the agitation effect.

Continuous agitation of the digester during the first set of feedings resulted in some erratic electrode behavior. Potential trends could be detected but the electrode agreement was not always good. In an attempt to improve the condition, the continuous agitation was stopped. This proved very successful.

Although it did not completely eliminate all erratic behavior, the electrodes in an individual digester showed excellent agreement. This effect was a little surprising since it was thought that the stirring would give more accurate and rapidly responding electrodes due to mass transfer effects as had been found by various authors. Moore, Rucchoft and Wattie(96) noted more divergence in electrode readings in E. coli sewage cultures when quiescent than when agitated. They felt this was due to stratification and possible poisoning of the electrode. Ward(66) used intermittent agitation in order to get better agreement of duplicate electrodes in a synthetic culture media since stratification caused different readings. However, the agreement between different synthetic broths was not as good and when the stirring was put on or off, a potential fall resulted in some and a potential rise in others. It should be added that agitation in bacteriological and biochemical experiments was almost always done by the passage of nitrogen gas through the solution and not by mechanical means.

The reason for the adverse effect of agitation found in this research in contrast to the above authors was probably due to the type and degree of agitation used. The method used in this research involved movement of a heavy sludge and therefore, a more violent type of agitation was needed. The movement of sludge solids in the digester could have provided more than a simple stirring effect due to impingement on the electrode surface.

Because of the improved condition resulting from the cessation of agitation, it was decided to use agitation only as a mixing device during the feeding sequence. Therefore, the effect of this agitation on the potential was investigated in order to attempt to differentiate the potential changes produced by the feed and the mixing. The sludge solution was periodically agitated in order to investigate this effect on the gold and platinum electrodes. The agitation was usually done at a time when the effects of the previous feeding would not be a complicating factor. The usual potential trend was in the negative direction but the magnitude of the change was not consistent. Certain of these agitation periods will be presented to illustrate some of the general characteristics since no previous quantitative data has been published for any bacteriological or biochemical systems.

The test shown in Figure 27 was done in two stages. The first part consisted of a 23 hour agitation period in order to investigate the long term effect. Three days later the second part was done with an agitation period of five hours in order to check the reproducibility of the agitation effect on a shorter time basis.

The results indicated that a rapid negative trend developed when the sludge was agitated. The potential then became more positive reaching an approximately constant level which was more negative than the premix potential. The time of the beginning of the constant period ranged from two to twelve hours depending on the electrode. In Figure 28 this occurred near ten hours.

The cessation of the agitation yielded a rising potential towards the premix potential level. The time duration of this change was a variable depending on the electrode, the length of agitation, and the potential difference between the premix potential and the potential when the agitation is stopped. The first stage required about 20 hours while the second never did quite reach the premix potential. A difference of five mv was important in determining the time necessary to reach the premix potential and this made the time estimation difficult in many cases. However, the curves did illustrate that a certain degree of reproducibility was possible and the effect of agitation was mainly transitory and not permanent.

The initial period of the agitation test described above is shown more clearly in Fiugre 28. In addition another test which was done with these electrodes at a later time is also included in this graph. This latter test produced good electrode agreement and a lack of erratic electrode behavior. The beginning of the five hour mixing was more representative of the many agitation tests with the exception of erratic electrode behavior. This was shown in the initial stage of the 23 hour mixing. However, all did indicate the usual negative potential trend when agitation was begun.

The tests described above were done with the same three gold electrodes. There were many other attempts to establish the potential pattern resulting from agitation with both gold and platinum electrodes. The results were not always as favorable as the above tests and it became apparent that there was no way to definitely predict the potential behavior. However, certain generalizations could be made concerning the electrode behavior.

The direction of the potential change was mainly toward the more negative potential. There were instances of positive changes as well as no change at all. The reasons for these differences were obscured as the experimental conditions were often similar. The activity of the solution did not appear to bear any relationship to the direction and magnitude of the change.

The negative potential trend due to agitation was found by others. Boyd and Reed(14) using sterile beef broth as the media stated that this was the result using gas stirring. Lepper and Martin(57) found that when a cooked meat media was stirred, a sudden drop of 50 mv was produced. The media took several hours to recover its original potential.

The quantitative evaluation of the potential change was not possible since the direction and magnitude of the change varied. If the negative changes within the first ten minutes of agitation were considered, the range covered zero to twenty mv excluding any sudden or erratic potential changes. The positive changes were in a smaller range of zero to ten mv. From these results it could possibly be concluded that the best prediction of the potential change upon agitation would be five to ten mv in the negative direction. It must be stressed that this range represented a semi-quantitative estimation with a good possibility of being violated.

Gold seemed to have more tendency to sudden large changes than did platinum. However, both metals did exhibit this phenomenon. The magnitude of the change tended to be larger for gold although the differences were often not appreciable. Some gold electrodes showed little change and some large changes. This applied also to platinum. All in all the agreement between the gold electrodes was usually as good as the platinum electrode agreement and the agreement of the gold and platinum electrodes. The variability that existed in each electrode pointed out the necessity of using more than one electrode in experiments in which potential measurements are taken.

The main object of these tests was to differentiate the potential changes produced by the feeding and by agitation. On a qualitative basis, the direction of the potential change was positive for the feeding and usually negative for the agitation. Thus, the potential changes would tend to counteract each other. The quantitative evaluation of the net effect was not found to be possible as both the feeding and agitation gave variable results.

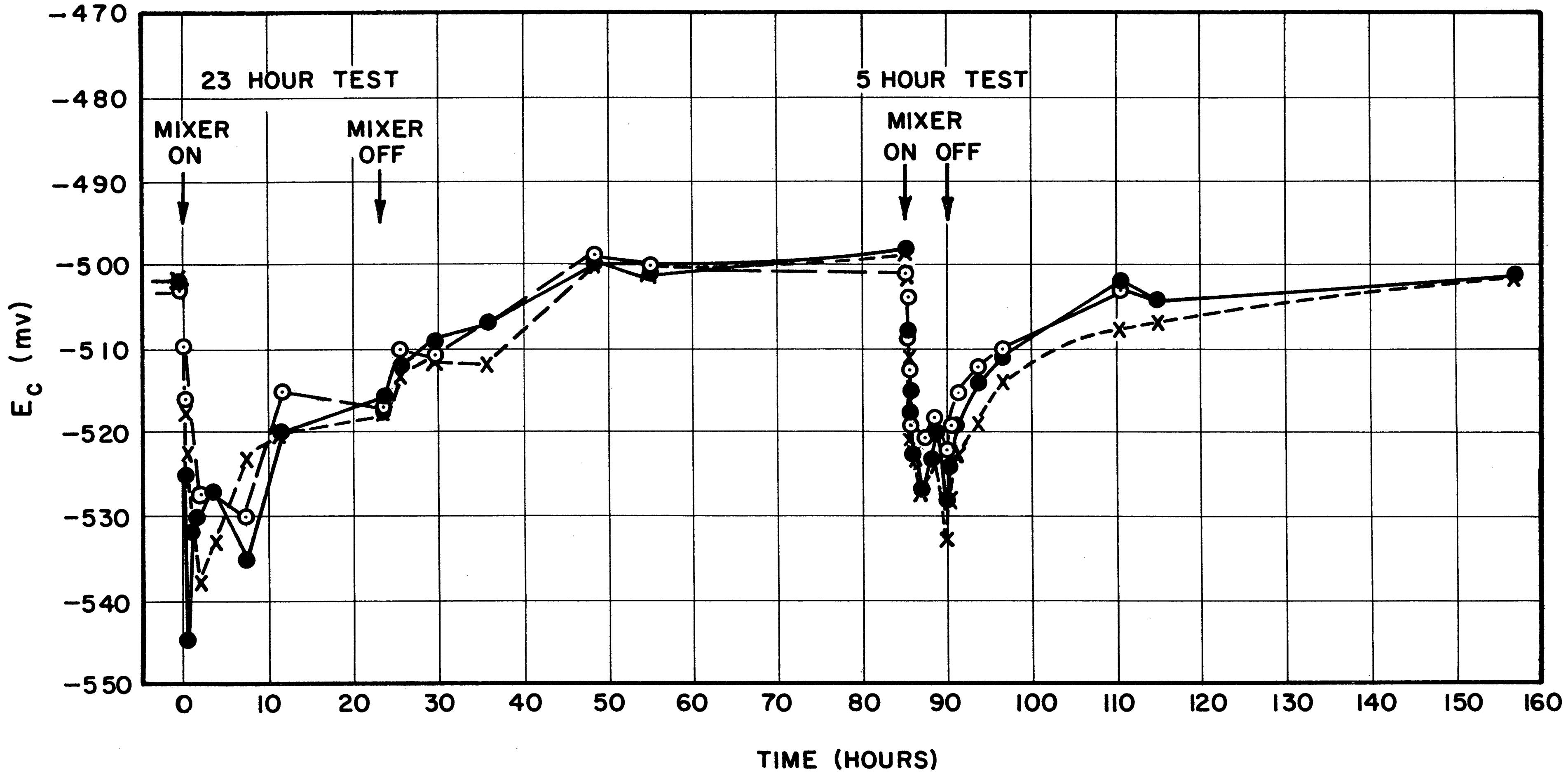


Figure 27. Effect of Agitation on the Potential of Gold Electrodes

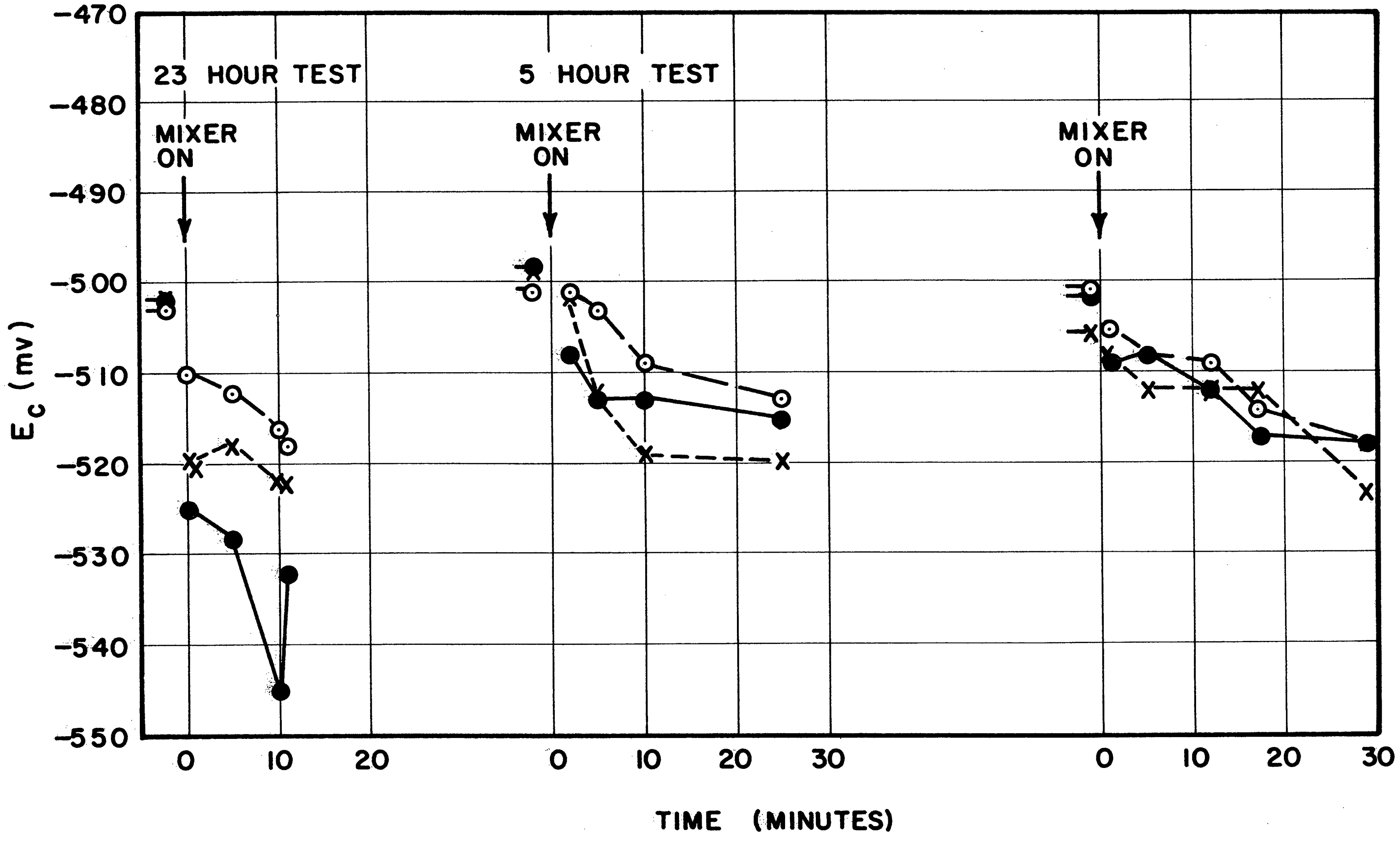


Figure 28. The Initial Effect of Agitation on the Potential of Gold Electrodes.

DISCUSSION

Although the indicating electrode provides the only difference in the components used to measure the redox potential and the pH, it is, however, this element which is responsible for the need of different considerations in the application and evaluation of either determination in a biological mixture such as digesting sludge. This sludge is a complex, heterogeneous mixture involving many bacterial and enzymatic systems, some of which contain oxidation-reduction reactions. These include reversible, semi-reversible or irreversible reactions.

The glass pH electrode is inert in this mixture and only indicates the hydrogen ion concentration. In contrast to this, the metal redox electrode cannot be considered as an inert indicator and the system or systems responsible for the potential are not known. These characteristics of the potential determination result in a situation whereby the measuring and measured systems are imperfectly understood due to their complex nature. Thus, interpretation of the data can become somewhat speculative since evaluation can be difficult even when the characteristics of either the measuring or measured system are known.

Although an equation exists to aid in the evaluation of the potential, the development of this basic oxidation-reduction equation relating the concentration of the oxidized and reduced components in a quantitative manner is based on reversible systems for which the equation for the reaction is known. Unfortunately, a digesting sludge cannot meet these requirements and the equation, therefore, can only be applied in a qualitative or semi-quantitative manner.

Although a simple, direct explanation cannot always be given for the electrode potential changes that occurred in the sludge, these potential measurements can still be of considerable value. They can now, as in the past, contribute towards an improved knowledge of the biological processes and provide an analytical device for better plant control. Although this research involves two imperfectly understood systems, digesting sludge and electrode potentials, it is felt that the results will aid in the further understanding of each.

There are two methods by which the oxidation-reduction potential of digesting sludge can be determined. The first consists of an individual measurement on a sludge withdrawn from the digester. This is similar to most analytical tests such as the volatile acid test in which a single spot value is obtained from a sludge sample. If the electrode is allowed to remain in the digesting sludge, a series of potential values can be obtained which would provide a continuous indicator of the digestion process. This second technique would add to the existing methods of continuously following the digestion such as the measurement of the gas production and composition. It should be noted that these tests plus the pH are the only methods of continuously following the digestion process in situ. Therefore, the addition of the electrode potential to this list is a valuable goal.

The single potential measurement can be done on the sludge sample withdrawn by the sewage treatment plant operator for tests such as volatile solids. Since the required experimental apparatus is similar to that used for pH measurements, facilities would be available for most sewage plants to utilize the potential measurement in control operations and to add this technique to the analytical tests commonly done for digester operation.

There are, however, certain precautions to follow when using this technique. The previous investigators who have published data on sludge potential values (88)(98) apparently were not conscious of these precautions since their recommended procedure and resulting potentials were found to be erroneous. This was due to the two factors that are of prime importance in this measurement--the time for the electrode to reach equilibrium and the condition of the metal electrode.

It was found in this work that the adjustment period, or time necessary for the electrode to reach equilibrium with the sludge potential, was a variable factor. However, it was much longer than the previously recommended period of 30 minutes. Under quiescent conditions the adjustment period ranged from ten to fifty hours depending on the condition of the sludge and the electrode. Since this time would not have been conducive to field measurements and rapid process control, several methods were considered which would reduce this time interval.

Agitation of the sample was successful in reducing the required time to near four hours. However, erratic electrode behavior proved to be a disadvantage. To combat this, mild agitation was tried but, as would be expected, the necessary time increased. Although the overall adjustment time was decreased by stirring, it was found that the initial phase of the adjustment was not appreciably changed.

The general form that an electrode followed when inserted in a sludge consisted of a rapid initial drop in potential followed by a decreasing rate of change. As the electrode approached equilibrium, the slope became smaller and thereby created long adjustment periods as seen in Figure 9. It was this latter phase that agitation aided by increasing the potential-time slope. The initial slope during the first 30 minutes was not appreciably affected. Since the sludge was agitated quite vigorously, it was felt that this extreme condition reliably defined the extent of the agitation effect.

When utilizing agitation as an aid in the adjustment, there must be no accessibility to air or the results would be affected as shown in Figure 10. The investigator should be aware that merely placing a rubber stopper in a sampling container would still allow contact with the air gap between the level of the sample and the stopper. Therefore, the sludge level should be in contact with the stopper such as was done in the dissolved oxygen test.

If the test was done under quiescent conditions, no special precautions were necessary for possible oxygen interference. The results of this research indicated that the test could be done in an open beaker with the electrodes about three inches below the surface. It appeared as if the sludge surface provided a buffer against the entrance of air.

The next attempt in reducing the adjustment time consisted of conditioning the electrodes in the sludge to be tested. The results were encouraging although the adjustment was sensitive to the time that the electrode was exposed to the air before reinsertion into the sludge. It appeared that part of the residual effect of the conditioning was lost rapidly.

This led to the use of a solution with a more negative potential than the sludge for conditioning the electrode. Although the work done was very limited, it appeared that this technique could provide a method of measuring the potential within a 30 minute period. It was felt that further work on this technique would be a very valuable contribution to the use of potential measurements in the sludge digestion process. The use of a conditioned electrode was opposed to the standard practice of cleaning the electrode surface by methods ranging from a water rinse to soaking in aqua regia. Since the condition of the electrode affected the adjustment period and cleaning affected the electrode condition, the method of cleaning the metal became of great concern.

An extensive literature survey revealed that there were many diverse opinions on which cleaning method was best. However, the effect on the adjustment period was not a factor in the selection. As a result, the literature survey was broadened in an attempt to evaluate the effect on the surface of the different cleaning agents as acids, oxidizing agents, heat, electrolysis, and abrasives. It was found that all the cleaning agents affected the metal surface and reproducibility of a surface was practically impossible by these techniques.

Experimentally, it was found that hot nitric acid yielded very variable results while rubbing with a wet cheesecloth proved to be a better method. It was interesting to note that nitric acid was used in the work that had been published on sludge potentials. Thus, in additon to the erroneous time interval used, their results were probably also influenced by the cleaning technique.

Whether or not this was responsible for a wide potential range (98) given for a digesting sludge potential was not known. But the figures were possibly significant. In describing the improvement of digestion by the addition of sulfate, the potential (E_h) range changed from zero to -100 mv to a range of -125 to -170 mv. Thus, the potential change ranged from 25 to 170 mv, a sevenfold difference. The experience in this research indicated that these values much be regarded as more qualitative than quantitative.

Although nitric cleaning has been used successfully by various investigators, the solutions tested were not digested sludge. The reason that this technique yielded variable results in sludge was believed to be due to the nature of the solution. Digested sludge was already an anaerobic biological solution and the conditions of testing were quite different from inserting electrodes into an aerobic broth. Thus, when inserted into sludge after a nitric acid cleaning, the electrode surface containing an oxidizing agent had to have the oxidizing condition of the surface reduced before the electrode could record the sludge potential. Since digested sludge did not exhibit the tremendous ability of E. coli to produce reducing conditions rapidly in a sugar broth, the residual effect on the surface due to cleaning had to be considered important.

The previous investigators of sludge potentials (98) in referring to the results obtained by taking measurements every few minutes and plotting them as a time-potential curve stated: "This slope will then be a measure of the dynamic character of the subject ...." By following their procedure, it has been found that this conclusion was completely erroneous. Apparently identical electrodes would yield different slopes and an active sludge could appear to be more sluggish than a less active sludge. The concept of indicating the dynamics of a system by a potential-time curve was not new, but any approach to make it a realization must be concentrated on the electrode itself since the condition of the electrode was often more important than the actual dynamics of the sludge.

The use of the potential to indicate other characteristics of the sludge beside the absolute potential would be a valuable goal. The absolute potential is a measure of the environment, but the adjustment period could indicate the capacity as well as the metabolic activity level of the sludge.

No test exists for measuring the activity level of a sludge. All analytical determinations simply measure the state of the sludge at one point. Methylene blue, an oxidation-reduction dye, is used to indicate the dynamics of more aerobic solutions. This dye has been applied to the sewage field as the relative stability test and is described in Standard Methods(114). The extension of this dye technique to sludge would not be feasible due to color interference from the sludge. Separation and clarification to produce the supernatant would not give a true picture of the situation. Thus, the metal electrode is the only method of obtaining these results by potential measurements.

In order to achieve this goal, some method must be used to provide reproducibility of the electrode surface so that the reference or starting potential will always be the same. In addition, it would be desirable to have the surface in an oxidative state. This has been done successfully for preparing electrodes for anodic oxidations(131)(132). After finding that the surface could not be reproduced by ordinary cleaning techinques, the electrodes were allowed to soak in a buffered solution of potassium permangenate to create a "controlled oxygen electrode." If this or a similar conditioning were applied to the electrode, an extensive testing program in establishing this technique could well contribute a reliable method of determining the metabolic activity level and capacity of a digesting sludge.

In order to follow the potential changes in a digesting sludge, the electrodes were allowed to remain in the sludge for long time intervals. It would have been impossible to detect rapid potential changes by the withdrawal of sludge samples and single potential determinations. This continued immersion of the electrodes in the sludge would also allow the measurements to be taken in situ which was advantageous for biological systems.

However, no previous experience existed on the long-time immersion of electrodes since no continuously-fed biological systems have been investigated utilizing this measuring technique. The longest that an electrode had been immersed was for about 20 days in an inoculated bacterial culture with apparently successful results(112).

The experimental results indicated that very long time periods did not affect the electrode behavior. Although this was contrary to the standard practice of cleaning the electrode to insure that the metal surface was not poisoned, this recommended procedure was not based on work in a digested sludge media. The insertion of new electrodes into the sludge at various times was done to determine if their behavior would differ from the electrodes immersed for several months. In addition the electrodes were removed from the sludge and reinserted after exposing the metal to air or rinsing the surface with distilled water. All tests indicated the electrodes were not adversely affected by the lengthy immersion period which extended up to six months.

The ability of the electrode to remain unaffected by the sludge was a very important result. This made it possible to follow the potential changes resulting from feeding the digesters without complications arising from the electrode adjustment. Thus, the potential can be added to those tests that can be used to provide a continuous record of the digestion.

The first use of continuously immersed electrodes was in following the potential changes resulting from feeding a lactose broth concentrate to a digested sludge. Since there were successive additions of the broth to the same media, this marked the first attempt of tracing the potential changes in a continuously fed, anaerobic, biological system. The work that has been published has been concerned only with batch bacterial growths. It is interesting that the feedings in this experiment could be classified as both batch and continuous because of the usual few days lapse between feedings and the rapid potential changes. Thus, the discussion of the data could be based on the results of a single feed or the overall results of the successive feeds.

The feedings of the lactose broth concentrate, a lactose-peptone-beef extract mixture, yielded a wide potential range of -405 to -560 mv during the series of feedings. This was a much wider range than shown by raw sludge feeds. The potential changes were also much more rapid as would be expected from a sugar-rich feed. In addition the potential changes correlated well with the gas production after a feeding. If a distinct lag occurred in the gas, the potential also exhibited a lag before reaching its most negative potential. With no lag in the gas production, the potential also reached its maximum negative potential without a lag. The potential became more positive after the gas production started to decrease.

There appeared subsequent potential changes after the gas production had nearly ceased which indicated a non-gaseous oxidation-reduction system was active. The pattern of these changes could be classified as a double reversal. These potential changes differed from the effects due to feeding raw sludge where there were no systematic rises and falls in the potential after gasification had ceased. This was not surprising since the feed composition was markedly different. This indicated that the measuring of gas rates due to a synthetic feed could possibly be misleading if the result was used to predict behavior due to the raw sludge feedings. This was because the potential indicated that the bacterial systems operating in the sludge were not the same. The use of potentials can be applied to check the assumption that synthetic sewage feeds act similarly to natural feeds.

The characteristic potential level of this system was difficult to determine due to the wide variation. However, it could be approximated at -440 to -470 mv or an E_h of -194 to -224 mv. The potential level did not seem to affect the behavior of an electrode. If one of the electrodes was at a different level than the others, the changes were still identical. This would seem to indicate that for this system the potential changes of the electrodes were relatively independent of the absolute potential within a certain potential range.

The raw sludge feedings did not yield rapid and relatively large potential changes as did the lactose-peptone-beef extract mixture discussed above. This was primarily due to the characteristics of the digesting sludge which acted like a solution with a high capacity to resist change. In addition, the metabolic breakdown of the complex materials in the raw sludge appeared to be slower than the utilization of the sugar in the synthetic feed.

Another very important factor concerns the highly anaerobic condition and potential of the sludge before the feeding. Batch type bacterial systems which have been widely investigated are relatively aerobic before inoculation and as a result, very large potential changes occur because of the natural tendency of the bacteria to create reducing conditions. However, the highly negative potential of sludge eliminated this initial large change and subsequently, the magnitude of the change was not great. Perhaps this is one of the reasons why potential measurements have not been applied to following the changes in a digesting sludge.

One of the more extreme examples of a small potential change resulting from feeding was found in a batch type feed where the maximum potential change during most of the gasification period was about ten mv. The electrodes yielded very consistent behavior and the average of the three electrodes in the digester was not difficult to determine. Electrode behavior often was not as consistent as in this case and the determination of an average representative potential became a very difficult task. Critical situations occurred where potential differences of less than five mv would alter the picture of the potential trend. In these situations the experience and judgment of the experimenter were a very vital factor.

Agreement of three electrodes within two mv was considered excellent, five mv good, and ten mv more the usual case. However, for averaging electrode values the agreement of the electrodes was not as important a factor as the consistency of the potential change of each electrode since a slight error in the potential level was not significant. But, the path of the potential change was very important. Part of the difficulty in determining the average potential was due to the impossibility of determining the potential over 24 hour periods during runs of which some extended over 800 hours. The solution to this would be a recording potentiometer which would record a continuous set of readings and detect changes that could occur while the experimenter was not present.

Another aid for increased accuracy in the potential measurement would be more than three electrodes in a digester if a recording potentiometer was not available. Frequent readings would reduce the recommended number to three since potential patterns could be evaluated accurately even with some erratic electrode behavior. It was found that three electrodes were not always adequate and it was felt that any decrease in this number would greatly affect the accuracy of the potential evaluation. From the results of this research it cannot be stressed too much that the use of a single electrode can very easily yield erroneous potential values and should never be relied on.

Agitation has been used as a means of increasing the electrode agreement. Attempts were made at first to use continuous agitation but erratic electrode behavior made it necessary to abandon this procedure. Improvement of the electrode behavior resulted from this although other workers had found stratification caused diverse readings. Settling in the digesters did not cause differences even when the electrodes were in the supernatant layer. There appeared to be no potential difference between the sludge and supernatant layer. This was possibly due to the "in situ" laboratory arrangement.

In addition to the electrode agreement within one digester, the potential agreement among different digesters under identical conditions was also a very important consideration. The simultaneous use of three digesters treated identically made it possible to find the degree of reproducibility that could be expected as well as the agreement between different digesters so that different feeding levels could be reliably evaluated. The results indicated that the potential behavior was not identical, but often similar for the same feeding levels. The batch feeding shown in Figure 21 exhibited excellent potential similarity and indicated that close agreement between samples was possible. However, in a biological system as complex as sludge there always existed a certain amount of divergence between identical samples. In addition the possible variability of the electrodes was also a factor especially when the potential changes were not large.

During the parallel feeding experiments it became apparent that low feeding levels to a normally digesting sludge would result in small potential changes and fairly constant potential levels. This would be expected for equilibrium conditions. On this basis further experimental work with non-parallel feedings was done when the sludge was not as capable of resisting potential changes. In this manner it would be possible to accentuate potential changes to aid in both the evaluation of the data and the potential comparison with the gas production.

The ability of electrode potentials to indicate the uniformity of the digestion was similar to the conclusions of Kaplovsky(43) who found that volatile acids were the least affected from day to day of all the analyses. He stated that with constant loadings, volatile acids should be fairly constant and that a constant level of acid accumulation was a good indicator of digestion uniformity.

Relationships were sought in the non-parallel feeding studies between the potential change, feeding level, and gas production. The short period after feeding yielded some instances where the difference in feeding level was reflected by the potential. However, much better results were obtained by using the potential changes after feeding was discontinued in batch-type experiments involving several successive feedings. This behavioral pattern was similar to that of the gas production which did not differentiate the different quantities of feed until the ultimate production was reached as shown in Figure 23. In this experiment the feeding rations of 3/1, 1/1 and 2/1 for Digesters one, two and three respectively corresponded to the same ratios based on total gas production. In addition the change in the potential from the minimum negative value to the first point where all three digesters exhibited constant potentials also corresponded to these ratios.

Another experiment with feeding ratios of 3/1, 3/1, and 1/1 for Digesters one, two and three only yielded gas production ratios of 2.5/1, 2.5/1 and 1/1 for the same digesters (Figure 26). This indicated that the efficiency of the digestion was somewhat less at the higher loading level. The results of the potential change were very significant as they reflected the gas production, not the feeding level, and thus indicated a reduced digestion efficiency. Although the calculation of the potential change ratios could be somewhat arbitrary due to the small change of the lightest loaded digester, the results were still of considerable value in evaluating digester operation.

From the gas production curves, gas rates were calculated to investigate the relationship of the changes in the gas rate and the potential. Since the gas rate was an indicator of the sludge activity, the comparison would indicate to what extent potentials reflect this activity.

Under conditions simulating a batch experiment where rapid changes are characteristic, variations in the potential and gas rate could be related.

However, in continuous digestion it was possible to have the gas rate constant and the potential changing and when the feeding was stopped, the gas rate changed while the potential remained constant.

This latter condition would indicate that the environment was not changing but the metabolic activity was. Thus, the potential measured changes in the environment, and the gas rates were an indication of the activity. From this, it appeared that the use of continuous potential measurements alone would not yield a clear picture of the digestion.

From the results of this research it has been found that a single potential determination of a sample of sludge would not be of much value unless the potential was outside the range of about -460 to -540 mv or a corresponding E_h of -220 to -300 mv. The range was determined from the potential values of normally digesting sludge in the laboratory digesters. Below this minimum negative value the sludge did not appear to be digesting normally. This was not an attempt to say that a potential more positive than -460 mv indicated the sludge was approaching failure. However, when sludges freshly drawn from plant digesters exhibited potentials near -460 mv, the sludges also had high volatile solid contents that were not indicative of a well digested sludge.

After any series of feedings was terminated, the potential returned to a constant value. During this period the last stages of gasification occurred. This potential was felt to be the most indicative of a ripe digested sludge. The most representative of these values was about -500 mv or an E_h of -260 mv. But it must be cautioned that a value of -500 mv was exhibited by sludges during active gasification and this value could not be used to state that the sludge was in a ripe stage.

The Eh potential range of -220 to -300 mv did not agree with that stated by Hood(88) of -100 to -200 mv for optimum digestion. The reason for this discrepancy was felt to be due to the method of determining the potential which was discussed previously and shown to be erroneous. It was of interest to note that the -100 to -200 mv range has been included as a standard in the sewage treatment text by Babbitt(1). It was encouraging, however, that the oxidation-reduction potential was included as an analytical test for the sewage field.

Another very important phase of the study was concerned with the potential changes starting immediately after the feeding. Because of the ability of the electrodes to remain immersed in the sludge, it was possible in this work to follow continuously the conditions resulting from the feed. This type of potential response could provide a valuable contribution to sludge digestion control if it was possible to determine the ability of a digesting sludge to absorb a feed without deleterious results. This possibility was based on the concept that when a more aerobic solution was added to a less aerobic solution, the resulting mixture would yield a potential dependent on the original solutions. The quantities of each solution, their capacity and poising power would determine this final potential which would be between the limits of each individual potential.

The effect of oxygen on the sludge potential was an excellent example of adding an oxidant to a more reducing solution. This was shown in Figure 10. The degree of mixing and oxygen diffusion was reflected in the potential rise which illustrated the possible effect of different feed levels to the digester. The sludge was able to overcome the immediate rapid potential rise and return the potential to the premix value.

Additions of oxidants to anaerobic solutions has been done by others. Using oxygen in nitrogen gas it was found that a reversal of the negative potential trend was caused by a two percent oxygen content, temporary checking at 1.4 percent and a very slight effect at 0.1 percent(76). A fixed amount of air added to a peptone broth containing 0.01 percent sodium thioglycollate caused the potential to rise rapidly and continue to drift in a positive direction whereas at a 0.1 percent concentration of the reducing agent the potential rose about 45 mv followed by a return to the original potential in about three hours(78). Clark et al.(49) stated that the action of small doses of oxidants would produce temporary checks or reversals on a time-potential curve followed by a very decided recovery of the negative drift.

Thus, it would be anticipated that the raw sludge feed would cause a temporary positive trend followed by a slower negative recovery to the original potential of the solution. Also, the larger the quantity fed, the longer the recovery would be prolonged. It might be possible that for a feed too large for the capacity of the sludge, the negative recovery would be retarded or eliminated as was the case with high concentrations of oxygen as observed by others. This could indicate a failure condition of the digestion.

The initial effect of feeding was toward a more positive potential. However, the addition of raw sludge did not consistently produce the rapid rise and recovery of the potential described above. Some examples of the the potential becoming more positive after feeding and then returning towards the more negative prefeed potential were seen in Figure 19.

In addition to the sludge feeding the potentials were also influenced by agitation of the digester contents. Thus the effect of agitation on the potential had to be determined since it was necessary to mix the digesters after feeding in order to blend the raw sludge with the digesting sludge. Intermittent mixing was necessitated by the erratic behavior of the electrodes resulting from continuous agitation. Separate agitation tests were attempted to evaluate this effect quantitatively but this was not successful. The potential change usually went in a more negative direction. This was a transient effect after which the potential returned to its premix level. The magnitude of this change was not consistent. Thus, mixing of the feed put two opposite forces in action. This masked the effect of feeding upon the potential and no quantitative measure was possible. A different method of agitation might improve this situation and the relative potential could then be accurately compared for different feeding levels.

The largest immediate changes in the potential resulted when the feed was not preheated. This was anticipated by evaluation of the temperature effect on the standard oxidation-reduction equation. Part of this effect was probably due to the metal electrode since during the initial stages of the mixing there still existed a colder mass of sludge due to the feed. The temperature of the digester sludge on an overall basis was lowered very slightly.

Large feed quantities usually caused greater immediate changes than the lower amounts. However, the results were not always consistent possibly due to the effect of agitation. In addition equal feeds could also give different responses which falsely indicated unequal loadings.

Constant loadings to an actively digesting sludge should result in a fairly constant potential level. The trend to a more positive potential due to the feed was opposed by the capacity of the sludge to resist this change. Since this capacity was not rapidly mobilized, the potential became more positive at first and then returned to the prefeed potential as the reaction of the sludge increased.

If the loading were more than the sludge capacity could handle, it would be anticipated that the potential would rise rapidly after the feed. This would be followed by a drop and a rise in the potential. The second rise would indicate an abnormal condition. On the other hand, after the initial rise the potential could continue to become more positive without any tendency to return to its prefeed potential.

Both of these types of potential responses occurred where overloading conditions were present as shown in Figure 25. Although these results appeared to be indicative of abnormal conditions, the potential changes often were not distinct enough to yield conclusive results after a single feeding. Thus the overall potential trend would be needed to supplement the results of one feed. However, the potential did not appear to be able to detect a failure of the sludge digestion process clearly enough to supplant other tests.

From the results of this research, it was felt that further experimental work along this line could possible establish a definite pattern which would indicate impending failure without the volatile acid test. It was noticed that the carbon dioxide content of the gas increased appreciably before the rapid drop in the gas rate occurred. Since this test could be done on a continuous basis, it would be an excellent supplement to the potential measurements which could also be taken continuously. This would aid in the investigation of the metabolic changes occurring in the critical phases of digestion and give more insight into the entire process.

A rising potential did not necessarily indicate an approaching failure condition. The process of activating a dormant sludge produced a rising potential level after an initial drop to a more negative level. This rising potential reached a maximum and then became more negative again. The trend toward a more positive potential did not indicate an impending failure but was simply a reflection of the activation of the sludge. The most positive potential reached was near -465 mv which fell within the limits previously defined where digestion was still satisfactory.

The first reaction to the feed by the dormant sludge was toward a more negative potential. Since there was practically no gas production during this period, it was felt that the change was due more to the hydrolytic systems than the methane bacterial systems. However, because both systems were probably affecting the potential, the relative effect was impossible to determine. There were various oxidation-reduction reactions in both systems and the study of each phase by potentials would be of great value in evaluating the mechanism. Since the most sensitive part of the process was the production of gas by the methane bacteria, the determination of the potential characteristics of this phase would set the optimum level for sludge digestion and gas production. This would not only aid digestion operation per se, but would also help in the evaluation of the basic factors affecting the process.

A very important part of this study was the comparison of gold and platinum electrodes. Based on experimental work in quinhydrone which indicated gold was more sensitive than platinum and a literature survey which also indicated gold might be a better electrode, gold was selected as the electrode metal. However, since no data was available on the relative value of each metal in digesting sludge, platinum was used in a supplemental manner to provide a comparison.

The immediate response to the raw sludge feeding, as well as the overall potential results during the digestion did not show any significant difference between the two metals. Similarly, the response to digester overloading did not appear to be differentiated. The differences that were exhibited were not beyond the normal variability of the electrodes. The only contrast was provided by agitation of the sludge which caused a greater amount of erratic behavior in the gold electrode although both metals were affected.

Comparison of the gold and platinum electrodes during the adjustment period indicated more dissimilarity than during the digestion experiments. This was especially apparent in fresh plant digester sludge where the average equilibrium potential of the platinum electrodes was more negative. However, on an individual basis a few gold electrodes were more negative than some of the platinum group. The difference between the average potential of each metal was usually within 20 mv.

The platinum electrodes usually required less time to reach the equilibrium potential. The potential of the gold electrodes in a high volatile solids plant sludge exhibited a plateau before reaching the final value. The phenomenon of poising the electrodes temporarily at an intermediate potential was not apparent with platinum. The cause was probably due to a weak oxidation-reduction system which could not be detected by the platinum as was the case in quinhydrone.

Electrode adjustment tests done in the laboratory digesters also indicated that platinum required less time to achieve an equilibrium potential. However, the difference between platinum and gold was less than in the fresh plant digester sludge and agreement between the electrodes was usually within ten mv. The form of the adjustment curve was also similar for the two metals. This improvement in the electrode agreement was apparently due to the characteristics of the sludge since the equilibrium potential was usually independent of the electrode metal.

The most apparent difference between the plant and laboratory sludges was in the degree of digestion. This was based on the volatile solids which indicated that the laboratory sludge was usually more digested. It therefore appeared that the less digested sludges contained substances which caused greater divergence between gold and platinum electrodes. These substances evidently were removed upon further digestion and decreased the effect of the specific metal used as the electrode.

An important factor in the explanation of electrode behavior arose from the gas-metal effect. This was especially significant in digested sludge studies since carbon dioxide, methane and possibly hydrogen were present in the sludge. The electrode metal and, in turn, the potential could be affected by these gases. Another gas, oxygen, was also of interest when the electrode adjustment was studied.

The studies of French and Kahlenberg(17) have shown that when the gas flow was changed from oxygen to hydrogen, the platinum electrode adjusted rapidly while the gold responded slowly. From hydrogen to oxygen, the platinum responded slowly while the gold changed rapidly. This possibly indicated why platinum would adjust to the anaerobic equilibrium potential more rapidly than gold since the oxidative condition of the metal had to be changed to a reduced condition.

Another possibility arose from the fact that platinum was a better catalyst than gold. Thus, the removal of oxygen from the surface would be facilitated yielding a more rapid adjustment of the platinum.

The effect of air on the electrode when immersed in sludge was greater on the platinum than the gold as seen in Figure 10. This did not correspond to the fact that platinum responded slower than gold when the gas was changed from hydrogen to oxygen. However, when the electrodes were removed from the sludge temporarily, platinum was less affected by the air exposure than gold. It was of interest that a 0.25 minute exposure of the platinum made a readjustment necessary. This indicated the effect of oxygen was a definite factor with both metals.

The gas-metal effect could become quite complex and, in addition, could be influenced by the inertness of the metal. Although the complexity of this subject extended beyond the scope of this thesis, it was felt that an adequate understanding of the oxidation-reduction potential would not be possible without some consideration of the gas-metal effect.

The choice of either platinum or gold as the electrode metal has not beem completely resolved by this research. Although their behavior could be very similar, there were instances where large differences occurred. This was especially true for the single potential measurement for which the adjustment period played such an important role. It appeared that the more well digested sludge produced better electrode similarity. However, for digested sludges with high volatile solids, there existed distinct differences. Unfortunately, it was not possible to determine which metal yielded the most representative potential results. It is possible that both metals by their differences could contribute more together than if used separately.

SUMMARY AND CONCLUSIONS

1. Oxidation-reduction potentials are of considerable value in detecting abnormal digestion conditions and in providing a continuous measure of the sludge digestion process which can lead to better process control and to a better understanding of the process itself.
2. The addition of a lactose broth concentrate to digested sludge exhibits different potential behavior than do raw sludge additions. This indicates different bacterial systems are operating and therefore comparison of gas yields from the two types of feeds can be misleading.
3. Additions of raw sludge to a normally digesting sludge will usually result in a potential rise followed by a return to the more negative pre-feed potential. The potential rise is increased by low temperature feeds and decreased by agitation.
4. Under normal digestion conditions the potential will remain fairly constant. A continued positive trend of the potential can be indicative of overloading.
5. The optimum range for sludge digestion was from -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.
6. A single electrode potential reading of a digesting sludge cannot define the degree of digestion if the value is within this potential range. The potential changes are usually more indicative than the absolute potential value for digester operation.

7. The potential change in certain cases reflects the ratios of the ultimate gas production and relative efficiency of differently loaded digesters after feeding is discontinued.
8. The potential changes and gas rate changes are related for batch experiments. For continuous operation where conditions are relatively steady, there is no relationship exhibited. Gas rate changes can take place and not be reflected by a constant potential level indicating that the metabolic activity, but not the environment, is changing.
9. The time for an electrode to reach equilibrium with the sludge potential ranges from 10 to 50 hours under quiescent conditions depending on the condition of the electrode and the sludge. Agitation can reduce this time to four hours with the electrodes often exhibiting a certain amount of erratic behavior. The time can be reduced further by preconditioning the electrode in digested sludge or in a solution more anaerobic than the sludge to be tested.
10. Agitation usually results in a negative trend of the potential which returns towards the premix value when the agitation is stopped.
11. Electrodes immersed for long periods in digesting sludge do not loose their sensitivity.
12. A minimum of three electrodes should be used for any sludge measurement. This is not just important, it is necessary for reliable data.
13. Gold and platinum did not differ significantly during the laboratory digestion studies. Adjustment trials on sludge withdrawn from plant digesters revealed distinct differences which became less as the sludge

became more digested. Platinum usually adjusted more rapidly and was less affected by agitation than gold. Gold appeared more sensitive to weak oxidation-reduction systems. Platinum was more sensitive to oxygen when immersed in the sludge.

APPENDIX A. DERIVATION OF OXIDATION-REDUCTION EQUATION

The basic oxidation-reduction equation relates the oxidative state of the system with the potential. The derivation of Michaelis(16) based on chemical affinity will be followed.

If a ferrous-ferric ion solution is at equilibrium, there will be no tendency for change. This can be represented as system I:

$$Fe^{++} = Fe^{+++} + e$$

$$\frac{Fe^{+++}}{Fe^{++}} = k$$

If another ferrous-ferric ion solution is not at equilibrium, there will be a tendency to change, i.e., system II:

$$\frac{Fe^{+++}}{Fe^{++}} \rangle k$$

However, there will be no change since the electronic equilibrium would be disturbed.

If an inert electrode which does not participate in the system, but merely acts as a conductor of electrons, is placed in each solution, and if the solutions are joined by a semi-permeable membrane and the electrodes connected to complete the circuit, then there will be a tendency of Fe^{+++} in system II to be reduced to Fe^{++}, and this will be accompanied by an oxidation in system I. This results in electrons being transferred through the electrodes and an electromotive force, E, is produced. The volumes are assumed to be so large so that no measurable concentration ratio change is produced.

Sufficient current is passed so that one mol of Fe^{+++} is reduced to Fe^{++} in system II and the converse occurs in system I. Thus one mol of Fe^{+++} will disappear in system II and appear in system I.

The work done in this reversible isothermal reaction for the transportation of Fe^{+++} from concentration $(Fe_1{+++})$ to concentration $(Fe_o{+++})$ through the semi-permeable membrane is equal to:

$$RT \int_{Fe_o{+++}}^{Fe_1{+++}} \frac{1}{(Fe^{+++})} \, d(Fe^{+++}) = RT\ln \frac{(Fe_1{+++})}{(Fe_o{+++})}$$

The work for the Fe^{++} change is:

$$RT\ln \frac{(Fe_o{++})}{(Fe_1{++})}$$

The total work will be the sum of these two, and is equivalent to the electrical work for the passage of one faraday across the cell with electromotive force E.

$$E = \frac{Rt}{F} \ln \frac{(Fe_o{}^{++})}{(Fe_o{}^{+++})} + \frac{Rt}{F} \ln \frac{(Fe_1{}^{+++})}{(Fe_1{}^{++})}$$

Since $\frac{(Fe_o{}^{+++})}{(Fe_o{}^{++})} = k; \quad E = k + \frac{Rt}{F} \ln \frac{(Fe_1{}^{+++})}{(Fe_1{}^{++})}$

As this electromotive force constitutes only one-half a cell, another half cell will have to be added in order to complete the circuit. This reference cell is taken as the reversible hydrogen electrode at one atmosphere pressure in a solution containing hydrogen ions at unit activity. The potential of this electrode is assumed to be zero at all temperatures.

The general reaction equation for the completed cell is:

$$\text{Reduced state} + nH^+ \ (a_{H^+} = 1) = \text{Oxidized State} + 1/2nH_2 \ (1 \text{ atm}).$$

Since the activities of the hydrogen gas and ions are unity in the standard hydrogen electrode, the following equation results:

$$E_h = E_o + \frac{RT}{nF} \ln \frac{(\text{Oxid})}{(\text{Red})}$$

where E_h = potential of the system referred to the normal hydrogen electrode (volts)

E_o = specific constant for system being measured (volts)

R = universal gas constant

T = absolute temperature

F = Faraday constant

n = number of electrons transferred in the oxidation-reduction reaction

APPENDIX B. CLEANING METHOD EFFECT ON THE METAL ELECTRODE

To evaluate the different cleaing methods, the effects on the electrode metal of chemicals, heat, gases, and abrasives were studied. Acids will be considered first since they are most commonly used in cleaning electrodes. Based on the electromotive scale, metals above hydrogen react with acids replacing hydrogen. Since noble metals fall below hydrogen, they are therefore inert to this type of action. However, acids can have functions other than behaving as an acid in the normally defined manner.

Hydrochloric acid can act as a reducing agent releasing chlorine in the presence of strong oxidizing agents such as manganese dioxide, potassium permanganate, potassium dichromate and nitric acid. Cold or dilute sulfuric acid acts only as an acid, with the concentrated form acting less rapidly to displace hydrogen than the dilute form. However, concentrated sulfuric acid is an active oxidizing agent when heated, being reduced to sulfur dioxide. In this capacity it reacts with metals above platinum in the electromotive series. It is not as strong an acid as hydrochloric or nitric. In combination with potassium dichromate it is a strong oxidizing agent releasing atoms of available oxygen. This material can also release free halogens from the halic acid. Nitric acid can act as an acid, oxidizing agent or nitrating agent. It will react with all metals except gold, platinum, iridium, titanium, tantalum and rhodium. The concentration and temperature of the acid determine its oxidizing ability. At 68°C or higher, it is readily decomposed by heat to water, oxygen and nitrogen dioxide. If mixed with three parts of hydrocloric acid, aqua regia is formed. This will dissolve gold, platinum and other metals which are not affected by the acids individually. The chlorides of gold and platinum are formed, probably due to the action of atomic chlorine.

From the above general description, it would appear that platinum and gold are relatively inert. However, a study of Mellor's(121,122) extensive work on inorganic compounds yields a different picture.

Platinum is readily dissolved by aqua regia and solutions containing chlorine. Under reducing conditions it is attacked by alkalis, nitrates, cyanides and phosphates. Carbon alloys with it, and therefore the metal should not be heated in a smoky flame. There is some solution in boiling sulfuric acid, and boiling a long time in water yields a small quantity of colloidal platinum. Pierce and Haenisch(123) in discussing the care of platinum crucibles, state that the metal should be kept away from oxidizing agents such as chlorine, bromine and ferric chloride. No compounds of sulfur, phosphorus, arsenic, selenium, mercury, lead, bismuth, silver, tin or antimony should be ignited in platinum since they will alloy with the platinum if in elemental form. A reducing flame causes formation of crystalline deposits which will penetrate the metal. Strong bases, or salts which give strong bases, i.e., barium carbonate, should not be heated in platinum. Scouring with talc and cleansing with hydrochloric acid is the best method of cleaning.

Gold is not attacked by sulfuric acid if pure and no oxides such as manganese and lead are present. It is not completely inert in hydrochloric acid unless air is kept out. Alkalis do not appreciably attack gold. It is dissolved by aqua regia, mixtures of hydrochloric acid with an oxidizing agent which liberate chlorine, water containing the halogens (chlorine, bromine, iodine in solution), and solutions which can generate halogens, i.e., chlorides, iodides and sulfuric acid. Gold is attacked by boiling ferric chloride, alkaline sulfides and thiosulfates, and substances which can give large quantities of oxygen, i.e., manganese dioxide, potassium permangenate, nitric and sulfuric acids, and potassium cyanide solution in the presence of air. Chlorine water slowly attacks gold.

Since both of these metals are affected by electrolysis, and polarization has been used to treat the metal electrode, its effect on the metal is of interest. In electrolysis, platinum becomes rough and dull in hydrochloric acid, forms a finely divided film in potassium hydroxide, and forms platinum black in hypochlorite solution. As an anode, its behavior depends on the previous history of the electrode. There is a possible oxide film when used as an anode, according to Bowden(124). Glasstone(50) states that platinum and gold are regarded as unattackable, due to the fact that they are nearly always in the passive state. Although less noble than gold, platinum is rendered passive more easily, especially in solutions of oxyacids. If ammonia or hydrochloric acid is in the solution, the anode will suffer appreciable attack, particularly if in the finely divided form. Rideal and Wansborough-Jones(125) point out that a platinum anode is soluble in hydrochloric acid and the amount of oxygen in the platinum bears a constant and simple relationship to the amount dissolved.

With gold as an anode the previous history is also important. It has been stated that it is more readily polarized than platinum. It will dissolve in a hydrochloric acid-cyanide solution, and in a neutral solution of sodium or potassium nitrate.

The effect of heating on the metal warrants considerable attention since this operation is usually performed at some time during the life of the electrode. This will most probably occur during the construction of the electrode although heating of the electrode metal is sometimes used as a cleaning method in an attempt to degasify the metal or to burn off imbedded material. In order to evaluate the actual extent of the metal degasification, the following factors are considered: (1) to what extent are different gases sorbed on a metal surface; (2) does heating degasify the surface; and (3) how can the gas be removed.

Sorption of gases occurs on all metal surfaces. The metals of interest, platinum and gold, sorb all gases but each to a different degree. From reviews of the literature, gold appears to sorb less quantities of oxygen and hydrogen than platinum(121)(122)(126).

The sorption of gases on metals can be important when the metal is heated in a gas flame because of the possible contamination of the surface. It is of interest to note that in various laboratories different gas compositions are used in the burner used in heating the electrode. This can cause different degrees of contamination due to the varying percentages of component gases and the specific adsorption characteristic of the metal for each gas. Also, the location of the metal in the flame can be important due to incomplete combustion of the gas in certain zones.

The next point of interest is how easily these sorbed gases are removed. According to Mellor(122) ordinary platinum contains much occluded gas which is very difficult to remove. Once freed, the surface is recharged with

with more gas than before. The gas is held very tenaciously and can be recovered only by heating to redness in vacuo(122)(126). When describing the temperature of platinum, authors often use the color of the metal. The color is dull red, cherry red and orange in the temperature range of 600-850, 850-1000, and 1000-1100°C, respectively. At 300°C, Langmuir(127) finds that oxygen is wholly irreversibly adsorbed on platinum and can only be removed by reacting with a reducing agent such as hydrogen. At least 360°C and the best vacuum is needed to remove oxygen from platinum. The oxygen film is not removed by heating alone even at 1200°C. At higher temperatures oxygen begins to attack the platinum.

Although degasification of the gold surface has not been as extensively studied as the platinum surface, it appears that the same general conclusions apply to both metals(121)(128)(129). For oxygen removal at 130°C, Benton and Elgin(130) used hydrogen gas since the use of a vacuum was unsuccessful.

The above data seem to indicate that heating alone will not degasify the surface. This points out the fallacy held by some investigators that heating alone can remove gases from the electrode surface. A technique has been reported in the literature which overcomes the difficulty of removing the sorbed gas. It is done by controlling the initial oxygen content of the metal and in this manner, it is possible to standardize the initial oxygen-electrode equilibrium.

This was done by Goard and Rideal(131) who first tried boiling with hydrochloric acid, washing and heating in a methyl alcohol flame. However, the best accuracy obtained was up to 30 mv. Then, in addition to the above procedure, the electrodes were placed in a solution of 90cc borate buffer pH 9 and 10cc 0.1N potassium permangenate for 30 to 45 minutes with vigorous stirring. They were then washed and put into the measuring system. The authors found good reproducibility and accuracy by this technique for irreversible systems. Glasstone and Hickling(132) had difficulty in reproducibility for the anodic oxidation of thiosulfate with platinum. This was overcome by controlling the initial oxygen content of the anode. This was accomplished by washing the electrode with water and warm nitric acid, heating to redness, stirring in 0.1N potassium permangenate and buffer solution of borate pH 11 for 30 minutes, washing with water and using immediately.

Although heating alone will not degasify the metal surface, it can affect the metal itself. Platinum is not acted upon by air or oxygen at ordinary temperatures and scarcely affected chemically at any temperature. It is doubtful if oxidation occurs below 1300°C. Gold is not acted upon by air or oxygen at any temperature. It only combines indirectly with oxygen as in the case for platinum. Platinum does not volatilize appreciably at 900°C but can be volatilized to some extent at higher temperatures. Gold begins to volatilize just below its melting point of 1063°C and the loss is probably nil at or below this point.

Besides volatilization of the metal, there can also be changes in the metal surface due to heating. McBain(126) stated that Berliner's work(133) showing that platinum heated to redness in vacuo sputtered when given up occluded gases, made it evident that a smooth surface could no longer be considered perfect after such treatment. Stromberg(134) presented photomicrographs of platinum foil evacuated for two hours at bright red heat. He stated that the furrowed surface was due to the twinning of countless visible crystallites. On the assumption of a wholly superficial effect, he allowed 40 percent of extra surface. Mendenhall(135) found from photoelectric studies that there were complications due to gases on the surface. Heating in vacuum not only affected the removal of gases, but the surface characteristics were also changed by the heat treatment. Frazer, Patrick, and Smith(136) stated that platinum was roughened by alternate heating and cooling. This was so called "activation of surface." They believed that the activation of platinum by heating in air was due to the formation of finely divided platinum on its surface. Finch and Stimson(128)(129) found that heating resulted in an electrical charge on the metal surface which became dissipated as the metal was cooled. However, their data indicated that platinum would have a residual charge at 25°C if heated to 970°C or cherry red. This was not apparent for gold.

To achieve more insight into the heating effect on the metal surface, it will be necessary to briefly look into sintering, the preliminary step in annealing. The sintering temperature of gold is 200°C and platinum is 700°C. This is the temperature where the microcrystalline and amorphous arrangements of the atoms on the surface begin to change rapidly into the macrocrystalline form. This indicates that a structural change can result from heating. Rideal(137) stated that after sintering, the surface activity of the deposited metal progressively became less in adsorption and catalytic activity. Finch and Stimson(129) found that freshly rolled platinum was in an unstable state and needed alternate heating in oxygen and hydrogen to achieve a constant and reproducible charge-temperature relationship. This was also the case for nickel where heating alone was not sufficient. However, it was found that heating alone was sufficient for gold. They felt that the sintering temperature was possibly the reason for this and perhaps the normalizing involved a structural change.

Other cleaning methods also affected the metal surface. After burnishing, boiling in 96 percent alcohol, boiling in concentrated HNO_3, washing with distilled water and drying at 150°C, Stromberg(134) allowed 100 percent for unevenness for gold foil. Photomicrographs showed innumerable crystallites and furrows. Frazer, Patrick, and Smith(136) found that surfaces were not plane from a molecular point of view after cleaning with acid or rubbing. Highly polished platinum in x-ray diffraction no longer showed characteristic lines, but the structure of an amorphous substance. McBain(126) added that it was very likely the surface was also contaminated with impacted polishing material.

By changing the metal surface and increasing the accessible area, acids could create a catalytically active surface(138). Langmuir(139) described Faradays' experiment of boiling platinum foil in concentrated sulfuric acid and washing. The platinum was brought to a condition where it caused combination of oxygen and hydrogen at room temperature. Platinum boiled in aqua regia, hydrochloric acid, or nitric acids was made more active in its ability to displace gold from its salt(122). This did not occur with sulfuric acid.

Attempts have been made to quantitatively measure the change on the available surface resulting from various treatments which affect the metal. From Bowden and O'Connor(138) some accessible area-apparent area ratios based on nickel were obtained. They were: rolled metal, 2; sandpapered, 6-10; alternate oxidation and reduction, 46; and metal solidified from liquid state, 1.5-1.7. With the latter method the surface was fairly smooth but when the surface layer was removed by polishing or etching, cracks and irregularities developed which relieved the strains. They stated there was evidence of narrow cracks penetrating deeply below the surface of polished metals. McBain(126) summarized the work of Bowden and others on platinum, nickel, gold and other metals. For bright foil platinum the ratio between the true surface and apparent surface was 2.2. If cleaned in acid and heated in a flame the ratio was 3.3, an increase of 50 percent. Silver after being finely sandpapered had a ratio of 16. Newly polished nickel had a ratio of 75 which decreased to a ratio of 9.7 when old. These figures indicated that the metal surface was an unknown varying factor and could help to account for different potential readings when the electrodes were given identical treatment.

The effect of mechanical treatment has been investigated in terms of potential measurements in addition to being expressed as the apparent area change as presented above. Differences of potential in distilled water between platinum and platinum rubbed with sandpaper, filter paper or linen were found by Gaugain(140). In addition to possible mechanical strain resulting from cleaning, the construction of the electrode offers another instance where the metal was mechanically handled. Any resulting strain could set up small voltaic cells since the strained portion was less noble than the unstrained part. Also small crystals are less noble than large ones. Glasstone(50) stated that the effect on the single electrode potential of bending or straining the electrode could be measured on a student potentiometer except in the case of the softest of metals. Gold and platinum have a Moh's hardness of 2.5-3 and 4-4.5 respectively. Since the hardness scale ranges from one to ten, it would appear that gold would be less affected than platinum.

APPENDIX C. GAS-METAL ELECTRODE EFFECT

The observations of Fredenhagen(141) concerning the effect of gases on a potential reading indicated this effect could be appreciable. He found that the platinum potential in an oxidizing solution was sometimes reached quickly and sometimes slowly and concluded that the velocity of reaction of ions in the oxidizing solution with gases absorbed on platinum was quite variable. It was further stated, that in oxidation elements platinum always became charged with gases; in some cases the potential was entirely due to the gas charge and was in no way conditioned by the giving up of electrons from ions of the solution to the electrode. Chang(142) also concluded that the evaluation of the platinum potential was complicated by the presence of dissolved oxygen. According to Ward(66), a poorly poised media exposed to air during bacterial growth created an oxygen-platinum electrode effect.

An extensive investigation by French and Kahlenberg(17) resulted in the conclusion that metals formed gas-metal electrodes with gases. The resulting electrode potentials were specific for each metal and gas, and were related to the absorbing power of the metal for the gas and the affinity of the metal for each gas in a mixture. The total potential was due to: (1) absorbed gas and (2) a condensed film on the surface. The potential depended not only on the proportion of gas, but the relative affinity for the metal.

They tried many metal electrodes including platinum and gold. The electrodes were freshly sanded and put in an air-saturated normal solution of potassium chloride. The zero time was recorded when the potential leveled off and gas was then passed through the solution. The electrode was a flat plate half-immersed in the solution. The results were not reproducible but checked in a semi-quantitative manner.

Carbon monoxide and methane altered the potential of platinum and palladium materially while on other metals the effect was slight. With hydrogen, gold remained essentially constant but fell off after the gas was shut off. Platinum quickly dropped approximately 500 mv before leveling off and continued to drop and then rose slightly after the gas was shut off. All metals except those of the platinum group were rapidly changed from hydrogen to oxygen potentials while it took considerable time to get the hydrogen potential. Platinum was opposite with the hydrogen potential being rapidly attained while the oxygen changed the potential slowly.

Platinum was found to be unsatisfactory unless stablizied with a gas such as hydrogen in which the metal assumed a constant potential.* It exhibited a specific behavior with gases, quite different from most other metals. Gold was the only metal which could not be polarized by hydrogen after being exposed to oxygen for some time.

To prevent condensation of the gas film, either the electrodes were coated with a material like collodion or else the solution was agitated. With the gas flow on, the electrodes read the same whether coated or not. But if not coated, the potentials fell after the gas was shut off. This condensation film on the surface was given as the source of variable electrode behavior upon agitating or accidentally moving the electrode or electrode vessel. The effect of a rapid change was particularly noticeable with hydrogen and platinum or nickel and slightly less noticeable with gold.

It was thought that the potential produced was due to the dissolved gas, not to the gas in the gas phase. However, greater changes of potential which occurred when the electrode was completely immersed opposed the authors theoretical conclusion that a partly immersed electrode gave a greater effect.

The effect of hydrogen could be further considered in connection with the hydrogen electrode. This type of electrode has been extensively studied and yielded a linear relationship between the potential and pH by catalyzing the reaction:

$$H_2 = 2H^+ + 2e.$$

Beans and Hammett(143) concluded that bare platinum was a poor catalyst and that platinized platinum was an excellent one. Michaelis(16) found that blank platinum acted somewhat differently than platinized platinum. The latter gave a potential dependent upon the pressure of the hydrogen atmosphere due to its catalytic effect on the hydrogen equilibrium. The blank platinum acted qualitatively like the hydrogen electrode but it was a slow reaction and equilibrium was never reached. The potential was almost always uncertain, and varied as to the individuality of the electrode, Gold-plated platinum usually gave a potential further from the true value than pure platinum. Solid gold reacted but slightly.

The gas effect has also been investigated for electrodes in buffer solutions. Gold yielded a well-defined potential which returned to its original value a short time after polarization according to Michaelis(16). The potential of the gold electrode was scarcely altered whether air, hydrogen, or nitrogen was introduced. There was always a small difference between air in the positive direction and hydrogen in a negative direction. Some sensitive electrodes gave differences up to one volt but gold and sometimes blank platinum gave differences much less than 0.1 volt. The differences with platinum were larger and depended on the surface. In spite of the differences with respect to hydrogen and oxygen, various "indifferent electrodes" behaved alike in well-poised solutions such as quinhydrone where the oxygen content did not affect the readings.

Lepper and Martin(15) investigated special gold-plated platinum and iridium electrodes in weakly poised and unpoised buffer solutions under the effect of gas. Iridium is a member of the platinum family. The gold plate electrode was made by heavily gilding a platinum plate electrolytically, drying, heating several times in a blowpipe until a deep gold color resulted and then finally electrolytically depositing gold. These were found much less sensitive to hydrogen and oxygen than merely gilded platinum.

In a weakly poised solution the gold plate changed little with decreasing concentrations of poising agent but iridium at the lower concentrations approached the hydrogen electrode potential under the influence of hydrogen. In an unpoised buffer the gold plate showed little change with hydrogen. However, the iridium showed a marked drop in potential. Oxygen, bubbled immediately after the hydrogen, caused a slight rise in potential with gold, but the iridium rose much more in relation to its low potential with hydrogen. The iridium rose to a higher positive potential than the gold did. The gold appeared to be more sensitive to oxygen than hydrogen in this case.

In order to create conditions more closely associated with biological growth than salt or buffer solutions, Boyd and Reed(14) studied the effect of hydrogen, nitrogen, carbon dioxide and air on platinum, gold and mercury in an anaerobically aged beef extract broth at 0°C. The platinum and gold were used in the form of polished foil. Air caused a gradual increase in the potential of 100 to 200 mv. The potential rose when the gas was shut off. Due to the slow response, the authors felt this indicated the inert nature of the electrode to air. Nitrogen had no effect on platinum and a very slight effect on gold and mercury.

Hydrogen had no effect on gold and mercury beyond that predicted by the standard deviation and caused by stirring. With platinum the change was much greater producing a drop to approximately -250 mv. The potential dropped further after the gas was shut off. Since this fall was not exhibited with the other gases it was concluded that the hydrogen effect was not due to stirring. These investigators also investigated the effect of bubbling hydrogen through broth for five hours. They compared their results with the work of French and Kahlenberg who treated a potassium chloride solution in the same fashion. In both media the drop in the platinum potential of 500 mv was practically the same. They felt this general agreement of the platinum increased the significance of the gas-metal electrode.

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