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ELECTRODE POTENTIALS DEVELOPED  
DURING SLUDGE DIGESTION

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## INTRODUCTION

The digestion of sewage sludge is an inherently complex biochemical reaction. The process essentially consists of a chain or succession of interdependent steps, many of which are imperfectly understood. Included in this chain are oxidation-reduction reactions. These reactions enable the living cells to satisfy their immediate needs for energy as well as to store energy for future utilization. Hewitt<sup>(1)</sup> states that oxidation-reduction systems are so essential that life might be defined as a continuous oxidation-reduction reaction.

Since an oxidation-reduction reaction involves an electron transfer, it is possible to make quantitative studies of certain chemical reactions by measuring the resulting potential change. This technique has been adapted successfully to pure bacteriological and biochemical systems and it would appear possible to apply a similar technique to the mixed culture utilized in sludge digestion with some degree of success.

The use of oxidation-reduction potentials in the field of sewage treatment was first reported in 1906<sup>(2)</sup>. Since that time, some efforts have been made to utilize such measurements in sewage processes but principally in the area of activated sludge with relatively few applications to anaerobic sludge digestion<sup>(3,4)</sup>.

A complete review of the basic principles of oxidation-reduction potentials would be beyond the scope of this article. Several sources of such information are available, of which Michaelis<sup>(5)</sup>, Clark et al.<sup>(6)</sup>, and Hewitt<sup>(1)</sup> are outstanding.

Various methods are presented by the above authors which relate the oxidative state of a thermodynamically reversible system to the resulting potential. All of these methods lead to the same equation:

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

$E_h$  is the potential of the system referred to the normal hydrogen electrode and  $E_o$  is a specific constant for the system being measured. Both 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 conversely if the ratio of oxidant to reductant gets smaller, a more negative potential results. A high positive result is shown by chlorine, an oxidizing agent. Conversely, hydrogen, a reducing agent, will exhibit a high negative potential. In the same manner, we can speak of an aerobic or oxidizing solution as basically having a positive potential and an anaerobic or reducing solution as basically having a negative potential.

In any case, the potential developed is dependent only on relative concentrations and not absolute quantities. Thus, oxidation-reduction potentials determine the level of intensity, but not the capacity of the oxidizing system.

Some of the other factors which have a bearing on the oxidation-reduction potential are the altering of the ionic equilibrium by pH changes and the degree of reversibility of the reaction. This

latter factor has caused the use of O-R potential to be rejected by some authorities, as applied in many biological systems, since the lack of reversibility invalidates the basic equation. There are many, however, who feel that this limitation should not preclude the use of oxidation-reduction measurements where proper precautions are taken (1,7,8,9,10,11,12).

There are two methods of obtaining the 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.

Metal electrodes, however, provide the most reliable method of obtaining oxidation-reduction potentials. The measurement reflects the difference in potential between an inert metal electrode, such as platinum or gold, and a reference electrode, such as the calomel half-cell. The calomel half-cell may in turn be referenced to hydrogen. It is important that the inherent characteristics of the metal electrode do not affect the potential of the system to be measured. In addition, vacuum tube potentiometers with high resistances are used for potential measurements in order to avoid polarization of the metal electrodes. This is especially important in biological systems where a slight polarization of the electrode can cause serious errors in measurements.

#### Oxidation-Reduction Potentials in Biological Systems

The fields of bacteriology and biochemistry provide an excellent source of background information for the application of electrode potential measurements to digesting sewage sludge. From such information it can be

substantiated that strict anaerobic organisms cannot grow under aerobic conditions. However, they can grow if facultative anaerobes first reduce the potential to a low enough level. One distinguishing feature of aerobic and anaerobic growth is the potential range in which their growth is initiated. According to Hewitt<sup>(1)</sup> 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 may span the entire potential range.

Many authors have had difficulty in measuring the potential of biological systems. Hewitt<sup>(1)</sup> 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 that observed variations were 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.<sup>(6)</sup> These authors observed 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. 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 extensive study of electrodes was carried on by Michaelis<sup>(5)</sup>. 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 where two apparently identical gold or platinum electrodes in the same solution differed by more than 100 mv, this author concluded that 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 poisoned 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<sup>(13)</sup>. 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 cultures.

#### Experimental 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 in measuring pH, no such uniformity exists 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.

The most thorough investigations covering the comparison of gold and platinum as an electrode were performed on the same system by two different authors<sup>(5,14)</sup>. The results produced two different opinions. Gold has been said to be more sensitive in bacteriological studies<sup>(10,15)</sup>, but other investigators did not find that the two metals differed in this respect<sup>(6,16)</sup>. Although reference to the greater sensitivity of gold was found, this research has not disclosed any instance where platinum was alleged to be more sensitive than gold.

From the literature survey 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 in various quinhydrone mixtures, were other factors in favor of the 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 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 a valid comparison might be made.

The construction of either type of electrode was similar. The metal was fused or soldered to copper wire and then sealed into glass. The possibility of sealing gold into glass was achieved through the use of a special lead glass having an expansion coefficient similar to that of gold.

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<sup>(17)</sup> who found that large platinum foil with a surface area of four square centimeters gave no better results than small wire electrodes in anaerobic bacteriological studies.

The model digesters used for the experimental work were constructed from plexiglas. The cylindrical portion, or body, of each digester consisted of an 8-inch section of plexiglas tubing with an 8.25 inch inside diameter and 0.25 inch wall thickness. The bottom of each digester was made from one inch thick plexiglas and had a diameter of 9 inches. The bottom was sloped at an angle of approximately 10 degrees. The cylindrical body was glued into a slot machined into the bottom plate. The top of each digester was also 9 inches in diameter and was made from 0.312 inch thick plexiglas. It was so constructed that it could be fastened to six lugs equally spaced around the inside of the body of the digester. In order to insure air tightness, a soft rubber gasket 0.25 inch thick was placed between the

walls and the top of the digester. The digester contained a drain in the bottom and a sampling tube located in the body of the tank about one and a half inches below the liquid level. A schematic drawing of the model digester is shown in Figure 1.

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

The digesters were placed in a water bath and the temperature held constant at 35°C by use of heating coils and a thermostat.

The digesters were continually mixed using a specially constructed impeller, with a mercury seal to exclude air.

Potentials were measured with a Beckman Zeromatic Model 9600 pH meter using the inert electrodes described previously. Each digester contained two gold and two platinum electrodes. The electrodes were brought together in a shielded 16 point switch box so that each electrode reading could be obtained by dialing its position on the switch. The resulting potential measurements are reported throughout this work as observed  $E_c$  values. This terminology was used in preference to a calculated  $E_h$  term, which might create controversy regarding the system being measured, its degree of reversibility, and the subsequent validity of such observations.

Gas was collected in polyethylene jugs inverted in a box containing an acidified salt solution as the confining liquid. The box was painted with an epoxy resin to protect it from the effects

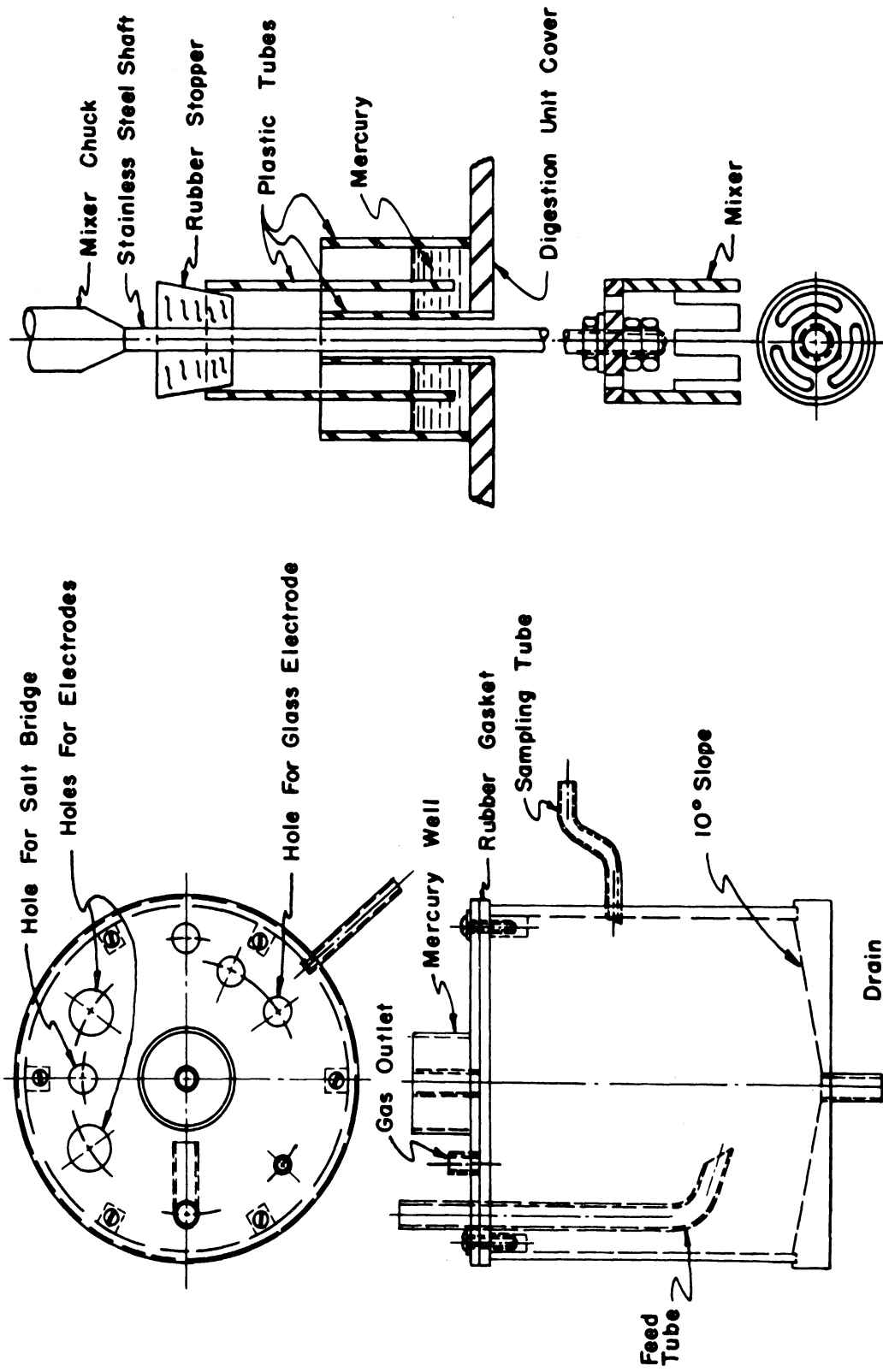


Fig. 1 Digestion Unit and Mixer Assembly

of the liquid. All gas analyses were carried out using a Burrell Gas Analysis Apparatus.

Adjustment of the Metal Electrode to the Sludge Potential

The determination of the potential of a digested sludge did not appear initially to be a complex technique. Although previous work on this subject was limited, the recommended procedures consisted of short time electrode immersion. Hood<sup>(18)</sup> 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 that such readings might not be valid, especially for a poorly poised solution. However, agitation with a magnetic stirrer was recommended by Eckenfelder and Hood<sup>(19)</sup>. They stated that readings should be taken with a platinum electrode every few minutes for a total of 30 minutes.

A study of the literature of the bacteriological and biochemical fields disclosed that the electrode adjustment period used by various workers was much longer than 30 minutes. Six to eight hours were used by Knight<sup>(20)</sup> with freshly gold-plated electrodes; Lepper and Martin<sup>(21)</sup> with special gold-plated and iridium electrodes autoclaved a meat media after inserting the electrodes and allowing the mixture to equilibrate overnight; Reed and Orr<sup>(22)</sup> found a few hours were needed with platinum for a reducing agar with sodium thioglycollate; and Michaelis<sup>(5)</sup> used four to six hours in a cysteine solution for platinum and a slightly longer time for gold-plated platinum.

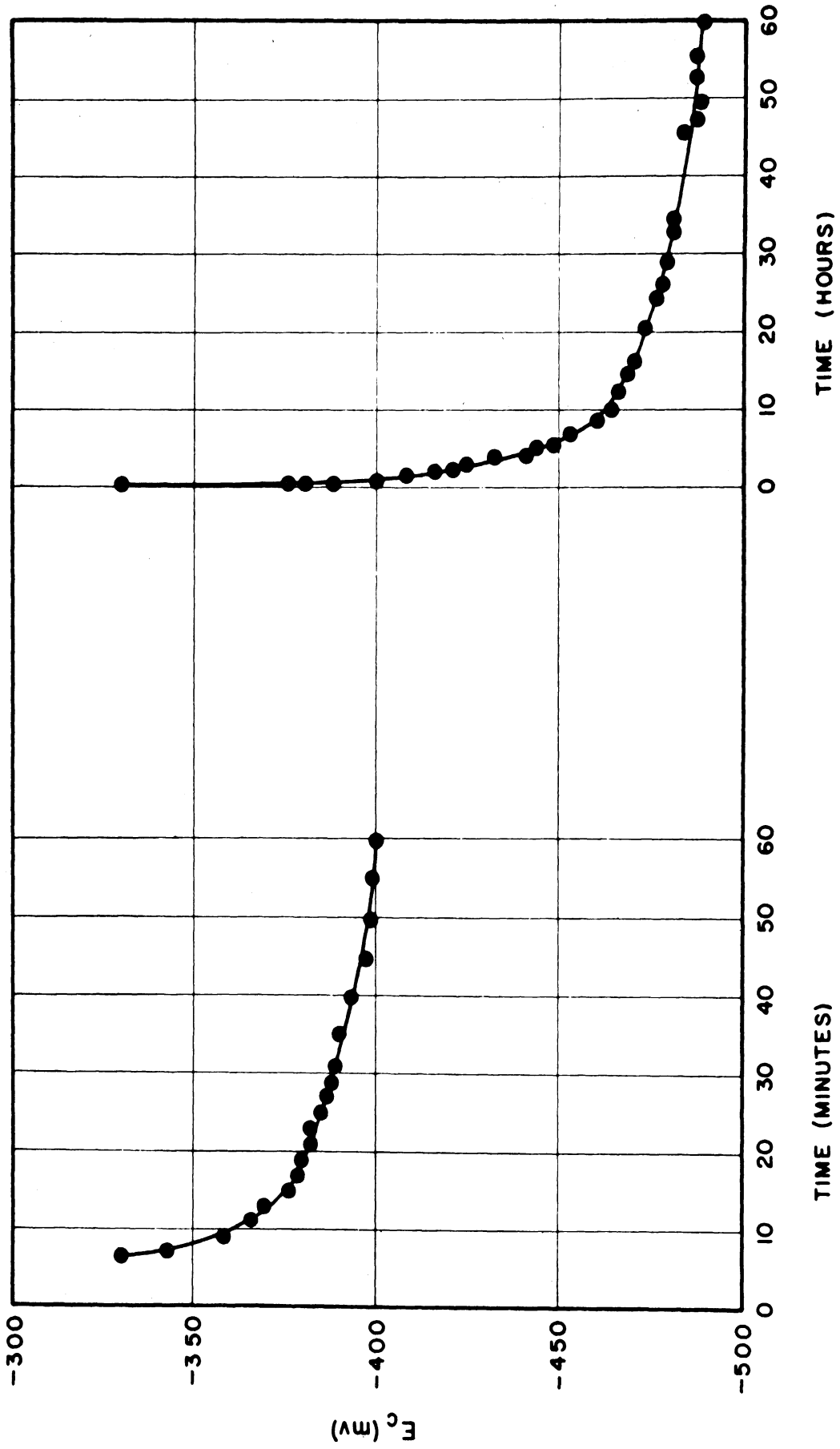


Fig. 2 Adjustment of a Platinum Electrode in a Digested Sludge

The potential-time relationship shown in Figure 2 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 municipal 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.

An adjustment trial was made with a magnetic stirrer to follow the recommended procedure in the literature<sup>(19)</sup>. The results in the short time interval were not significantly different from that under quiescent conditions. This was also shown by other trials with agitation.

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<sup>(5,16,17,23)</sup>. It was shown repeatedly throughout the work that any contact of air with previously digested sludge caused the sludge to have potential readings from 50 to 100 mv more positive than the normal optimum level for an actively digesting sludge mass. The importance of this fact cannot be minimized since the sample so



exposed does not return to its optimum level for an extended time interval, and this return is only possible if the environment is kept air and oxygen free.

Figure 3 shows the effect of addition of a normal raw sludge feed to an actively working sludge digester. The potential departs from the optimum and then slowly returns to the optimum level over a period of some six hours. Thus, with raw sludge fed twice daily there is opportunity for poor potential levels to exist in the digester for some twelve hours per day. This fact serves to substantiate the recommendation for frequent feeding of digesters operating at high rates.

#### Observations of Electrode Potentials in Laboratory Digesters

Initially a digester was inoculated with previously digested sludge and fed twice a day at a rate of 0.1 lbs. of volatile matter per cubic foot per day. Raw sludge representing a mixture of primary and waste activated sludge averaging 3.13 per cent solids and having 72.8% volatile was fed. The average detention period was 14.2 days and the run lasted for 16 days. Figure 4 presents the results obtained. Apparently the initial sludge inoculum was rather dormant. This is indicated by the low initial production of gas, the tendency for the pH to fall off with feeding, and the immediate rise in volatile acids. The electrode potential followed the volatile acid trend almost exactly rising to a peak on the fourth day and finally leveling off at -525 mv at equilibrium.

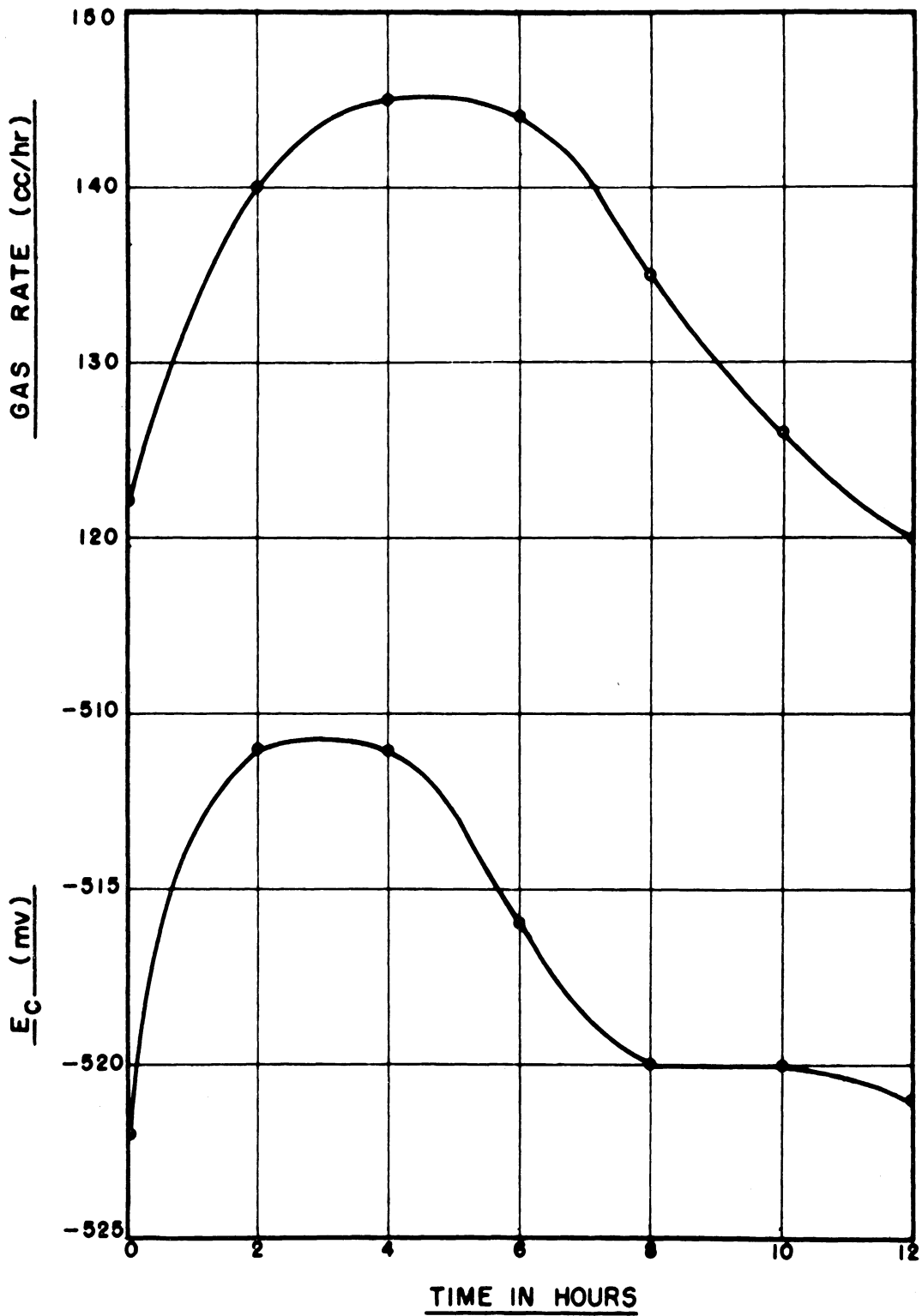


Fig. 3 Change in the Electrode Potential and Gas Rate Between Feedings

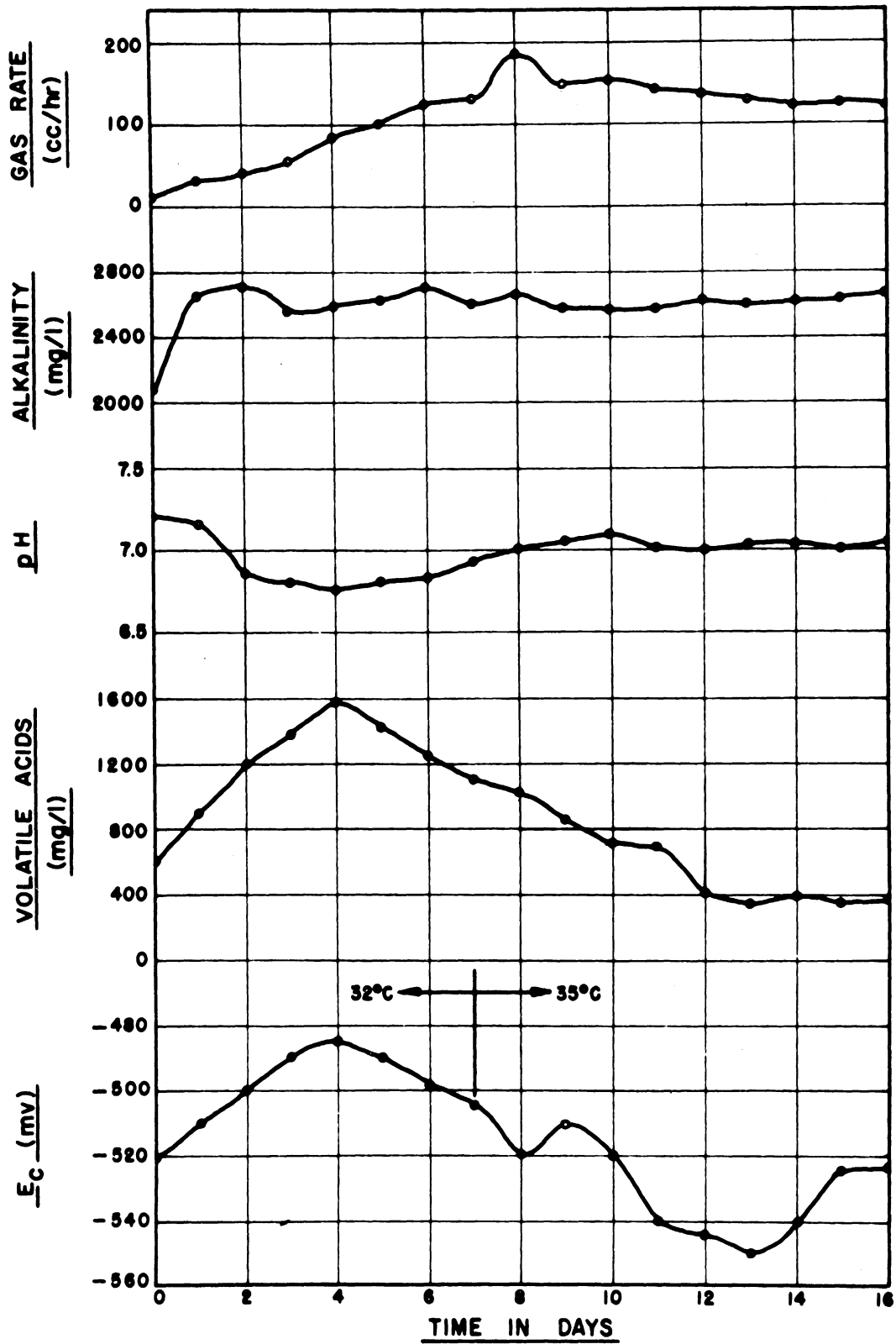


Fig. 4 Digestion Parameters during Slow Start-Up

Three digesters were next set up to check reproducibility between units. Digested sludge seed in this run varied between units but the raw sludge fed to each digester was identical. Figure 5 presents the results of a 30-day run. Again, after equilibrium was established, the electrode potential values were found to be consistently between -520 and -530 mv. Moreover, it seemed that the electrode potential measurement was somewhat more indicative of the trend of things to come in the digester than were the more customary parameters.

To further check these observations, it was decided that sludges from five Michigan cities would be studied with the objective of determining what potential levels would be obtained from widely varying types of sludge. For this purpose Detroit sludge was selected to represent a large primary installation with industrial wastes, while sludge from Ypsilanti represented the small primary type of plant. The city of Saline was chosen because it utilizes a recirculating trickling filter. Chelsea was selected to represent the very small type of activated sludge plant, while Ann Arbor sludge was used since it was convenient and could be considered representative of a large metropolitan type of activated sludge plant. All laboratory digesters were seeded with the respective local digested sludge and fed twice a day with the respective local raw sludge. The loading was held constant at a level of 0.075 lbs. of volatile solids per cubic foot per day for a total of 12 days in all units. All sludges appeared healthy and gave normal levels of pH, volatile acids, carbon dioxide, and alkalinity. The electrode potential values were also quite uniform

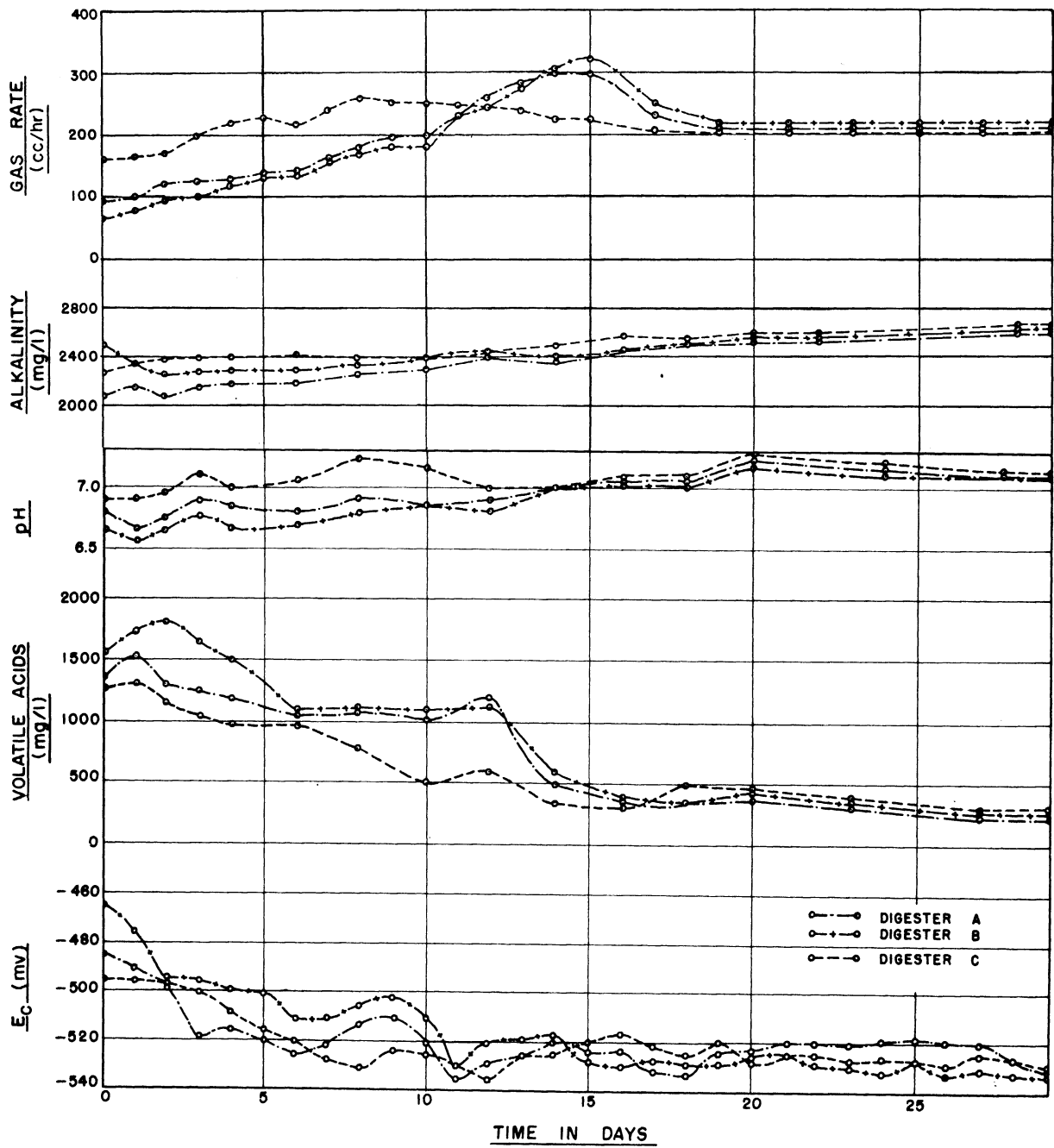


Fig. 5 Electrode Potentials, Volatile Acids and pH during Start-Up and Operation

except for a slight rise at the beginning of the curves which reflected the exposure of the seed sludge to air during transfer to the laboratory. The results are tabulated in Figure 6. Of the parameters measured, the electrode potential is unquestionably the most uniform and appears to fall in all cases within the same range as previously determined (-520 to -530 mv).

The second phase of the work involved the observation of effects produced with deviation of the electrode potential from the optimum level as determined above. The first attempt to shift the potential utilized a feed of hydrogen peroxide. Such small quantities of chemical were required to be fed on a continuous basis that frequent difficulties were experienced. For this reason the use of an electrolytic control similar to the one used by Hanke and Katz<sup>(24)</sup> was designed. In essence the control mechanism consisted of a source of D.C. voltage, a salt bridge, and two large inert electrodes. When the positive pole of the supply was placed in the digester and the negative pole connected to the digester by means of a salt bridge, the potential of the digester was increased. When the leads were reversed the potential was decreased. The adaptation of this method for use in a laboratory digester of the size and type being used in this study was not without difficulty. However, the presently designed electrode and salt bridge system works extremely well. Figure 7 shows a line diagram of the system in use.

Using this equipment, one digester was started in the same fashion as previously outlined and allowed to operate for five days until equilibrium was apparently established. At that time the electrolytic control was activated and the electrode potential increased at a

Tabulation of Digestion Parameters  
for Five Sludges

Sludge	Electrode Potential mv.	Volatile Acids mg/l	Gas Rate cc./hr.	Gas Production cu. ft./lb.	CO <sub>2</sub> o/o	pH	Alkalinity mg/l
Ann Arbor	-524	400.	155	8.25	32	7.1	2800
Saline	-528	350	187	10.0	36	7.0	2690
Detroit	-521	340	185	9.87	38	7.05	2700
Ypsilanti	-521	440	162	8.64	36	7.02	2650
Chelsea	-522	525	140	7.5	35	7.05	3250

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

Fig. 6

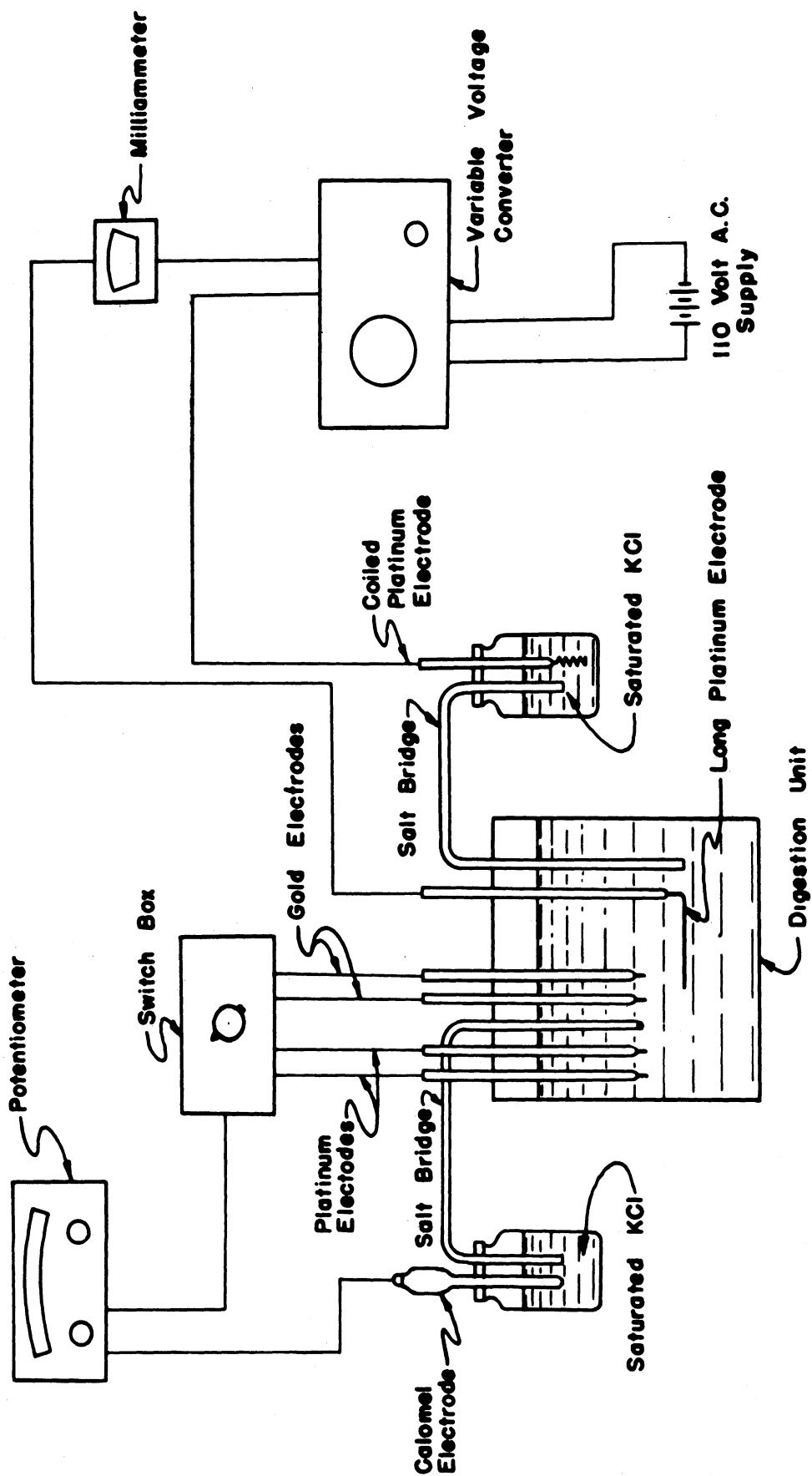


Fig. 7 Electrode Potential Measurement and Electrolytic Control Circuits



slow rate. The objective was to increase the potential but not so suddenly as to upset the bacterial flora. In 20 days the electrode potential was raised from -520 to -250 mv. Figure 8 indicates the results. The volatile acids began to increase immediately and rapidly rose from a level of 500 to above 2000. The gas rate fell off rapidly and declined to a level of essentially zero. Alkalinity and pH also fell at the same time.

At the 25th day the potential was decreased rapidly in a period of five days to the original optimum level of -525 mv. The volatile acids continued to increase, the alkalinity and pH returned to normal levels but the gas rate remained zero for another 12-day period. Obviously, the acid forming bacteria were functioning, but the adverse potential trend had been too severe for the methane producing bacteria to recover in any reasonable period of time.

The next test was set up in a similar fashion with similar loadings but using four digesters. Digester D was to be the control while the potentials in Digesters A, B, and C were to be poised at -430, -460 and -490 mv respectively for a 10-day period. At this time the units were to be returned to the optimum level. For five days no control was used and the digesters behaved in a predictable fashion. Figure 9 shows the results of the next 30 days' observations. From this figure it is apparent that the control unit produced almost constant results. The pH in Digester C indicated no apparent difficulty but Digesters A and B were quite acid. Volatile acids were apparently seriously affected in A and B but C showed no effect for about 12 days

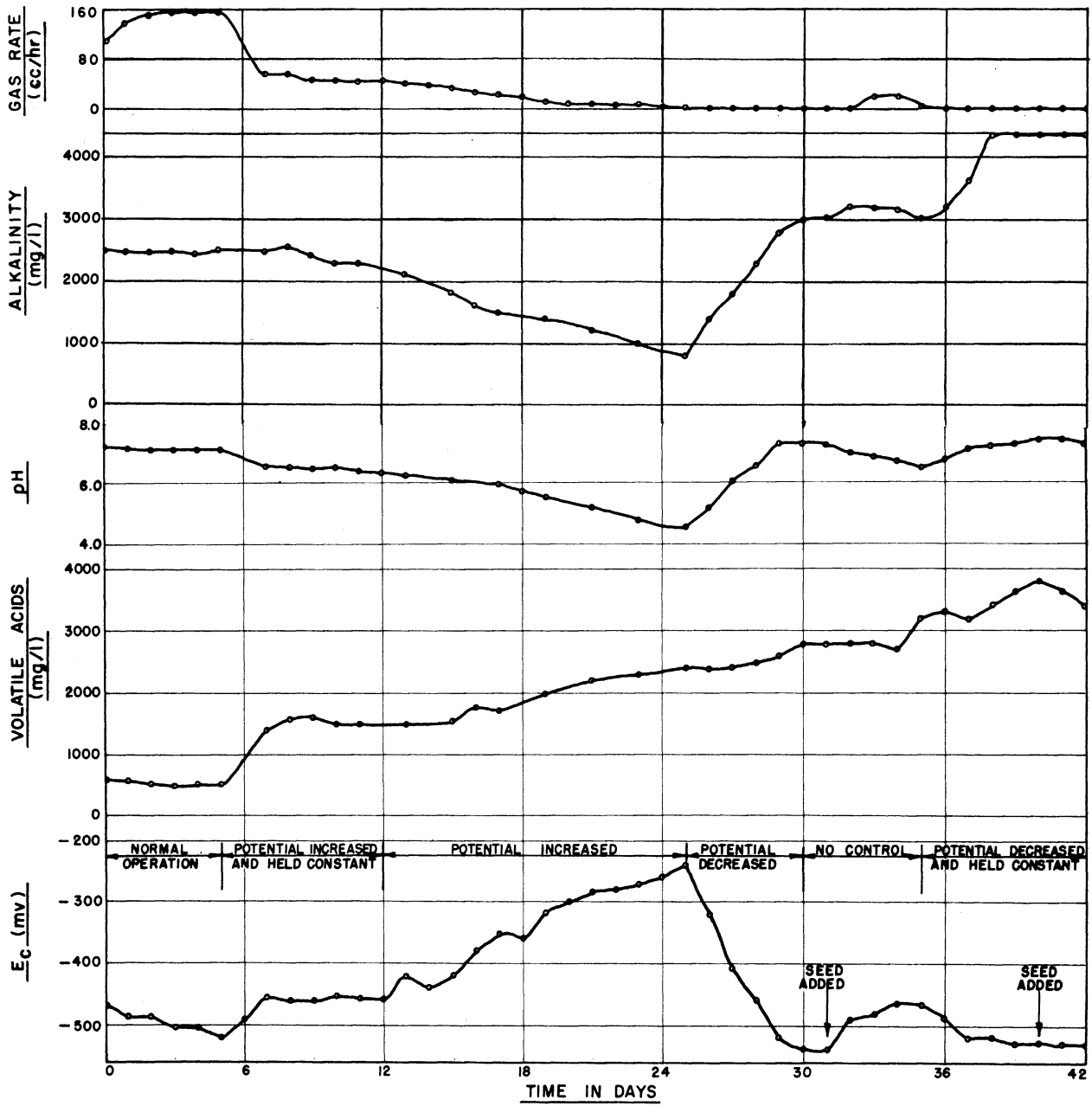


Fig. 8 Electrode Potentials, Volatile Acids and pH during Electrolytic Control Changes

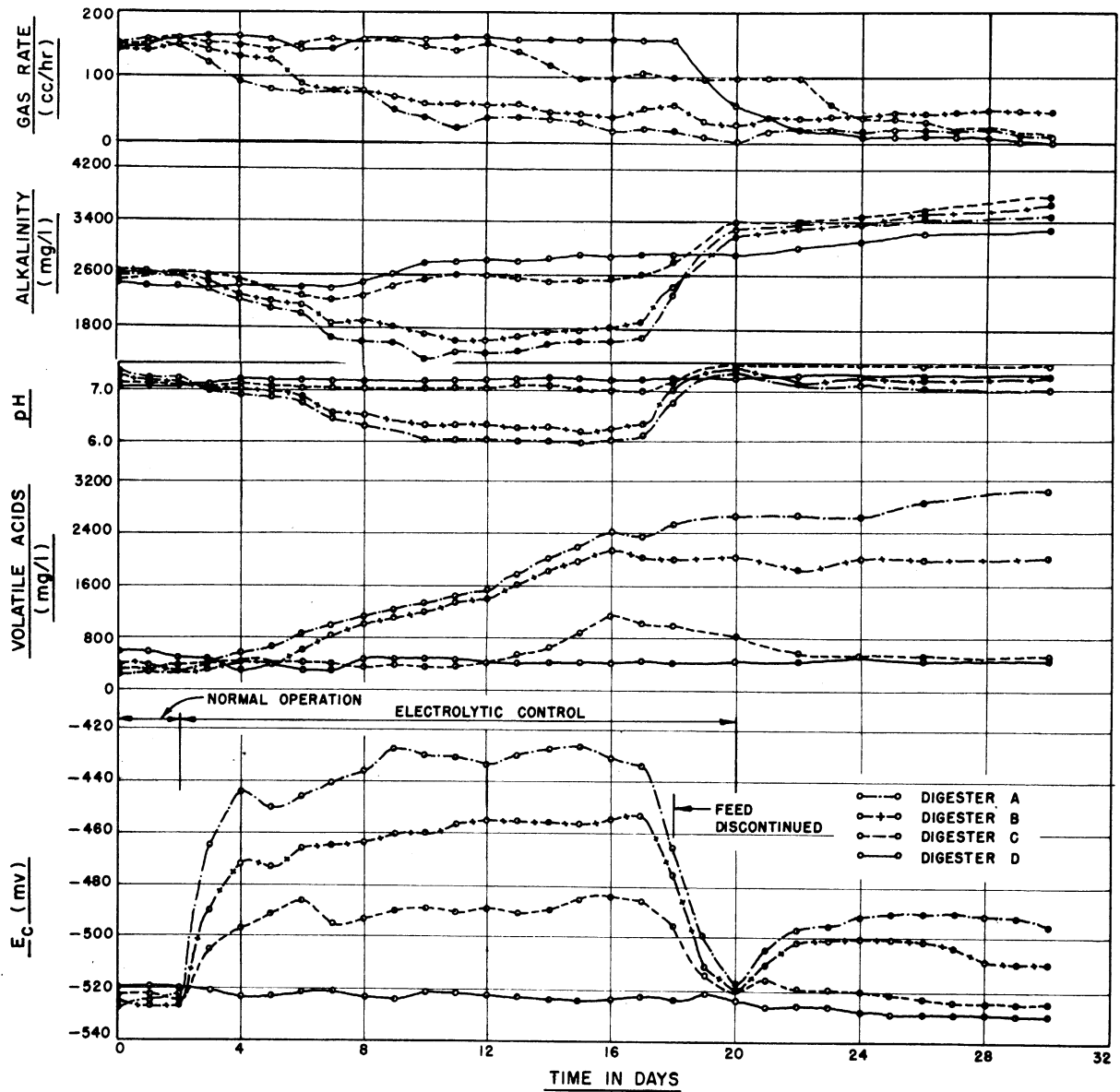


Fig. 9 Electrode Potentials, Volatile Acids and pH during Electrolytic Poisoning of the Potential

after which interval a sudden increase occurred. The gas rate fell off as might be predicted from the volatile acid behavior.

On the 17th day of this run the potential was returned to -520 mv, the control shut off, and the feed discontinued. The digester poised at -490 mv continued to produce gas and its volatile acids returned to a normal level. Digesters poised at -460 and -430 were apparently pretty well stuck.

The next run was designed to show the effect of overloading on the electrode potential and to note if any similarity to the conditions produced by potential control could be observed.

No electrolytic control was to be employed initially and the Digesters A, B, C, and D were loaded at rates of 0.30, 0.225, 0.150 and 0.075 lb. of v.s. per cubic foot per day. The raw sludge feed was not concentrated so that detention time in the digesters also varied, being 5.7, 8.6, 11.4, and 22.0 days in the respective digestion units. On the basis of work by previous investigators recommending an 8 to 10 day minimum detention time, it was felt that certainly Digester A would fail by overloading.

The digestion units were allowed to come into equilibrium using the level of feed for control unit "D". After equilibrium had been established, the increased rate of feeding was initiated and the results are as indicated in Figure 10.

Conditions of digestion in Unit B, loaded at a rate of three times that of the control were not far from ideal. The average potential was -512 mv (about 10 mv off its optimum). The pH was 7.0 while the alkalinity averaged about 2700 mg/l or around 500 mg/l below that of the

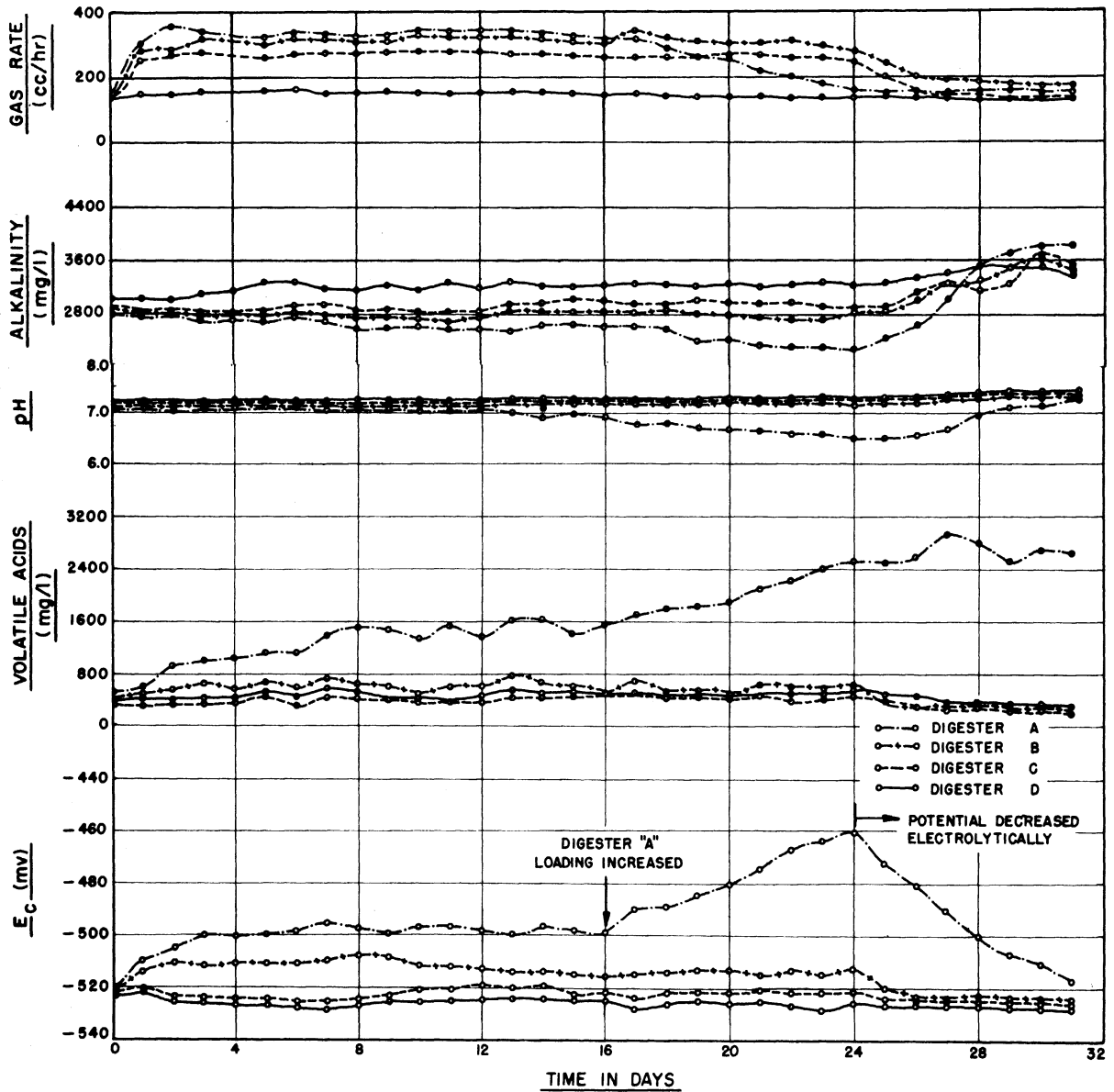


Fig. 10 Electrode Potentials, Volatile Acids and pH Developed during Overloading

control. The concentration of volatile acids averaged about 150 mg/l above that of the control but at no time did they exceed 700 mg/l which is far from being critical. The shorter detention time is reflected in the reduced gas rate. The gas produced amounted to about 21<sup>4</sup> per cent of that from the control digester although the loading rate was three times the load applied to the control.

Digester C behaved even better than B. However, Digester A appeared to be in a critical condition. The potential rose to -496 mv, volatile acids rose to 1400 mg/l, the alkalinity dropped as did the pH. The unit appeared to be just barely holding its own. At this point and after 16 days of such observations, the load to Digester A was increased slightly and it immediately responded by a rapid increase in volatile acids. The result would indicate that at an electrode potential value of approximately -490 or -495 mv, a digestion unit has reached its critical level as far as a healthful environment for methane producing bacteria is concerned. Above this point, the acid formers are apparently quite active but the methane organisms just will not continue to function.

These observations seemed to indicate that a desirable upper limit of potential does exist for methane producers. The next set of runs was set up to define this point more closely, and to determine whether overloading and electrolytic potential control produce similar limitations on the bacterial flora.

The four digesters were again established at the uniform rate of 0.075 lbs. of v.s. per cubic foot per day and equilibrium

established. Electrolytic control was applied to produce a potential level of -476 mv for A, -496 mv for B, and -510 mv for C. Digester D was again the control unit. Figure 11 shows the results. Digester A immediately began to develop an extremely acid and unproductive condition. At a volatile acid concentration of 1500 mg/l the electrolytic control was applied and the potential brought back to -525 mv. For a period of days the volatile acids continued on an upward trend as the methane producers struggled to redevelop a highly active culture. The rate of gas production tells the story. By the time the electrode potential reached -510 mv, the gas production was increasing rapidly. It eventually exceeded that of the other units, using up the excess volatile acids accumulated. This resulted in a return of the volatile acids to the optimum level. In this case, electrolytic control would seem to have demonstrated some ability to correct the environment of mildly acid or overloaded digesters. This point will definitely need further study.

To complete the picture on the desirable electrode potential range for methane bacteria, the digestion units were again readied in the same fashion as previously described. This time the potential was depressed below the optimum level. Results are as indicated in Figure 12. The lowest unit (Digester A) poised at -575 mv indicated distress at about the 6th day. At this time volatile acids began to increase almost exponentially. At 1500 mg/l of volatile acids, the potential was returned to optimum and the digestion recovered, following a similar pattern to that previously observed for the unit which had been poised at -475 mv.

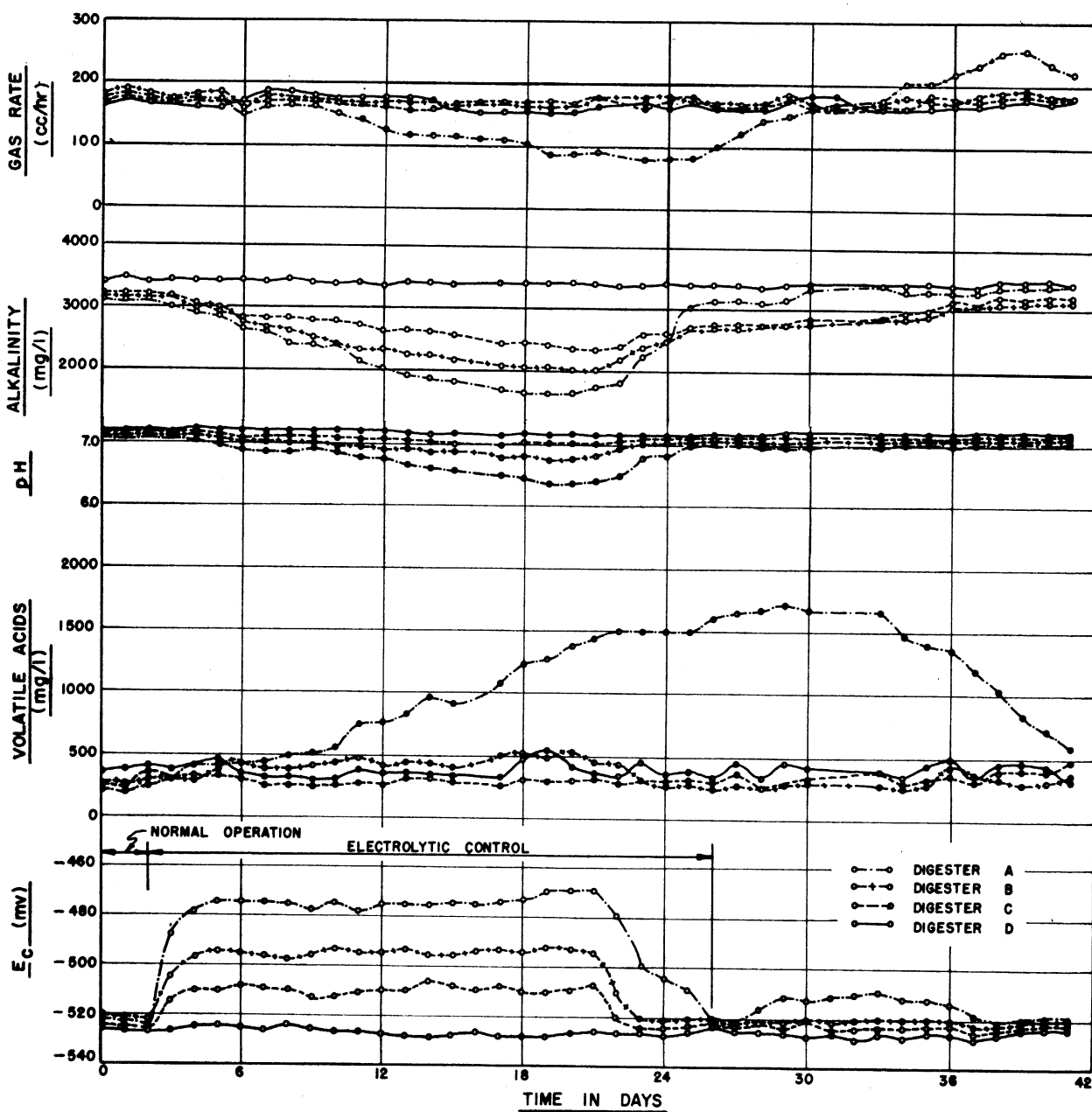


Fig. 11 Electrode Potentials, Volatile Acids and pH during Electrolytic Increase of Potential



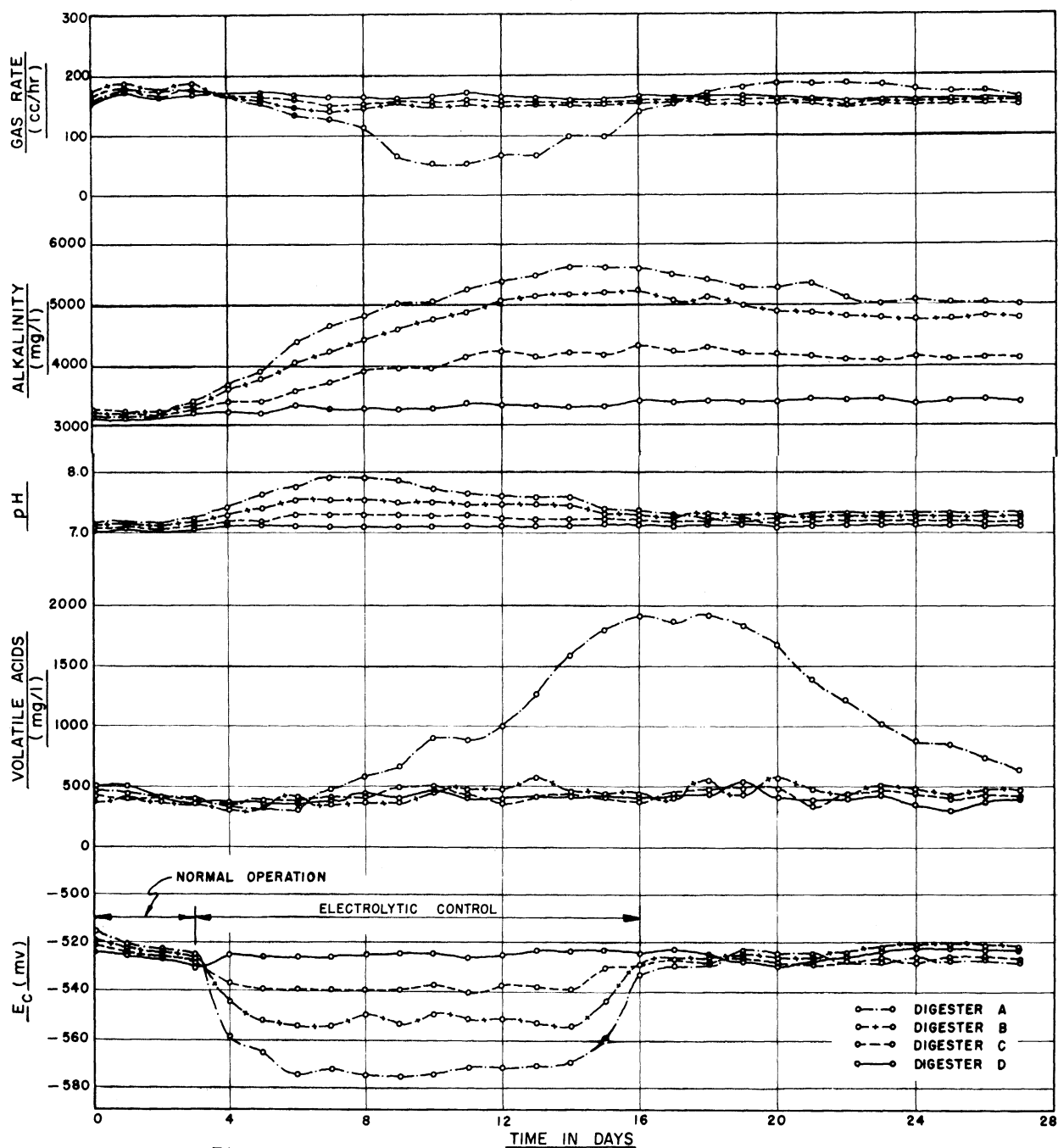


Fig. 12 Electrode Potentials, Volatile Acids and pH during Electrolytic Decrease of Potential

## SUMMARY

Electrode potential measurements when properly observed can be extremely informative in the interpretation of the behavior of an anaerobic digestion process. Such observations can be, in contrast to previously reported results, highly consistent and reproducible.

Within the limitations of the equipment used, optimum digestion appears to be a function of a healthy methane producing flora which seems to thrive best at an  $E_c$  level between -520 and -530 mv.

These organisms will continue to function over a range of  $E_c$  from -490 to -550 mv. The extremes of this emf range appear to be relatively critical regions for dependable growth of methane organisms. -510 to -540 mv is considered at the present time a safer range.

It must be cautioned that technique in measurement is important, and that a few isolated readings will not suffice. Readings should be taken frequently and the trend of the data established.

There is some indication that electrolytic control of digestion is possible. It is extremely early in the research to say whether such control will definitely work and whether it is economical or not. If such control proves practical, it would provide an added safety factor for those installations contemplating high rate digestion.

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