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Anerobic Biological Treatment of Liquid Wastes from Pyrolysis Processes

Final Report

Richard R. Dague

The University of Iowa
Iowa City, Iowa 52242

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NOTICE

ACKNOWLEDGEMENTS

Most of the work presented in this report was done by several graduate students in the Environmental Engineering Program of the University of Iowa. They are Gary Benjamin (M.S., May 1979), Timothy Fisher (M.S., May 1980), Mark Veenstra (M.S., May 1980), and David DeChant (M.S., Dec. 1980). Other students who have contributed significantly to the work include Karen Hagelstein and William Harris. The effort put forth by these students was of great significance in the success of the project.

A special acknowledgement is due to Dr. Roger C. Splinter, Associate Director of the University of Iowa Hygienic Laboratory, and Dr. James C. Walker, Chemist with the University Hygienic Laboratory. There assistance in the characterization of the PUROX pyrolysis wastes and the effluents from the anaerobic reactors was of great value.

A word of thanks is also due to Dr. Donald K. Walter of the U.S. Department of Energy for his technical advise and counsel throughout the period of the study.

As noted above, six students have worked on this project while pursuing graduate degrees in Environmental Engineering. Four have completed their work and the other two are near completion. Thus, in addition to the technical findings detailed in this report, considerable educational achievements have been made possible by the U.S. Department of Energy funds provided through this project. This support is gratefully acknowledged.

ABSTRACT

Wastewaters from Union Carbide's PUROX pyrolysis process are high in oxygen demanding substances (COD of = 30,000 mg/l) and contain polynuclear aromatic hydrocarbons (PAHs) and other organics, some of which are toxic.

Both suspended and attached growth anaerobic biological processes have been applied to the treatment of strong wastes. The purpose of this research was to evaluate these two anaerobic processes for application to the PUROX wastes.

The suspended growth experiments were conducted using three, five-liter, completely mixed, anaerobic reactors operated at 35^{o}C. The reactors were fed primary wastewater sludge and pyrolysis wastes in variable percentage mixtures to maintain solids retention times (SRTs) of 15 days and liquid retention times (LRTs) of either 15 or 5 days.

The anaerobic microorganisms were acclimated to the toxic pyrolysis wastes by introducing the wastes in very low (one to five ml/day) initial amounts followed by gradually increasing feed rates.

It was found that not more than 17% of the total daily feed to the suspended growth units could be pyrolysis wastes when operating at a 15 day SRT and LRT. When operating in the anaerobic contact mode, with an SRT of 15 days and an LRT of 5 days, a pyrolysis wastes feed rate of 51% of the total feed was possible without inhibition.

Once acclimated to the PUROX wastes, the suspended growth anaerobic biological systems were able to remove 70% of the COD of the pyrolysis wastes.

The attached growth anaerobic units consisted of two sets of two columns in series, each four feet in height. Thus total column depth

was eight feet. The columns were 5-1/2 inches in diameter and were filled with 5/8 inch plastic media. The columns were fed various percentage mixtures of a soluble synthetic substrate and the PUROX pyrolysis wastes. The temperature of the columns was maintained at $35^{o}C$.

As with the suspended growth units, it was necessary to acclimate the attached growth reactors to the pyrolysis wastes. This was done by feeding pyrolysis wastes at a very low initial rate. Over a period of 45 days, the rate of pyrolysis wastes feed was increased from 5% of the total feed COD to 45% of the total feed COD (33.3% of the volume). This 45% rate of pyrolysis waste feed resulted in inhibition of the reactors. It was found that the maximum rate of feed of pyrolysis wastes without inhibition was approximately 30% on a COD basis (22.2% on a volume basis).

Under equilibrium operational conditions, it was estimated that the anaerobic columns were removing approximately 70% of the COD of the pyrolysis wastes.

The application of activated carbon to the PUROX pyrolysis wastes was also investigated. Adsorption isotherms developed for both the raw pyrolysis wastes and the effluent from the anaerobic reactors indicated a high level of adsortive capacity. Carbon column tests, however, indicate that application of carbon to the raw pyrolysis wastes is not economically feasible. The costs of such treatment would be about $0.23 per gallon. However, application of carbon columns to the effluent from the anaerobic reactors may be feasible. The estimated cost of such an application is $0.0084 per gallon of anaerobic reactor effluent.

Practical systems for the treatment of the PUROX pyrolysis wastes may include suspended growth anaerobic reactors receiving mixtures of pyrolysis wastes and the usual sludges from a city (to provide the necessary dilution for the pyrolysis wastes). Another practical system might include the treatment of the pyrolysis waste in an anaerobic column using wastewater from a municipal treatment plant for dilution water.

The effluent from the anaerobic units is still relatively high in organics and contains organic compounds which may be toxic. Therefore, the effluent could not be discharged directly to the environment. It would be necessary to treat the effluent by one or a combination of activated sludge, activated carbon, or chemical oxidation using ozone, hydrogen peroxide, chlorine, or chlorine dioxide.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

INTRODUCTION

1.0 BACKGROUND

This research project resulted from a proposal submitted by the writer to the U.S. Energy Research and Development Administration (now the U.S. Department of Energy) in July, 1976. The proposal was subsequently accepted and funded and the project began on July 1, 1977.

At the time this work began it was known that the liquid wastes from the scrubbing of product gases from the pyrolysis of municipal refuse were extremely high in organic pollutants. It had been reported by Union Carbide (Linde Division) that the wastewaters from their PUROX* process had a 5-day biochemical oxygen demand (BOD_5) and chemical oxygen demand (COD) averaging 52,000 mg/l and 77,000 mg/l, respectively. Prevelant concepts for handling the wastewaters at that time were to discharge them to the sewer or to treat them with an activated sludge process.

Anaerobic biological processes are ideal for application to the treatment of strong wastes. Rather than requiring an energy input, as do aerobic biological processes, a net energy output is possible as a result of methane (CH_4) gas production. Thus the process not only produces a fuel gas, but also eliminates the need to apply energy to treat the wastewaters aerobically. It was estimated that the anaerobic alternative to the treatment of PUROX pyrolysis wastewaters had the potential of increasing the net energy output from the PUROX process

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* Trade mark of the pyrolysis process patented by the Linde Division of Union Carbide Corporation

by about five percent (as a result of methane generation) and also to reduce the total oxygen consumption by about ten percent. Thus anaerobic processes appeared to offer great potential for making the PUROX pyrolysis process more cost and energy effective when applied to municipal refuse.

2.0 PURPOSE AND SCOPE OF RESEARCH

The purpose of this research was to evaluate the application of anaerobic biological treatment systems to the treatment of pyrolysis gas scrubber wastewaters. Specifically, the wastewaters from Union Carbide's PUROX process were to be evaluated. The basic questions that were foreseen as being important were listed in the original proposal as follows:

1) Is the wastewater treatable under anaerobic conditions?

2) What degree of treatment can be expected in terms of BOD and COD removal?

3) What is the quantity and quality of the gas produced?

4) How much excess sludge is produced?

5) What is the effect of the low wastewater pH on treatment performance and what is necessary to solve this potential problem?

6) Is the addition of N and P required for effective treatment and, if so, in what quantities?

7) What is the effect of temperature, detention time, and organic loading on the performance of the anaerobic system?

8) How does the anaerobic filter and the completely mixed reactor compare on the basis of performance and potential for full-scale application?

9) Based on the answers to questions 1 through 8, does the aerobic or anaerobic alternative offer the most cost and energy effective approach to the treatment of pyrolysis gas scrubbing wastewaters?

As is often the case in research, the scope of the work expanded considerably as the project progressed. As discussed in detail later, it was found that the pyrolysis wastewaters contained highly toxic organics that were strongly inhibitory to the anaerobic biological processes. As a result of this, question 1 above (Is the wastewater treatable under anaerobic conditions?) tended to dominate the entire project. Also, these problems lead to attempts to pretreat the PUROX wastewaters to enhance their biological treatability.

3.0 PROCEDURES

This research followed three major, inter-related tracks over the three-year project length as follows:

Track A: Suspended Growth Anaerobic Experiments

Track B: Attached Growth Anaerobic Experiments

Track C: Carbon Treatment Experiments

Specific details on the procedures followed for each research track are presented in Chapters IV, V and VI of this report. Only general procedures are described here.

The suspended growth experiments involved the use of three, five-liter anaerobic reactors that were fed a combination of primary wastewater sludge and PUROX pyrolysis wastes. The units were operated at a temperature of 35^{o}C at all times, but in a variety of solids retention time (SRT) modes and percentages of pyrolysis wastewater feed.

The attached growth experiments involved the use of two anaerobic columns filled to a depth of four feet with 5/8 inch plastic media. The columns were operated in a variety of modes in terms of feed rates and percentages of synthetic substrate and pyrolysis wastes in the raw feed.

The carbon experiments involved the determination of isotherms for the raw PUROX wastewater and the passage of the wastes through laboratory-scale columns to evaluate the effectiveness of carbon in removing organics. Other experiments with carbon involved the direct addition of powdered activated carbon to the suspended growth anaerobic reactors.

CHAPTER II

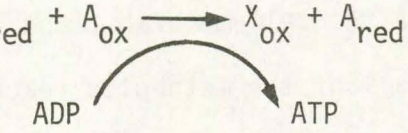
LITERATURE REVIEW

1.0 ANAEROBIC SYSTEMS

1.1 General Microbiology

All forms of living organisms perform a series of chemical reactions in which some are exothermic and others are endothermic. The principal carrier of biologically utilizable energy is adenosine-5'-triphosphate (ATP), and all energy-requiring processes in living cells are directly or indirectly coupled to the conversion of ATP to adenosine-5'-diphosphate (ADP). ATP contains a high-energy phosphate bond which upon hydrolysis provides energy for reactions within the cell. There are two basic mechanisms of generating ATP and ADP: electron transport phosphorylation and substrate-level phosphorylation. The first mechanism involves the flow of electrons through electron transport systems coupled to the synthesis of ATP from ADP and inorganic phosphate. Substrate-level phosphorylation refers to the transfer of a high energy phosphate group from an organic compound to ADP (1).

Most bacteria gain ATP by chemical reactions and are termed chemotrophs. These are commonly oxidation-reduction reactions where one substrate is reduced at the expense of a second:



Higher organisms can only use organic substrates as electron donors (X_{red}) and oxygen as electron acceptor (A_{ox}). However, in microbial

metabolism, alternate donors and acceptors can be employed. Bacteria can use oxygen, nitrate, sulfate, carbon dioxide, or organic compounds as terminal electron acceptors. The electron donor can be an inorganic or an organic compound (1). The chemotrophic bacteria are divided into two groups: chemolithotrophs, those which use inorganic electron donors as energy sources, and chemoorganotrophs, those using organic electron donors (1,2). Table II-1 shows the various types of metabolism carried out by chemotrophic bacteria. The bacteria of importance in anaerobic systems are the chemoorganotrophs which use sulfate and organic substrates as terminal electron acceptors and the chemolithotrophic bacteria which reduce carbon dioxide to methane or acetate.

Most of the chemical reactions involved in bacterial metabolism are catalyzed by enzymes. These are proteins that the organism must synthesize in response to inducers or depressors and they must bear some structural resemblance to the compound involved in the reaction. Because they are extremely specific in the compounds in which they will act upon, the metabolic activities of microorganisms are controlled by the variety of enzymes they possess. There are two basic enzyme groupings: extracellular (or exoenzymes), which are responsible for hydrolyzing large molecules to a sufficiently small size so that they can pass through the cell membrane, and intracellular (or endoenzymes), which carry on all of the metabolic reactions within the cell. When enzymes act in a sequence, such that the product of one enzyme reaction are known as metabolic pathways.

Enzymes are large molecular weight proteins which are susceptible to influences and agents that are known to affect proteins. With

Table II-1. The Two types of Chemotrophic Metabolism

Type	Electron Donor	Electron Acceptor	Carbon Source	Examples
Chemoorganotrophy	organic substrate	O_2	organic substrate	pseudomonads bacilli
	organic substrate	NO_3^-	organic substrate	
	organic substrate	SO_4^{2}	organic substrate	sulfate reducers
	organic substrate	organic substrate	organic substrate	clostridia, lactic acid bacteria
Chemolithotrophy	H_2	O_2	CO_2	hydrogen-oxidizing bacteria
	H_2S	O_2	CO_2	thiobacilli
	H_2S	NO_3^-	CO_2	*Th. denitrificans*
	Fe^{2+}	O_2	CO_2	*Th. ferrooxidans*
	NH_3	O_2	CO_2	*Nitrosomonas*
	NO_2^-	O_2	CO_2	*Nitrobacter*
	H_2	CO_2	CO_2	methanogenic bacteria
	H_2	CO_2	CO_2	*Acetobacterium*

From Reference 1

the exception of thermophilic species, enzymes are rapidly denatured at temperatures of 50°C and over. Their catalytic activities are notably affected by pH and heavy metal ions interfere with their active sites (3). Enzymes normally function with the aid of a prosthetic group called a coenzyme. These are complex heat-stable compounds which must be present in many enzymatic reactions and often function as carriers.

When a new substrate enters a bacterial environment, the ability of the organism to catabolize the compound largely depends upon its abaility to synthesize the enzymes necessary to enter the compound into the metabolic pathways present within the microbe. This synthesis may or may not occur, depending upon the organic compound and the broadness of the substrate specificity present in the microorganism. If catabolism of the new substrate is possible, the production of new enzymes will take time and it is commonly referred to as an acclimation period.

1.2 Anaerobic Metabolism

The anaerobic decomposition of complex organic matter to carbon dioxide and methane involves a wide variety of interacting species of bacteria. Complex organics, such as cellulose, lipids, proteins, and carbohydrates, are hydrolized and fermented to acetate, short chain organic acids, alcohols, H_2 and CO_2 (4). These products are then further reduced to CO_2 and CH_4. Until recently, anaerobic digestion was thought to be accomplished by two basic groups of bacteria: the acid formers and the methane formers. However, new techniques to grow methanogenic bacteria in pure cultures has led to a greater understand-

ing of their catabolic activities. It is now widely accepted that methanogenic species cannot degrade compounds other than methanol, formate, acetate, CO_2 and H_2 (1,4,5,6,7,8). Therefore, the two-step theory of anaerobic decomposition must be modified to include an intermediate group of bacteria which produce acetate, CO_2 and H_2 from the organic acids and alcohols produced by the acid formers.

The first stage of anaerobic digestion is performed by a wide variety of fermentative bacteria. Some are facultative anaerobes while others are strictly anaerobic species. Their reactions include hydrolysis of polysaccarides, cellulose and proteins and subsequent fermentation to H_2, CO_2, alcohols, acetate, lactate, propionate, butyrate, and other fatty acids. They include the lactic acid bacteria (genera *Lactobacillus, Sporolactobacillus, Streptococcus, Leuconostoc, Pediococcus,* and *Bifidobacterium*), the butyric acid bacteria (genera *Clostridium, Butyrivibro, Eubacterium,* and *Fusobacterium*), and the mixed acid and butanediol bacteria (genera *Escherichia, Salmonella,* and *Shigella*)(1). These acid forming bacteria are faster growing and generally less sensitive to pH or dissolved oxygen than the methanogenic species. They generally are not the rate limiting step in digestion processes except that the hydrolysis of insoluble macromolecules could be rate limiting in some systems (6,9).

The products of the acid forming bacteria other than those used by the methanogenic species are decomposed by the acetogenic bacteria. These organisms degrade long-chain fatty acids, alcohols and other organic acids to acetate, H_2 and CO_2 which can be utilized by the methanogens.

A well documented example of an acetogenic bacterium is in the degradation of ethanol. *Methanobacillus omelianskii* was thought to produce methane from ethanol. It was shown, however, that this fermentation was actually accomplished by the synergistic association between two different species of bacteria. The first, an acetogenic organism termed the S organism, oxidizes ethanol with water to acetate and H_2. This was thermodynamically possible only if the partial pressure of H_2 was kept quite low by the second organism, *Methanobacterium* MoH, which utilized CO_2 and H_2 to form methane (1,4). Similarly, *Desulfovibrio* species will only oxidize ethanol and lactate, in the absence of sulfate, when methanogens are present to keep the pH_2 sufficiently low. The acetate, CO_2 and H_2 produced can then be utilized by the methanogens (4,10).

McInerney et al. (8) recently isolated an anaerobic bacterium that degraded the even-numbered carbon fatty acids, butyrate, caproate, and caprylate to acetate and H_2. This bacterium was also able to degrade the odd-numbered carbon fatty acids, valerate and heptanoate, to acetate, propionate, and H_2. This acetogenic bacteria could only be grown in the presence of a H_2 utilizing organism such as *Methanospirillum hungatti* or a *Desulfovibrio*. Based upon thermodynamic considerations, the growth of this organism depended upon the maintenance of a very low partial pressure of hydrogen, even lower than that required by the acetogenic S organism (4,7,8). McInerney and his co-workers determined that even though this acetogenic bacteria was slow growing (generation time of 84 hours at 35°C) it was present in large numbers in anaerobic digesters. The most probable number of this fatty acid catabolizing

bacterium found in digesters is 4.5×10^6 organisms per gram of wet sludge (8). The vital role of methanogens in the catabolism of long chain fatty acids in anaerobic environments is their ability to maintain a very low partial pressure of H_2.

The methanogenic bacteria are the key to the successful operation of any anaerobic process. They are the microorganisms which actually stabilize the waste to carbon dioxide and methane. They are strictly anaerobic, sensitive to pH, slow growing, and are frequently the cause of digester upsets. They appear as rods, spheres, spirals or aggregates and often display differing intracellular organizations (7). All species are able to couple the oxidation of hydrogen to water with the concomitant reduction of carbon dioxide to methane. Many species can also utilize formate provided they contain the enzyme formate dehydrogenase for conversion to CO_2 and H_2 (1). Acetate is by far the most important methanogenic substrate in anaerobic digestion processes, being used by *Methanosarcina barkeri*, *Methanospirillum hungatii*, and several other species. Tracer studies show that methane is formed entirely from the methyl carbon and the carbon dioxide is exclusively from the carboxyl carbon of acetate. Similar results were obtained with methanol but various strains of *Methanosarcina* are the only species isolated capable of utilizing this substrate (1,3,4,7,11).

Methanogenic bacteria possess two unique coenzymes; F_{420} and C_oM (2-mercaptoethane-sulfonic acid). F_{420} is an electron transport coenzyme which replaces such carriers as Ferredoxin found in other bacteria. It is a strongly fluorescent compound found only in methanogenic species. The use of fluorescence microscopy is therefore an easy

way to identify methanogens in mixed cultures (1,12). C_oM serves as the active carrier of the methyl group during methane formation.

1.3 Interspecies Hydrogen Transfer Among Anaerobic Microorganisms

CO_2 and H_2 are the preferred substrates of all methanogens and these compounds are rapidly removed from digester environments. By effectively removing H_2, methanogens maintain a low pH_2 which causes changes to occur in the metabolic activities of the nonmethanogenic population. Fermentative bacteria often reoxidize NADH by reducing organic compounds such as pyruvate to lactate. The low pH_2 created by methanogens permits direct reoxidation of NADH by causing electron flow to shift towards hydrogen production rather than production of organic electron sink products. This causes an increase in production of acetate and H_2 and a decrease in such sink products as lactate, ethanol, and succinate (1,4,7,13,14). This type of nonobligatory interspecies hydrogen transfer between acid forming and methanogenic bacteria benefits both species by (7):

1) Increasing substrate utilization,
2) Increasing ATP generation by nonmethanogens, and
3) Increasing overall growth of both species.

On the other hand, acetogens which convert fatty acids, ethanol, and benzoate to acetate depend upon hydrogen transfer to methanogens to create thermodynamically favorable conditions for these reactions to occur. Interactions of this type appear to be obligatory as studies on fatty acid fermentations have shown that the presence of methanogens or H_2 utilizing *Desulfovibrio* were essential (8).

There is some competition for H_2 among methanogens, sulfate reducers, and acetogenic bacteria in anaerobic environments. Sulphate reducing bacteria can competitively inhibit methanogens by removing H_2 for reduction of sulfate to sulfide (14). However, this phenomenon is not of major concern in digesters where the majority of the methane formed comes from acetate rather than H_2 and CO_2. Because of this alternate energy source the relative numbers of methanogens in digester environments are quite high and competition for H_2 by sulfate reducing bacteria has little overall effect. Certain acetic acid bacteria are capable of utilizing CO_2 and H_2 forming acetate and therefore compete with methanogens for these compounds. However, the relative numbers of these acetate forming bacteria found in digesters is quite low and, because acetate is also a substrate for methanogens, this type of competition does not inhibit the growth of the methanogenic species (15).

1.4 Gas Production

It is well established that acetate is the primary source of methane production in anaerobic digesters, accounting for approximately 70% of the total methane formed (6,7,8,11,16,17). The remaining 30% of the methane comes from the lithotrophic reduction of carbon dioxide with the concomitant oxidation of hydrogen to water. Figure II-1 shows a proposed scheme of substrate flow for the anaerobic stabilization of a wastewater sludge from a typical activated sludge plant. This flow scheme shows the significant effect that H_2 removal by methanogens has upon the microbiology of the nonmethanogens. As previously stated, a low pH_2 in the digester causes oxidation of reduced pyridine dinucleotides or ferredoxins via hydrogen production and allows more acetate

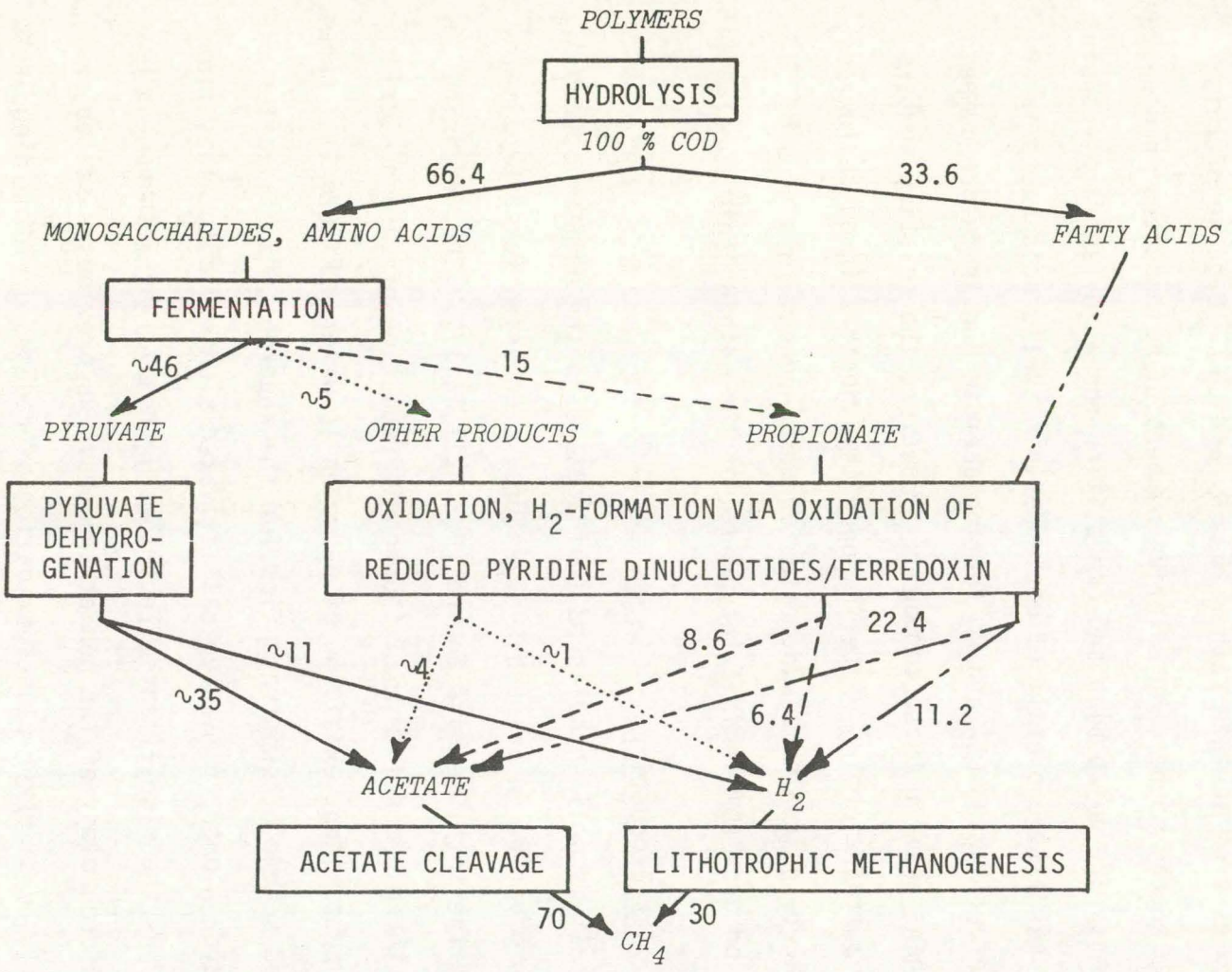


Figure II-1. Sources of Methane Fermentation in the Anaerobic Digestion of Raw Sludge from a Conventional Activated Sludge Plant. Unit: Percentage of COD. (From Reference 6.)

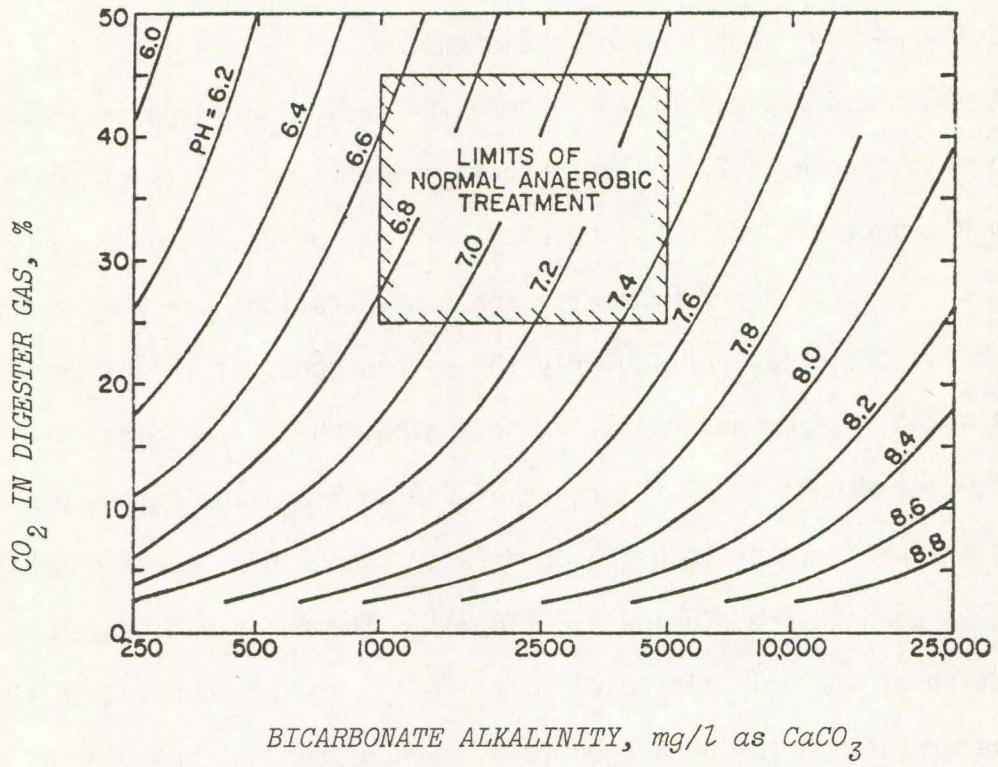


Figure II-3. Relationship between pH and Bicarbonate Concentration near 95°F. (From Reference 21).

1.7 Toxics

Molecular oxygen is toxic to strict anaerobes and its presence must be eliminated in any anaerobic process. When reduced flavoproteins or reduced iron-sulfur proteins come together with oxygen, two toxic compounds are formed: hydrogen superoxide and the superoxide radical. Aerobic bacteria contain catalase and superoxide dismutase for the enzymatic destruction of these compounds. Most aerotolerant anaerobes are devoid of catalase but contain superoxide dismutase. Strict anaerobes lack both of these enzymes and it is generally thought that the toxic effects of the superoxide radical are the cause of this aero-intolerance (1,27). The extreme oxygen sensitivity of the methanogenic bacteria may be associated with the oxidation of F_{420} (7).

Hydrogen and hydroxide ion concentrations can become toxic to anaerobic bacteria, particularly the methanogens, if the pH deviates substantially from neutrality. The optimum pH for the digestion of wastewater sludge is in the range of 6.8 to 7.2. Inhibition occurs when the pH is lower than 6.5 or greater than 7.6. Severe inhibition results when pH drops below 6.2 (18,21). The pH in a digester is a function of the volatile acids, alkalinity, and CO_2 content in the digester gas. A low pH is generally caused when the build-up of fermentation intermediates, namely volatile acids, exceeds the buffering capacity provided by the alkalinity present in the system. This build up of volatile acids can occur when the system is organically overloaded or the methanogenic population becomes inhibited by a toxic material. Figure II-3 shows the relationship between pH, bicarbonate alkalinity, and the CO_2 content of the digester gas. A bicarbonate alkalinity of from 2,500 to 5,000 mg/l generally provides sufficient buffering capacity to maintain pH control in most digesters.

for mesophilic bacteria are around 35°C while the thermophilic optimum is approximately 55°C (18,25,26).

Methanogenic bacteria are very slow growing organisms with regeneration times of from four to ten days at 35°C (18). Anaerobic processes must be designed such that the SRT within the reactor is sufficiently long enough to prevent the hydraulic washout of these vital organisms from the system. The minimum solids retention time (SRT min.) is defined as the shortest SRT which prevents washout of the methane forming bacteria. Since growth rates for bacteria are a function of temperature, the SRTmin is also temperature dependant. At 95°F the SRTmin equals ten days while this value doubles for each 20°F drop in temperature (21). The SRT of a reactor is defined as:

$$SRT = \frac{\text{total weight of suspended solids in the system}}{\text{total weight of suspended solids leaving the system per day}}$$

In a single stage completely mixed digester the SRT is equal to the hydraulic detention time. Most single stage digesters operate with a SRT of about 30 days to provide adequate stabilization of the sludge. In a two-stage digester sludge is settled and recycled from the second digester into the first such that the SRT is longer than the hydraulic detention time. A further advancement of this concept is the anaerobic contact process where hydraulic retention times are as low as six to twelve hours with loadings up to 4.0 Kg volatile solids/m^3-day (25). The SRT of an anaerobic contact process is largely dependent upon the ability of the sludge to settle and concentrate prior to recycle to the contact tank. Anaerobic filters are capable of maintaining very long SRTs as most of the solids remain in the system attached to some type of media.

poses approximately 11 percent of the dry weight of bacterial cells and therefore it is required in relatively large quantities for growth to occur. Phosphorus is also important because it accounts for about two percent of the dry weight of bacterial cells. However, since the cell yields for anaerobic bacteria are much lower than those found in aerobes, the nutrient requirements for anaerobic processes are significantly less (1,21). Sanders and Bloodgood determined that the minimum carbon to nitrogen ratio for anaerobic digestion was 0.0620 and substrates with a lower ratio would require supplemental nitrogen (23). In addition, trace amounts of sulfur, calcium, cobalt, copper, iron, magnesium, manganese, potassium, selium, and zinc are required for synthesis of certain cellular compounds. Domestic wastewater will provide all of the required nutrients for bacterial growth but many industrial wastes may be deficient in certain major nutrients such as nitrogen and phosphorus (21).

Temperature plays a key role in the regulation of metabolic activities of microorganisms. Growth rates and substrate removal rates generally increase with rising temperatures until an optimum is reached where further temperature increases result in a rapid decrease in activity and subsequent death. This is generally due to the denaturization of proteins within the bacteria at elevated temperatures. Most bacteria function within the temperature range of 20 to 45^{o}C and are termed mesophilic. However, some species of bacteria have adapted to higher temperature environments and are capable of survival and growth between 50 to 80^{o}C. These bacteria are termed thermophilic and are very similar to the mesophilic bacteria except that they possess macromolecules which are extremely heat stable (24). Optimum temperatures

production due to endogenous kinetics and the destruction of dead cellular material. Carbohydrates produce the largest cell yields while fatty acid metabolism results in very low solids production. This relationship between cell yield and substrate type is caused by the different ATP yields that occur during fermentation of these compounds. A study with an anaerobic filter, similar to the one used in this project, showed biological solids production to be 0.12 gram VSS/gram COD destroyed with a protein-carbohydrate waste. Operation on a volatile acids substrate produced only 0.015 gram VSS/gram COD removed (22). Comparison of these cell yields with Figure II-2 shows the advantage of anaerobic filters over conventional digestion processes in their ability to maintain much longer SRTs.

1.6 Environmental Requirements

Anaerobic bacteria require certain environmental conditions in order to digest organic material and maintain adequate growth. These requirements are: contact with food, availability of nutrients, proper temperature, adequate time for growth, and freedom from toxic materials.

Digestion cannot occur without the actual contact of the bacterial with the substrate. Some mixing does occur due to gas production within the reactor but it is not sufficient to prevent "dead zones" from forming in the lower corners of the digester. Most anaerobic processes use some form of mechanical mixing to increase digester performance.

The nutritional requirements for the growth of anaerobic bacteria are similar to those of aerobic heterotrophs. Nitrogen com-

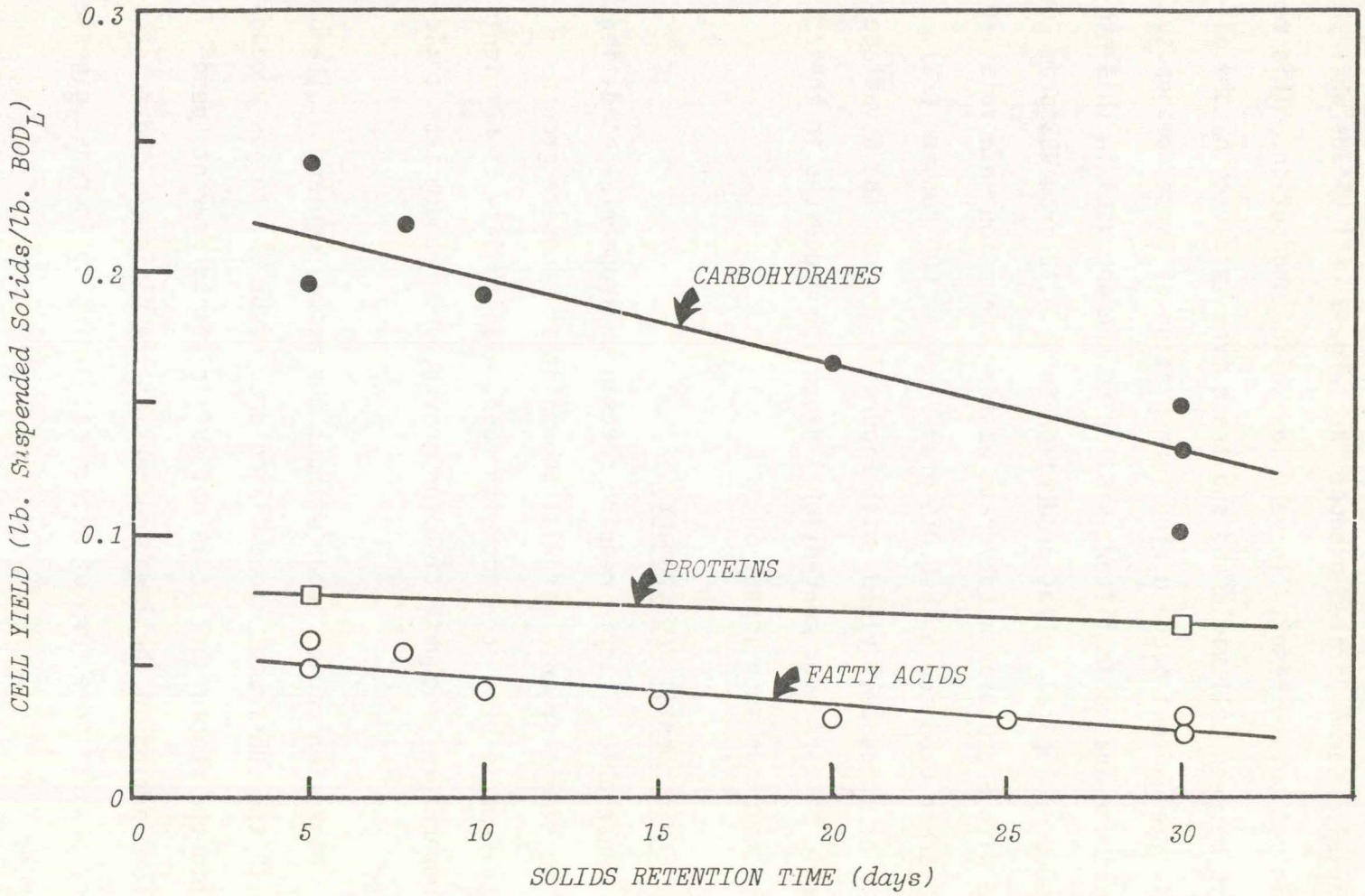


Figure II-2. Biological Solids Production Resulting from Methane Fermentation. (From Reference 21.)

the destruction of one pound of ultimate BOD, this converts to 0.35 liters CH_4/gram BOD destroyed (21). Total gas production would be 30 to 50 percent higher to account for the carbon dioxide content.

1.5 Solids Production

A comparison of aerobic and anaerobic metabolism reveals a major difference in the production of biological solids. Aerobic heterotrophs couple the oxidation of organic substrates to the reduction of oxygen or nitrate. This involves respiratory chains with high ATP yields and the substrate is almost completely converted to cellular material, carbon dioxide, and water. Fermentative anaerobes carry out oxidation-reduction reactions which result in little ATP generation. Therefore, the amount of cells obtained per mole of substrate is much smaller than with aerobes and, in addition to cellular material, large amounts of fermentation end products are formed (1). The anaerobic conversion of carbohydrate to methane and carbon dioxide yields a ten percent decrease in the potential energy, but ninety percent of the energy available through oxidation of the initial carbohydrate remains in the fermentation end product, methane (16). The greatest advantage of anaerobic treatment processes over their aerobic counterparts is that they stabilize organic wastes to a useful, high-energy end product rather than converting much of this available energy source to the production of microbial cells.

The biological solids generated from an anaerobic process is a function of the substrate composition and the solids retention time (SRT) in the reactor. Figure II-2 shows the relationship between cell yields, feed composition, and SRT. Longer SRTs result in lower sludge

production from pyruvate. The significance of acetate and H_2 production from fatty acids and other fermentation products by acetogenic bacteria is also shown.

Methane and carbon dioxide are the major components of digester gases. However, trace quantities of hydrogen sulfide, nitrogen, hydrogen, and oxygen may also be present. Approximately 65 to 75 percent of digester gas is composed of methane while the remainder is mostly carbon dioxide (18,19). The methane to carbon dioxide ratio depends upon the type of waste and the bicarbonate chemistry within the reactor. Table II-2 shows the specific gas production, the composition and heating value of gas produced from the three basic substrate groups (20). The total gas production per gram of substrate is higher for organic fats than that produced from hydrocarbons or proteins.

Table II-2. Gas Characteristics from Different Substrates

Substrate type	Total Gas Production (cm^3/gram)		Heating Valve (Kcal/Nm^3)
Hydrocarbons	800	50% CH_4 + 50% CO_2	4,250
Proteins	700	70% CH_4 + 30% CO_2	5,950
Organic fats	1200	67% CH_4 + 33% CO_2	5,650

From Reference 20.

Methane production in digesters is generally about 0.5 to 0.7 liters per gram organic matter destroyed (4,19). Theoretical considerations show that 5.62 cubic feet (STP) of methane are produced by

The alkali and alkaline-earth cations are stimulatory to anaerobic bacteria at lower concentrations but become inhibitory at higher levels. These cations include sodium, potassium, calcium, and magnesium. Table II-3 shows the effect that these cations have on anaerobic systems.

Table II-3. Stimulatory and Inhibitory Concentrations of Alkali and Alkaline-Earth Cations (mg/l)

Cation	Stimulatory	Moderately Inhibitory	Strongly Inhibitory
Sodium	100 - 200	3,500 - 5,500	8,000
Potassium	200 - 400	2,500 - 4,500	12,000
Calcium	100 - 200	2,500 - 4,500	8,000
Magnesium	75 - 150	1,000 - 1,500	3,000

From Reference 21.

Sulfide levels in trace amounts are almost stimulatory but become toxic at concentrations exceeding 200 mg/l. Ammonia concentrations in the range of 1,500 to 3,000 mg/l are inhibitory while concentrations greater than 3,000 mg/l are strongly toxic (21).

Certain heavy metals such as cadmium, lead, zinc, nickel, copper, and mercury are toxic to anaerobic bacteria. Most heavy metals will precipitate from solution in the presence of sulfides which are produced from the degradation of proteins and the reduction of sulfates (28). However, metal concentrations may exceed the capacity of sulfides to precipitate them in some industrial wastes.

Certain organic compounds will exhibit toxicity to anaerobic bacteria. Synthetic detergents such as aliphatic sulphonates and

alkyl aryl sulphonates are toxic. Chlorinated hydrocarbons and similar organic solvents, such as chloroform, are extremely toxic (28). Such molecular structures as chloro substitutions, aldehydes, double bonds, and benzene rings exhibit tocicity to unacclimated anaerobic bacteria. However, prolonged acclimation over several months will result in high levels of degradation of aldehydes, alcohols, and esters. Chloro substituted petrochemicals remain refractory even after long acclimation periods (29).

There are four basic methods to control toxic materials in anaerobic systems (21):

1) Remove the toxic material from the waste,
2) Dilute below the toxic threshold,
3) Form an insoluble complex or precipitate,
4) Antagonize the toxicity with another material.

2.0 ANAEROBIC DIGESTION

2.1 History

No reports prior to 1895 suggest anaerobic decomposition as a means of waste stabilization. Anaerobic decomposition was thought to be dangerous from the standpoint of public health. According to Fuller (29):

> "Septicization within the modern sense of the term dates from about 1896, when the so-called septic tank was developed by Mr. Cameron and his associates at Exeter, England."

The septic tank, which was actually a settling tank and digestion tank combined, was widely used for waste treatment in both the U.S. and Europe until 1906 (30). In 1906, Dr. G.L. Travis proposed the use of two-story tanks to separate solids settling from solids digestion. In the following year, Karl Imhoff devised what

became widely known as the "Imhoff tank." Thereafter, the use of the Imhoff tank for wastewater treatment spread rapidly. By 1916, 70 plants in the U.S. were serving a population of 600,000 (30).

Although beset with many problems, the Imhoff tank remained widely employed in new plant construction until well into the 1920's. The success of Imhoff tanks forestalled the use of separate sludge digestion until 1918. It was then that the first "separate" tanks for sludge digestion were constructed at Madison, Wisconsin. Only a few plants employing separate tanks for sludge digestion were installed prior to 1926.

The first mixed digester was put into operation in 1923 at Brownsville, Texas. The first application of sludge heating was at Antigo, Wisconsin, in 1926. According to Kivell (31): "...it was not until the advent of heated digesters that the process could be said to have arrived."

The use of separate, heated digesters spread rapidly after 1926. By 1931, approximately 100 separate sludge digestion systems, serving a population of 3-1/2 million, had been installed in the U.S. (31).

2.2 Solids Retention Time

The critical solids retention time (SRT) in anaerobic digesters operated at 35^{o}C is 10 days (32,33). The effects of SRT on Methane production, 5-day BOD, COD and volatile solids reductions are shown in Figures II-4 and II-5. At SRT levels below 10 days (shaded in Figures II-4 and II-5), gas production and the percentage removal

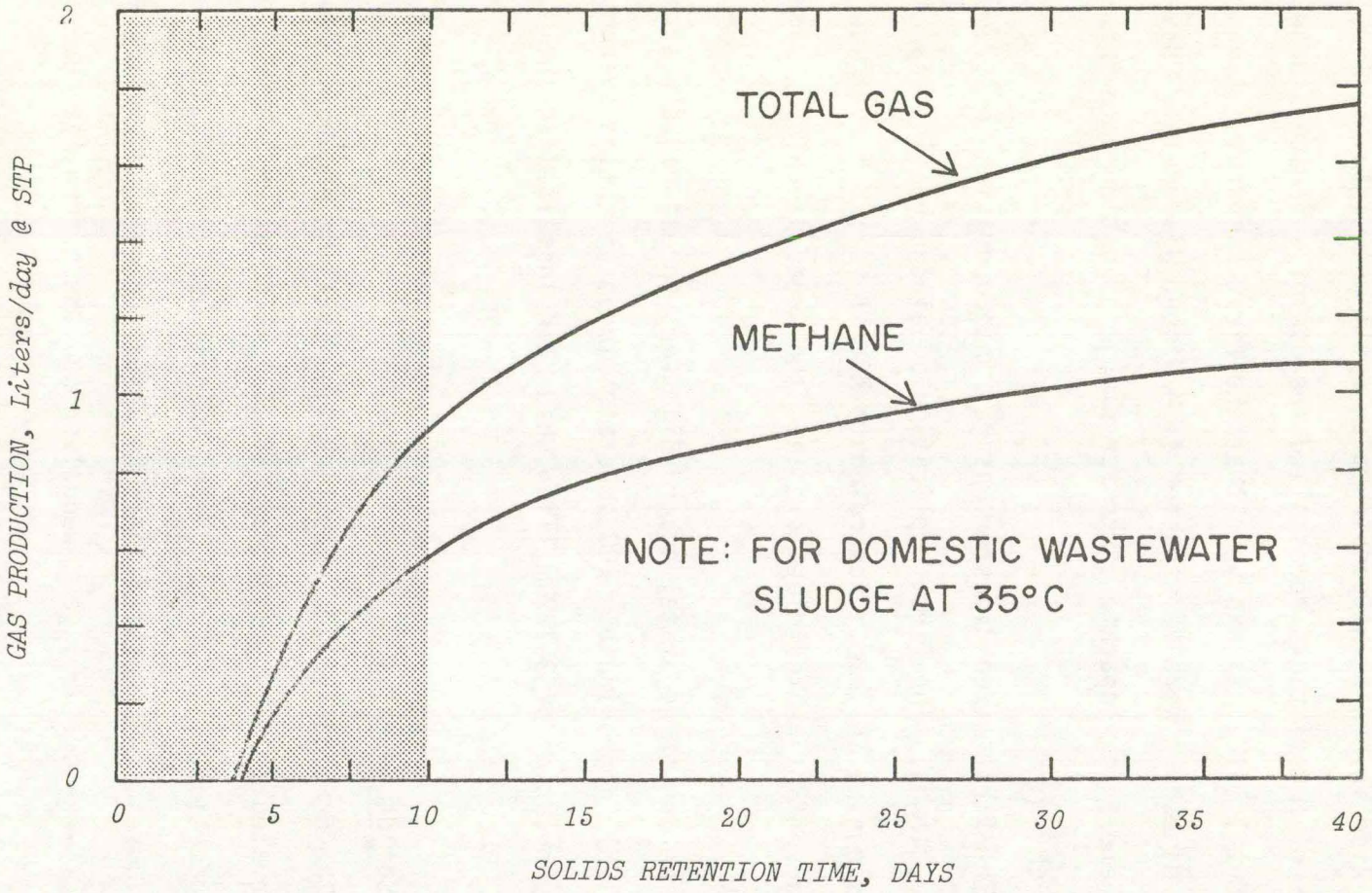


Figure II-4. Effect of Solids Retention Time on Gas Production. (From Reference 32.)

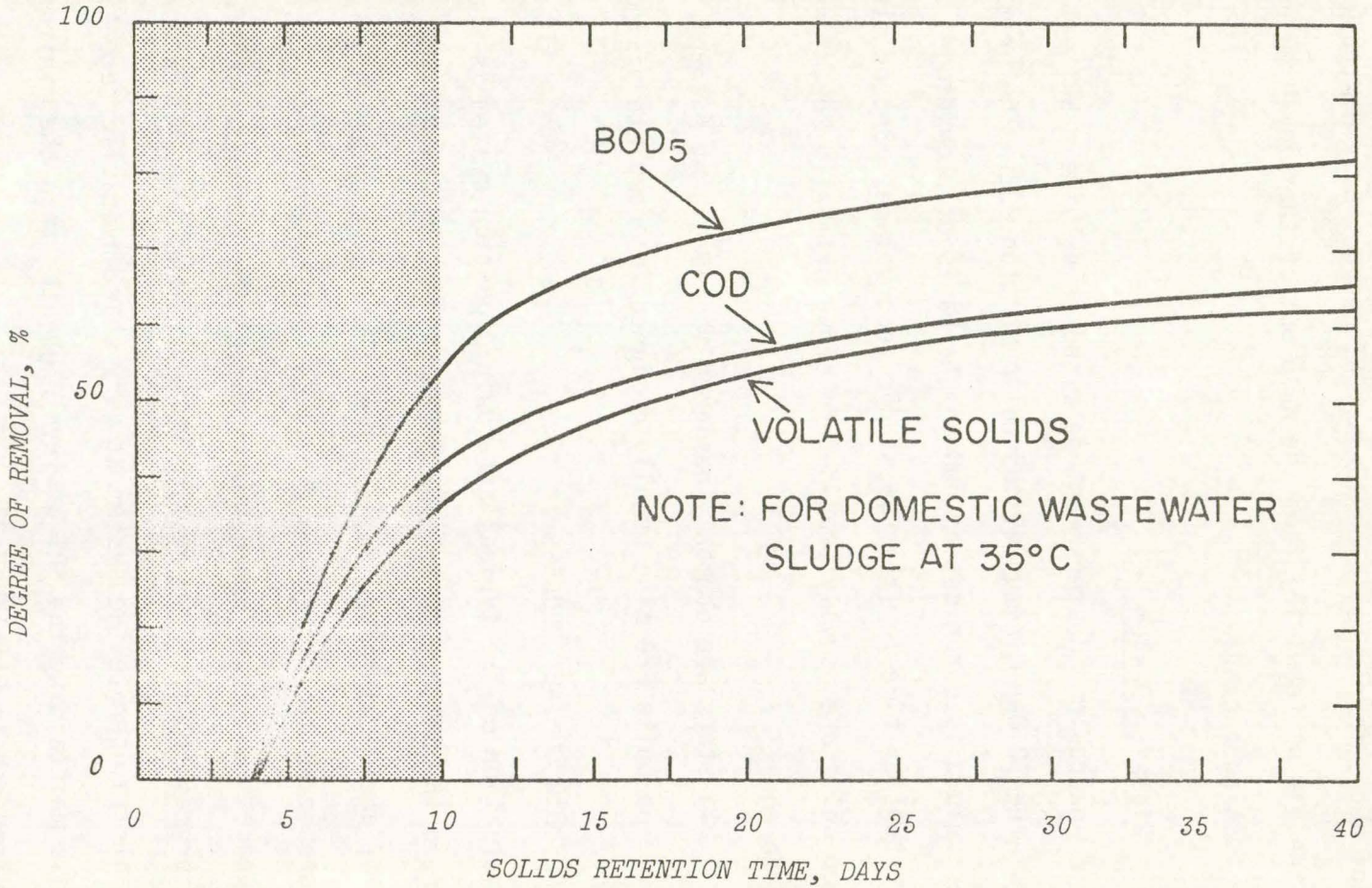


Figure II-5. Effect of Solids Retention Time of BOD_5, COD, and Volatile Solids Reduction. (From Reference 32.)

of BOD, COD and volatile solids decreases rapidly, reaching zero at an SRT of about four days. The 10-day SRT can not be violated without system inhibition resulting from the wash-out of the slow-growing methane forming bacteria.

2.3 Digester Design

Anaerobic digesters must be sized to provide a SRT well in excess of the 10 day minimum discussed in Section 2.2. The primary digester volume is often determined on the basis of providing a 20 to 30 day retention time for the raw sludge feed volume. Second stage digestion units are usually provided to serve primarily for digested sludge storage.

Digesters are commonly designed to operate at a temperature of 35^{o}C. The units are also usually designed for complete mixing.

3.0 ANAEROBIC CONTACT PROCESS

A variation on the typical anaerobic digestion system is what has been termed the "anaerobic contact process". The process involves the recycle of active biological sludge from a solids separation unit to the anaerobic reactor. The process is not unlike the aerobic activated sludge process and therefore has been called the "anaerobic activated sludge" process (34). By recycling solids to the primary reactor it is possible to operate the system at very short hydraulic retention time while maintaining the SRT at levels greater than the minimum values discussed in Section 2.2.

The concept of recycling sludge originated in 1950 when Rawn and Candell reported on research on multi-stage digestion conducted at the

joint disposal plant of the Los Angeles County Sanitation District (35). The digesters in this plant were designed for four-stage operation with the capability of recycling sludge from the bottom of the fourth tank to the top of the first tank. Average detention time for the entire four-tank system was 11 days, but the detention time in the first tank was only four days.

The anaerobic contact process got its true start in 1953 when Fullen reported on studies of the anaerobic digestion of packing plant wastes (36). At that time the treatment process had been under study for 3-1/2 years by Geo. A. Hormel & Co. at Austin, Minnesota. As Fullen reported, the process consisted of mixing the incoming raw waste with an "activated" anaerobic sludge at a temperature of 92^{o} to $94^{o}F$, and then effecting a separation of sludge from the mixture and returning it to the digester.

In 1955, Schroepfer el al., reported on a comprehensive study of the anaerobic contact process as applied to packing-house wastes (37). In these studies BOD removals of 95 percent were achieved at detention times in the 12 to 15 hour range.

Detention times as short as 12 hours were unheard of in an anaerobic process prior to the development of the anaerobic contact process. Over the past 25 years the process has been applied to a great many industrial wastes. In general, the process is most applicable to wastes that are quite strong (BODs over 1,000 mg/l) and also warm so that heat does not have to be added.

4.0 THE ANAEROBIC FILTER

In the anaerobic filter system, the development of a microbial film attached to the filter media provides for the biological conversion of organic wastes to carbon dioxide and methane. The primary advantage of fixed film processes over other biological treatment systems is their ability to retain microbial solids within the reactor for long periods of time without the need of recycling settled effluents. For example, the anaerobic contact process depends upon the ability of a settling tank to concentrate sludge for recycle to maintain a sufficient SRT and microbial mass within the contact tank for stabilization of the waste to occur. The settleability of the sludge coming from the contact tank is a critical factor in the successful operation of any anaerobic contact process (26). However, with an anaerobic filter, soluble organic wastes can be treated with very high efficiencies and low operational costs (22,39).

The fixed film concept has been used in aerobic processes for quite some time. Trickling filters were in operation long before the development of the activated sludge process where suspended solids are settled from the effluent and recycled to the aeration basin. However, the development of the anaerobic filter is relatively new with the first laboratory scale investigation of this process being completed in 1967 (22). This study, done by Young and McCarty, compared the anaerobic filter to other biological processes. They found that the ability of the filter to maintain a longer SRT provided several advantages over other anaerobic systems. The heating of the reactor contents which is required to maintain treatment efficiency in most anaer-

obic processes was not necessary. Young and McCarty observed COD removals of 80% at loadings in excess of 100 lb COD/1000 cubic feet per day while operating the filters at 25°C. Loadings as high as 212 lbs COD/1000 cubic feet per day with liquid detention times as low as 4.5 hours resulted in at least 60 percent removal of COD. Increased removals or higher loadings could be expected with elevated temperatures but heating is not required to provide efficient treatment as in other anaerobic processes. Another advantage of the anaerobic filter design is the low production of excess microbial solids. By maintaining a longer SRT, fixed film reactors produce lower cell yields and sludge wasting and disposal becomes minimal or non-existent. It was also found that anaerobic filters are more capable of accepting shock loads provided sufficient buffering capacity is available to maintain favorable pH conditions. This is similar to aerobic processes where trickling filters are often used to level widely fluctuating organic loads prior to treatment by activated sludge systems.

Since the equipment is not elaborate, sludge disposal is minimal, and heating is not required, the anaerobic filter is a very low cost form of treatment for soluble organic wastes. The application of this process to the treatment of a high-strength wheat starch waste resulted in COD removals of 75-80 percent with operational costs as low as 1.3¢ per pound BOD applied (39). Aerobic alternatives would have required substantially greater initial and operating costs while the use of the anaerobic contact process could have resulted in operational difficulty.

Studies on aerobic fixed film systems haveshown that fluid velocity has a positive effect upon the rate of substrate uptake (40,41).

Maximizing surface to volume ratio is also advantageous in improving performances but only if the surface is well distributed in the nutrient. It was also determined that aerobic microbial film systems operate under zero-order reaction kinetics such that the rate of film growth or substrate uptake is independent of the substrate concentration (40).

One of the difficulties involved with an anaerobic filter study is that the parameters used to evaluate performance, such as COD, pH, and volatile acids concentration, will vary within the reactor. This is due to the plug flow nature of the system and the different types of bacteria present in the filter. In a completely mixed digester the effluent has the same chemical make up as the contents of the reactor. However, in an anaerobic filter the COD, volatile acids concentration, and pH within the system is dependent upon the location the sample is taken from. Figure II-6 shows the relationship that filter height has upon the COD and volatile acids found in the anaerobic treatment of a protein-carbohydrate waste. It is interesting that the volatile acids concentration rises sharply and then gradually decreases with increasing filter height. This shows the rapid fermentation of the waste to intermediates and their subsequent conversion to methane and carbon dioxide. In an anaerobic filter the chemical make-up within the reactor is a function of geometry. Microbial populations will tend to segregate into regions where they are most adaptable. Also, the peak volatile acids concentration and the effluent COD increases with higher organic loadings. Therefore, an anaerobic filter that is operating at maximum loadings will require a

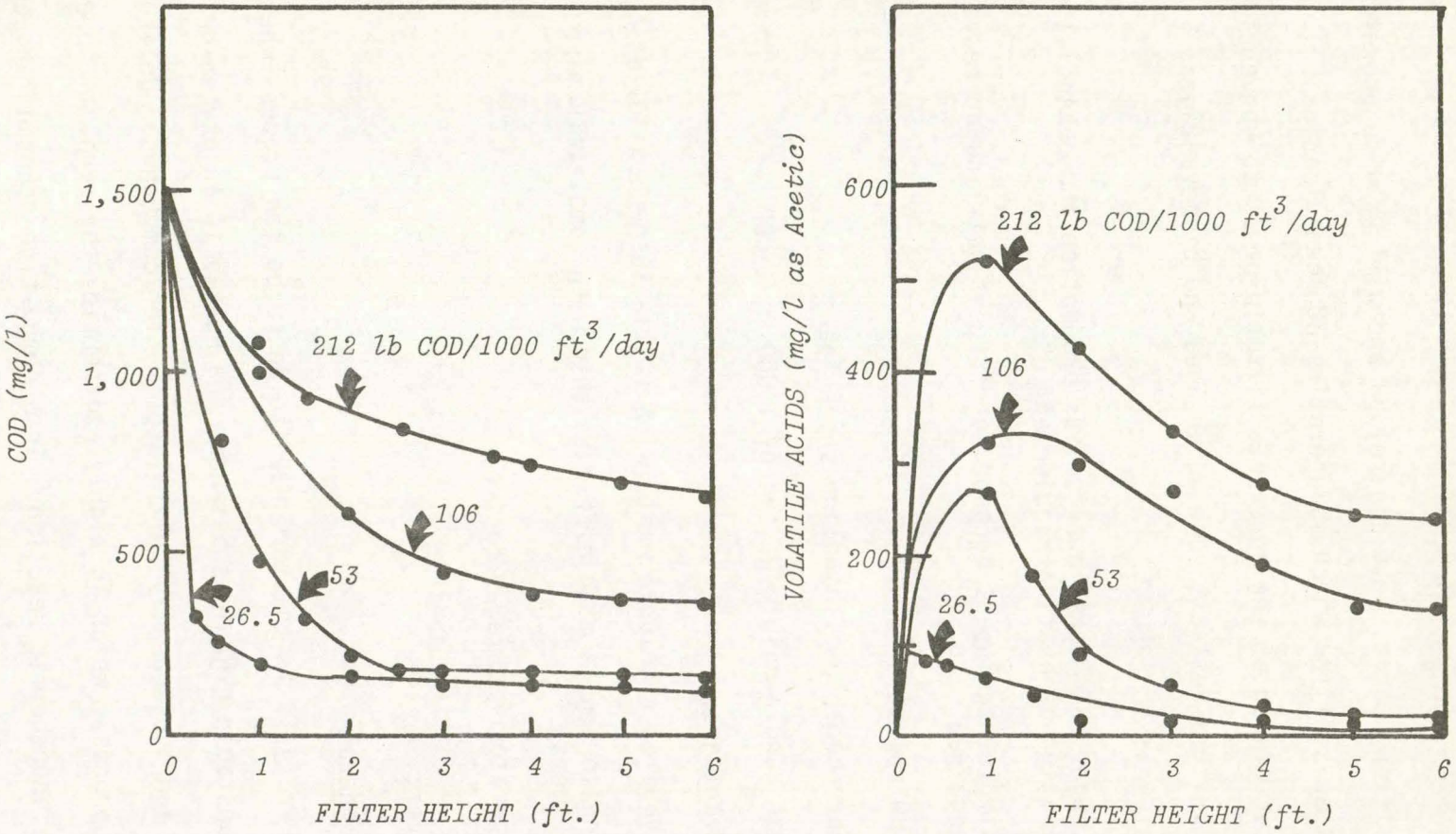


Figure II-6. Anaerobic Filter Processing a Protein-Carbohydrate Waste at Different Loadings. (From Reference 22.)

larger buffering capacity to control pH and will provide poorer COD removals than a filter which is operating at lower loadings.

The comparison of the anaerobic filter process to conventional digestion systems reflects some advantages and disadvantages:

Advantages:

1) Longer SRT means lower solids production and potential elimination of heating requirement.

2) Simpler equipment because no effluent settling or recycle is required.

3) Low operating costs.

4) More capable of handling shock loads.

5) Can handle dilute wastes of 1,000 mg/l COD.

Disadvantages:

1) Requires a soluble waste with little suspended solids.

2) Monitoring is more difficult than with completely mixed systems.

3) Operator has fewer controls.

5.0 PYROLYSIS

5.1 General

Pyrolysis is the term used to describe the process where thermally unstable organic substances are heated in an oxygen-deficient atmosphere and subsequently split into smaller compounds. Unlike the combustion process, which is highly exothermic, the pyrolytic process is a highly endothermic reaction. In a combustion reaction the energy of the organic compound is released by oxidation with air. This results in end products such as carbon dioxide, water, and inert ash material. However, in a pyrolysis reaction the organic substance is subjected to

extreme temperatures and, in the absence of oxygen, undergoes a combination of thermal cracking and condensation reactions. This results in end products which contain high levels of energy and are valuable as fuels or raw materials. The three major component fractions resulting from a pyrolytic process are:

1. A combustible gas composed primarily of hydrogen, methane, carbon monoxide, and carbon dioxide.
2. A liquid that contains pyrolytic oils, water and condensible organics such as acetone, methanol, acetaldehyde, and formic acid.
3. A solid residue consisting primarily of a carbon char plus any inert materials which have entered the process.

The relative yields of these end products varies dramatically with the temperature at which the pyrolysis process is carried out (42,43). Table II-4 shows data of pyrolytic yields as a function of the operating temperature. Higher pyrolysis temperatures favor the production of gases while lower temperatures produce more liquid and solid fractions. Gas composition also varies with pyrolysis temperature. Table II-5 shows that the production of hydrogen greatly increases while carbon dioxide content decreases at elevated temperatures. However, the composition of the liquid stream does not change drastically with temperature, as shown in Table II-6. The volatile matter found in the char product decreases with increasing pyrolytic temperatures as would be expected (43).

Several major pyrolysis processes are currently under development in the United States and are listed in Table II-7. Each system is designed to operate under different reaction conditions so that the desired end products vary with each process.

Table II-4. The Effect of Temperature on Pyrolysis Yields

Product Yield	Percent of Weight			
	900°F	1200°F	1500°F	1700°F
Gases	12.33	18.64	23.69	24.36
Oils, Water, and all condensibles	61.08	59.18	59.67	58.70
Char	24.71	21.80	17.24	17.67
Accountability	98.12	99.62	100.60	100.73

From Reference 46.

Table II-5. Gases Evolved by Pyrolysis

Gas	Percent by Volume			
	900°F	1200°F	1500°F	1700°F
H_2	5.56	16.58	23.55	32.48
CH_4	12.43	15.91	13.73	10.45
CO	33.50	30.49	34.12	35.25
CO_2	44.77	31.78	20.59	18.31
C_2H_4	0.45	2.18	2.24	2.43
C_2H_6	3.03	3.06	0.77	1.07
Accountability	99.74	100.00	100.00	99.99

From Reference 46.

Table II-6. The Effect of Pyrolysis Temperature on Organic Product Composition

Pyrolysis Temperature, °C (°F)	649 (1200)	816 (1500)
Weight % of Condensible Organics		
Acetaldehyde	13.0	10.5
Acetone	18.0	16.5
Methylethylketone	4.3	4.9
Methanol	20.6	23.5
Chloroform	1.0	2.1
Toluene	1.3	3.2
Formic Acid	14.4	11.2
Furfural	7.2	8.0
Acetic Acid	1.3	2.1
Methylfurfural	6.9	6.7
Naphthalene	1.6	1.8
Methylnaphthalene	1.3	1.4
Phenol	6.5	5.6
Cresol	2.6	2.5
	100.0	100.0

From Reference 43.

Table II-7. Large-Scale Pyrolysis Systems in the U.S.

Location	Key Participants	Process	Announced Tonnage	Products	Start-up Date
Baltimore, Maryland	Monsanto Environ-Chem Systems, Inc; City of Baltimore; EPA	Landgard™ Process: shredding, water quenching, magnetic separation	100 TPD	Stream, Ferrous, Glassy Aggregate	1975
El Cajon, California	Occidental Petroleum Corp; San Diego Co; EPA	Flash Pyrolysis™ process: shredding, air classification, magnetic, and other mechanical separation, froth flotation	200 TPD	Pyrolytic oil, ferrous aluminum, glass cullet	----
Erie County, New York	Carborundum Torrax, Inc: Erie County; EPA	Slagging pyrolysis system	75 TPD	Pyrolysis gas/steam	1974
S. Charleston, W. Virginia	Linde Division, Union Carbide Corp.	Purox™ oxygen converter, shredding	200 TPD	Pyrolysis gas, slag	1975

From reference 44.

5.2 Union Carbide PUROX Process

The PUROX system being developed by Union Carbide is a combination incineration-pyrolysis process to convert municipal solid wastes to a medium BTU fuel gas. The process can best be described by referring to Figure II-7. Solid wastes are first shredded and then passed through a magnetic separator to prepare the refuse for pyrolysis. This waste is then fed into a vertical shaft furnace through a charging lock located at the top. Pure oxygen is injected into the combustion zone at the bottom of the furnace where it reacts with the carbon char residue from the pyrolysis zone. Temperatures in this lower portion of the furnace are around 3000^{o}F and are sufficiently high to melt and fuse all of the noncombustible materials remaining from the process (44,45). This molten material overflows from the hearth into a water quench tank where it forms a hard, sterile granular product.

The hot gases formed by the reaction of oxygen and carbon char rise upward through the descending waste. In the middle portion of the furnace the refuse is pyrolyzed under an essentially reducing atmosphere to form a gaseous product high in carbon monoxide and hydrogen. As these gases continue to rise they dry the incoming material at the top of the furnace. This action further cools the product gas so that it exits the refuse converter at a relatively low temperature (about 200^{o}F) (45,46).

As it leaves the furnace, the gas mixture contains water vapor, some oil mist, various condensated organics, and fly ash. A gas-cleaning system is used to remove the undesirable components. The resultant gas is a valuable clean burning fuel. The typical composi-

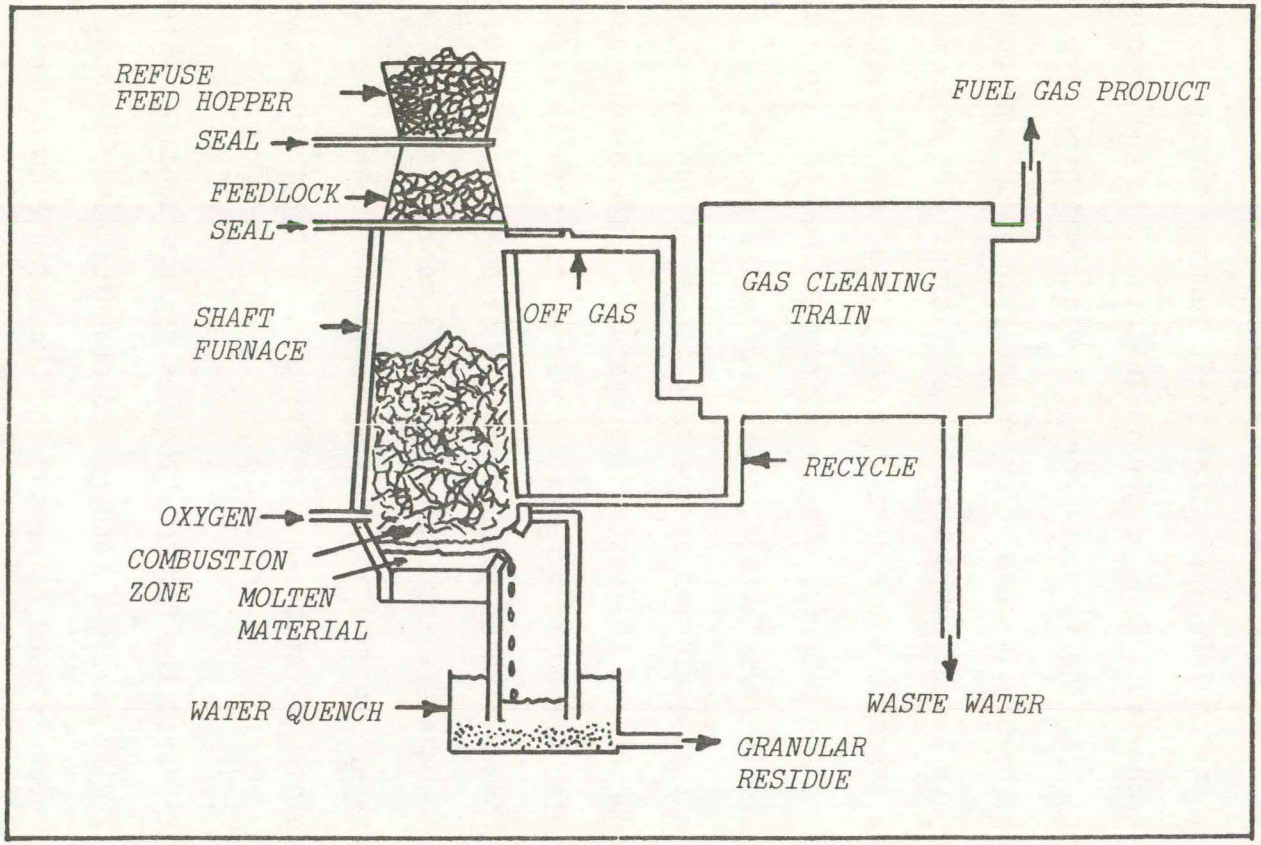


Figure II-7. Oxygen Refuse Converter. (From Reference 45.)

tion of this fuel gas is shown in Table II-8. The heating value is approximately 300 BTU per cubic foot. Since the product gas of the PUROX system is essentially sulfur-free and contains very little fly ash, it is an ideal fuel for all types of gas-fired furnaces. It could also be used as a supplementary fuel in an existing utility boiler without requiring extensive modifications (45).

The solid granular material produced by the PUROX process is free of any biologically active substances and is considered suitable as a construction fill material. The volume of this solid residue is only two to three percent of the volume of the incoming refuse. By contrast, conventional incineration of municipal solid wastes produces residues amounting to 10% or more of the volume of the refuse burned (45).

Table II-8. Typical Composition of Gases from PUROX Process

Constituents	Volume %
CO	47
H_2	33
CO_2	14
CH_4	4
C_2H_x	1
N_2	1
	100
Fuel Gas Quanity	7 million BUT/TON Refuse

From Reference 45.

A schematic diagram of the PUROX demonstration plant located at South Charleston, West Virginia is shown in Figure II-8. The gases leaving the furnace are directed to a scrubbing tower which utilizes a water spray to remove particulates and organic materials. The gas stream then passes through a wet electrostatic precipitator which further removes particulates. An oily residue and a small amount of condensed water is drawn from the electrostatic precipitator as well as particulate matter. The gas stream is then directed to the product gas condenser which cools the gas to about 100^{o}F (44). The bulk of the water vapor is removed in this unit. This condensate contains significant amounts of the organic material which is found in the PUROX wastewater.

The wastewater from the spray scrubber, electrostatic precipitator, and the product gas condenser is combined. This wastewater is vacuum filtered to remove char particles and is then recycled back to the spray scrubber. Because of this recycling, the characteristics of the wastewater that must finally be treated may vary. Higher strength wastewater will result if the gas scrubber water is recycled several times. A lower strength waste can be expected if the scrubber water is only used once. Therefore, the wastewater characteristics can be controlled somewhat by the operation of the gas cleaning system. However, the total pounds of organics removed per ton of gas produced is dependent upon the nature of the solid waste entering the pyrolysis process.

The typical characteristics of the wastewater produced in the PUROX process is shown in Table II-9. The waste is very high in

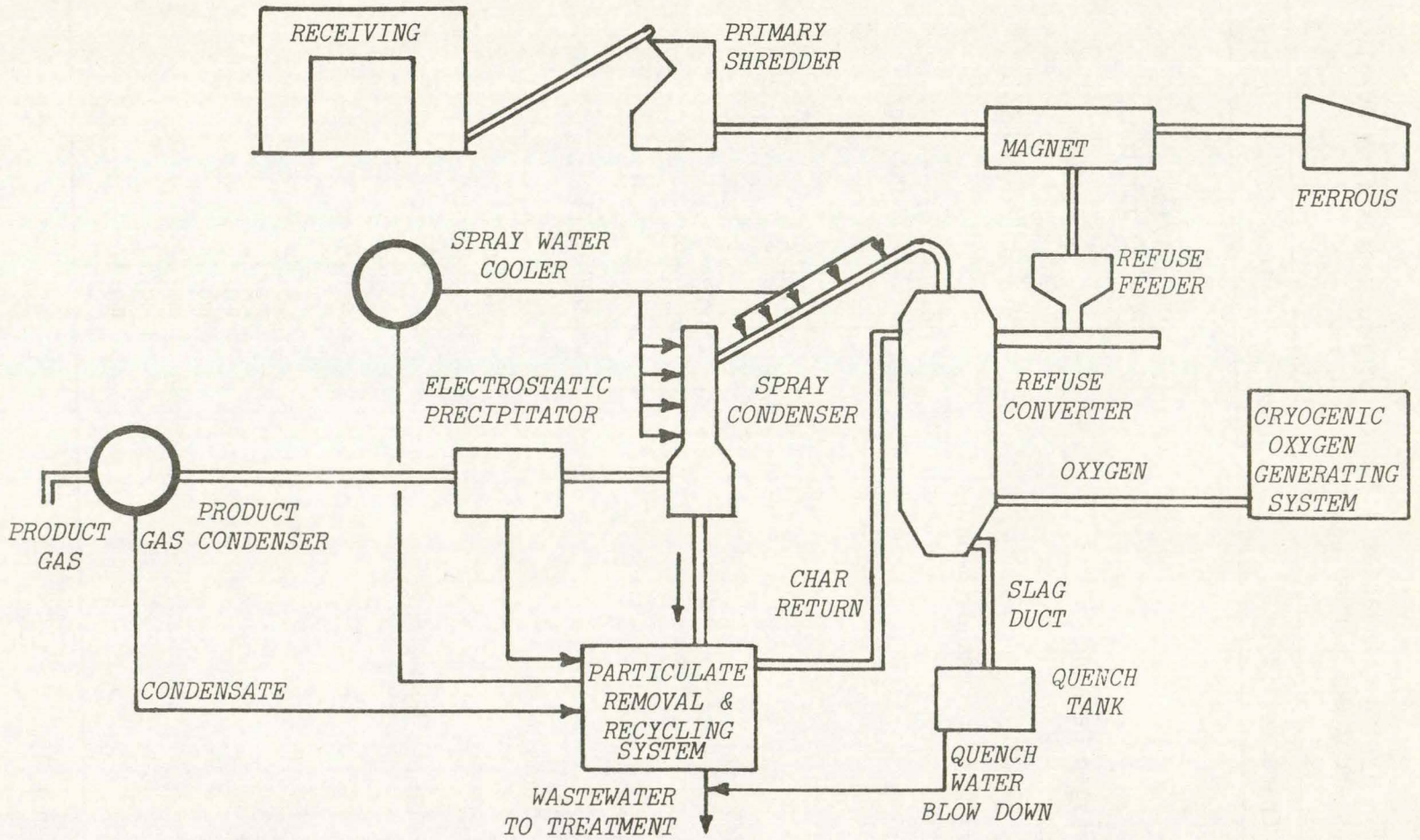


Figure II-8. Schematic Diagram of South Charleston, West Virginia PUROX Plant. (From Reference 44.)

Table II-9. Typical Characteristics of Liquid Wastes from Pyrolysis Fuel Gas Scrubbing

Characteristic	Quantity
Flow:	
Average	100 gal/ton
Range	80-120 gal/ton
Chemical Oxygen Demand:	
Average	77,000 mg/l
Range	60,000-90,000 mg/l
Biochemical Oxygen Demand (5-day):	
Average	52,000 mg/l
Range	40,000-60,000 mg/l
pH:	
Average	3.7
Range	3.0-4.5
Temperature:	
Average	100°F
Range	80-120°F
Oil & Grease:	
Average	1,000 mg/l
Suspended Solids:	
Average	20 mg/l
Range	10-50 mg/l
Total Organics, % by Weight:	
Average	4
Range	2.5-6.0
Metals:	
Iron	5 mg/l
Chromium	5 mg/l
Nickel	1 mg/l
Copper	1 mg/l
Cadmium	3 mg/l
Zinc	3 mg/l

From reference 49.

COD and BOD and would constitute a significant load on a municipal treatment plant if discharged directly to a sewer. If a city were to use the PUROX system to process all of its solid wastes, the resulting wastewater produced would add a 64 percent increase on the organic load applied to its wastewater treatment plant (47). Other wastewater characteristics of interest are the low pH and the presence of heavy metals. The warm temperature of the wastewater is beneficial because it could reduce or eliminate the heating requirement of many anaerobic systems.

Gorman et al., (48) did a study on gas scrubber wastewater samples from the PUROX process. River water was analyzed for organics and metals and then used for scrubbing the pyrolysis product gas stream. The resulting wastewater was not recycled and represented a once-through the system sample. The raw river water contained only trace amounts of aromatics and metals. The gas scrubber wastes had COD values of around 12,000 mg/l while the BOD values were nearly 5,000 mg/l. Phenolic compounds were found in significant concentrations (around 130 mg/l). A chromatographic analysis of the scrubber water samples detected the presence of benzene, toluene, ethylbenzene, and naphthalene. Concentrations of these aromatic compounds ranged from 1,000 to 4,000 µg/l. Phenanthrene, anthracene, and pyrene were found in lower concentrations. Metals were also detected with iron and zinc concentrations of around 5 mg/l.

6.0 POLYCYCLIC AROMATIC HYDROCARBONS

6.1 General

Combustion is the predominant process by which fossil fuels

are converted to energy. Combustion, particularly when inefficient, is also the primary technological source of polycyclic aromatic hydrocarbons (PAHs) released into the environment. The need for liquid fuels to supply the transportation industry, and for nonpolluting fuels for heat and power generation, provide the incentive to commercialize processes to convert coal, shale, and other solid organics, including mixed municipal refuse, to synthetic liquid and gaseous fuels. These processes represent a potentially massive new source of PAHs to the ever increasing load being placed upon the environment. Since the Union Carbide PUROX System is a high temperature pyrolitic process involving the various organic compounds found in municipal refuse it leads to the formation of PAHs, phenols, and other biologically refractory organics. Many PAH compounds are carcinogens. These include: benzo[a]pyrene (BaP), benzo[a]anthracene, benzo[c]phenanthrene, and 3-methylochloranthrene (MCA) (50,51,52). Because of the ever-increasing industrial development in many parts of the world, the annual production rate of PAHs is constantly rising, causing them to be of greater concern in recent years.

6.2 Sources of PAHs

The PAHs originating from man-made combustion processes are quantitatively the most significant sources of these compounds in the world environment (52). These consist of coke production in the iron and steel industry, catalytic cracking in the petroleum industry, coal tar pitch, carbon black, asphalt production, chemical processes, power generation, controlled refuse incineration, open burning, and internal combustion engines. Some biosynthesis of PAHs has been demonstrated

in plants, bacteria, and algae, but these natural sources are small in comparison to the man-made loads (52).

Most of the existing literature on PAH production centers on BaP, one of the most potent PAH carcinogens. BaP production generally constitutes between 1% and 20% of the total PAH load on the environment, but it has been singled out for most studies because of its well documented carcinogenetic potential to humans. Table II-10 shows the estimated esmissions of BaP into the atmosphere. By far the greatest source of BaP comes from the burning of coal, coke production in the iron and steel industry, and open burning. It is interesting to note that enclosed incineration accounts for less than 3% of the total BaP emissions into the atmosphere in the U.S. However, roughly ten times more PAHs are taken as solid residues from municipal incinerators than are emitted in the stack gases (53). Leaching of PAHs from the residues after landfilling may lead to contamination of ground and surface waters.

Transportation and processing of petroleum are the primary technological sources of PAHs found in the water environment. Further sources of waterborne PAHs are atmospheric fall-out, wastewater discharges from coke production, and domestic wastewater which contains PAHs from human excretion and runoff from streets. Wastewaters from coal and shale conversion processes and solid waste resource recovery systems are a potentially significant new source of PAH contamination of water supplies. Table II-11 shows the BaP content of various water samples. Table II-12 shows the concentrations of various PAH compounds found in coal and shale conversion waters.

Table II-10. BaP Emissions to the Atmosphere

Source of formation		BaP emission in tons/year		
		U.S.A.	Worldwide (excl. U.S.A.)	Worldwide
Heating and power generation				
using: Coal		431	1945	2376
Oil		2	3	5
Gas		2	1	3
Wood		40	180	220
	Sub-total	475	2129	2604
Industrial processes				
Coke production		192	841	1033
Catalytic cracking		6	6	12
	Sub-total	198	847	1045
Refuse and open burning				
Enclosed incineration:				
Commercial & industrial		23	46	69
Other		11	22	33

Table II-10. Continued.

Open burning:				
Coal refuse fires		340	340	680
Forest & agriculture		140	280	420
Other		74	74	148
	Sub-total	588	762	1360
Vehicles				
Trucks and buses		12	17	29
Automobiles		10	6	16
	Sub-total	22	23	45
Grand Total		1283	3751	5044

From reference 52.

Table II-12. PAHs in Coal and Shale Conversion Water (mg/l).

Constituent	Synthane gasification condensate	Solvent-refined coal raw process water	Simulated *in situ* shale retort by-product water
Naphthalene	0.2	5	0.1
2-Methylnaphthalene	1.3	2	0.3
1-Methylnaphthalene	<0.1	--[a]	0.1
1,3- + 1,6-Dimethylnaphthalene	0.1	---	0.2
Dimethylnaphthalenes	---	2.3	---
2-Isopropylnaphthalene	---	0.7	---
1-Isopropylnaphthalene	---	2	---
Biphenyl	<0.1	0.2	<0.1
Dimethylbiphenyls	---	0.7	---
Fluorene	<0.1	0.3	0.2
9-Methylfluorene	---	0.3	---
1-Methylfluorene	ND[b]	0.2	0.2
Anthracene/phenanthrene	ND	1.1	0.3

Table II-12. Continued.

Constituent	Synthane gasification condensate	Solvent-refined coal raw process water	Simulated *in situ* shale retort by-product water
2-Methylanthracene	ND	---	0.2
1-Methylphenanthrene	ND	0.2	0.1
9-Methylanthracene	ND	---	0.4
Methylphenanthrene	---	0.3	---
Fluoranthene	ND	0.4	0.1
Pyrene	ND	0.6	<0.1

a Not reported

b Not detected

From reference 51.

Table II-11. BaP Content in Various Water Samples

Waters	ppm BaP
Uncontaminated ground water	< 0.00001
Drinking water	< 0.00003
Contaminated by industrial effluent	0.01
Heavily contaminated by coking, oil shale, oil-gas processing	0.5 - 1.0

From Reference 51.

The end products of coal conversion processes generally contain higher concentrations of PAHs than does petroleum. Table II-13 shows the BaP content of some synfuels-related materials. Although enriched in BaP, relative to petroleum crudes, coal-derived crude oils contain significantly less BaP than do high boiling distillates and distillate residues such as coal tar, coal tar pitch, and petroleum pitch.

Table II-13. BaP Content of Synfuels and Related Materials

Material	∿ppm BaP
Petroleum crude oil	1
Shale-derived crude oil	3
Coal-derived crude oil	3
Coal tar	3,000
Coal tar pitch	10,000
Petroleum pitch	2,000

From Reference 51.

It is estimated that worldwide energy consumption in 1985 will produce atmospheric emissions of approximately 200 x 10^8 lbs of particulates and 130 x 10^8 lbs of hydrocarbons. Furthermore, about 40 x 10^6 lbs of nondegradable organics will be emitted as water pollutants (51). Because of the potential harm that these pollutants may cause to human health and the overall quality of life, it is important to review each new energy source relative to its contribution to the total load placed upon the environment.

In evaluating the potential production of biorefractory organics produced in the PUROX system, it is important to consider the potential pollution caused by alternate energy production. It is evident that the U.S.A. will depend more heavily on its vast coal reserves for future energy production. Inefficient burning of coal is one of the greatest sources of PAH compounds released into the environment. Processes to convert coal or shale to synfuels produces products with higher PAH concentrations than their petroleum counterparts. The fact that the PUROX system produces a clean burning fuel gas and traps most of the by product pollutants in the gas cleaning train could be very advantageous, provided this wastewater is effectively treated. Since the PUROX System is a refuse disposal process as well as a net energy producer, the production of pollutants from alternate refuse disposal processes should be considered. Land filling can lead to groundwater contamination and remote site locations lead to further depletion of relatively clean burning liquid fuels because of longer hauling distances. Incineration of municipal refuse produces problems with particulate emissions, stack gas pollutants, odor production, and potential

PAH leachate from disposal of solid residues. The key to the environmental soundness of the Union Carbide PUROX System appears to be in the effective treatment of the wastewater produced in the process.

6.3 Decomposition of PAHs

PAH degradation can be accomplished by two basic processes, physical oxidation and biological reduction. Photooxidation is quantitatively the most important process, occurring in the atmosphere as well as the water environment (52). PAH compounds released into the atmosphere form aerosols which remain suspended from a few days to several weeks depending upon particle size and meteorological conditions. These aerosols decompose very readily by reaction with ozone, nitrogen oxides, sulfur oxides, and various other oxidants present in the atmosphere (52). This reaction is dependent upon sunlight and will occur in the aquatic environment provided adequate oxygen, exposure time, temperature, and illumination are present.

Chemical oxidation of PAH compounds will occur in water and wastewater treatment plants which use chlorine, chlordioxide, or ozone for disinfection purposes. Reaction with chlorine, at concentrations employed in drinking water purification processes, will reduce trace PAH levels with a corresponding half-life of a few minutes (53). Many of the mechanical processes used in water and wastewater treatment have some capacity to remove PAH compounds. This removal generally occurs with those PAH compounds which are adsorbed to suspended particles. Activated sludge processes remove approximately 80 percent of the PAHs from wastewaters. However, this removal is not due to biodegradation but to the irreversible adsorption of the PAHs on the sludge (54). Co-

agulation, flocculation, and filtration operations can also achieve a substantial reduction in PAH concentrations. Solid residues from water and sewage treatment plants may contain significant concentrations of PAHs and their disposal could lead to groundwater contamination by leaching (53,54). Activated carbon appears to have the greatest ability to adsorb PAHs from water. Adsorption equilibrium can be achieved in as little as five minutes using powdered carbon with continual stirring. Filtration through beds of activated carbon will provide 99 percent removal of PAHs from filtered river water (54).

The microbial degradation of PAHs and other benzene-ring compounds (such as phenols) is accomplished to a limited extent with acclimated species enjoying far better success than unacclimated populations. Soil and water pseudomonads are extremely versatile in their catabolic activities and are the principal bacteria involved in PAH degradation in the environment. Most of the literature on the microbial decomposition of ring compounds contend that aerobicity is a key factor in hydroxylation and ring cleavage (3,55,56). It is generally accepted that dihydroxylation is a prerequisite for enzymatic fission of the benzene ring. The enzymes catalyzing the hydroxylation of the aromatic ring are called mixed-function oxidases. In such reactions one atom of oxygen is incorporated into the substrate molecule while the other atom of the oxygen molecule is reduced to water, provided a suitable electron donor is present (56). There are two different modes of ring fission, ortho and meta cleavage. Ortho cleavage results in the fission of the bond between the two carbon atoms bearing hydroxyl groups to form dicarboxylic acids. Meta cleavage occurs on a carbon-

carbon bond where only one carbon carries a hydroxyl group and leads to the formation of either an aldehyo-acid or keto acid. Both types of ring fission are catalyzed by dioxygenases enzymes which incorporate one molecule of oxygen into the ring (55). Figure II-9 shows ortho and meta cleavage of catechol, a key intermediate in the degradation of aromatic hydrocarbons by pseudomonads.

Studies on the dark conversion of PAHs adsorbed on activated sludge showed that anthracene and phenanthrene are partially metabolized by aerobic bacteria but that higher molecular weight polycyclics are not (53). Because PAHs are only sparingly soluble, they may accumulate in sediments below industrial outfalls to concentrations which greatly exceed those found in the stream itself. Herbes and Schwall (50) found that PAH turnover times in petroleum-contaminated sediments were a function of molecular weight. Turnover times in uncontaminated stream sediment were 10 to 400 times greater than in contaminated samples, while absolute rates of PAH degradation (expressed as micrograms of PAH removed per gram of sediment per hour) were 3,000 to 125,000 times greater in contaminated sediment. This study showed that sediments which received chronic PAH inputs and that supported microbial populations capable of decomposing two- and three-ring PAH compounds were unable to degrade four- and five-ring structures. Other compounds studied that were almost completely refractory included the carcinogens benz[a]anthracene and BaP. Herbes and Schwall concluded that the ease of transformation of PAH by microorganisms is inversely related to the number of rings. Acclimation of the bacteria greatly increases their ability to degrade polycyclics, but no microorganisms were iso-

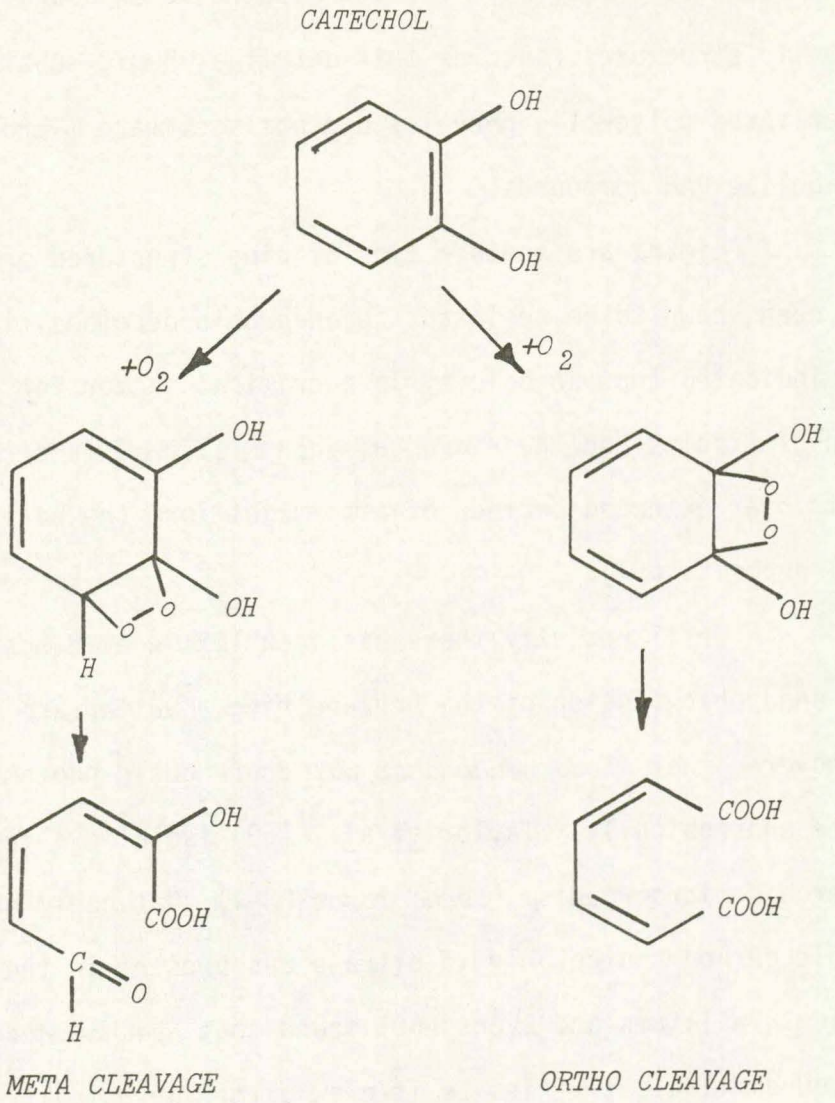


Figure II-9. Ortho and Meta Cleavage of Catechol by Pseudomonads. (From Reference 3.)

lated that could utilize four- and five-ring PAH compounds as sole carbon sources. They also found that chronic exposure to oxygenate aromatic structures (such as leaf detritus, humic substances, and interlinked polycyclic phenols) did not acclimate microorganisms to catabolize PAH compounds.

Ligins are another type of ring-structured organic which has been shown to be resistant to anaerobic decomposition. Research has indicated that aerobicity is a critical factor for the mineralization of lignins and their gradual accumulation in anaerobic environments over extended periods of time might form the basis for peat and coal deposits (57).

Until recently there has been little evidence to support the anaerobic fission of the benzene ring. Dutton and Evans (58) discovered that *Rhodopseudomonas palustris* could photometabolize benzoate anaerobically. Taylor et al., (59) isolated a facultatively anaerobic microorganism (*Pseudomonas* PN-1) that could use benzoate as a sole carbon source only if nitrate was present in the mineral salts medium. Williams and Evans (60) found that *Pseudomonas stutzeri* displayed similar activities as it grew either aerobically on benzoate or anaerobically on benzoate with nitrate or nitrite. Nottingham and Hungate (61) discovered that a completely anaerobic mixed population from a sewage sludge digester could decompose small concentrations of benzoate with or without acclimation. Ferry and Wolfe (62) confirmed these findings and concluded that benzoate degradation was accomplished by a coupled reaction between two types of bacteria. One type ferments benzoate to acetate by a reductive pathway in the absence of nitrate.

The methanogenic organisms would then serve to replace the function of nitrate by removing the fermentation products and thus provide thermodynamically favorable conditions for benzoate fermentation. Keith et al., (63) found a different mixed culture which degraded benzoate anaerobically with several short chain volatile fatty acids (heptanoic, valeric, butyric, proponoic, and acetic) as the intermediates arising from cleavage.

Probably the most promising study was done by Healty and Young (64). They found that both phenol and catechol could be completely degraded anaerobically by a mixed population from a sewage digester. Phenol decomposition began after a 2.5 week acclimation period while catechol required a 4.5 week acclimation. The work of these researchers indicates that the aromatic ring structure is not refractory under strict anaerobic conditions and that heterotrophic bacteria possess reductive pathways capable of ring cleavage. However, it should be noted that the aromatic compounds which have been proven to be anaerobically degradable are single ring structures which are hydroxylated or have an acid grouping to serve as a biological handle. To date there is no evidence of anaerobic decomposition of any polynuclear aromatic compounds.

CHAPTER III

SOURCES AND CHARACTERISTICS OF PYROLYSIS WASTES FOR STUDY

1.0 SOURCE

The pyrolysis wastewater used in this research was obtained from the PUROX demonstration plant located in South Charleston, West Virginia. A shipment of eleven, 55-gallon, plastic lined, steel drums of the PUROX process wastewater was received at the P.F. Morgan Environmental Engineering Research Laboratory of the University of Iowa in October of 1977. At the time the wastewaters were collected, the Union Carbide plant in South Charleston was demonstrating the pyrolysis of typical municipal refuse.

As indicated by the letter in Appendix A, the shipment of PUROX wastes was arranged through Dr. L.C. Matsch, Senior Engineering Fellow, of Union Carbide Corporation, Tonawanda, N.Y.

2.0 CHARACTERISTICS

A preliminary waste characterization of the eleven drums was performed at the time the wastewater was recieved. The COD values for the 11 different drums of PUROX waste ranged from 18,400 mg/l to 41,300 mg/l. The pH varied from 4.1 to 4.4. Five-day biochemical oxygen demand (BOD_5), volatile acids, and heavy metals concentrations were analyzed on the barrel of waste with the highest COD (41,300 mg/l). The results of this preliminary waste characterization are given in Table III-1. The Purox waste concentrations of these samples were lower than those given by Union Carbide, with the exception of certain metal concentrations (Table II-9). In a communication with people from

Table III-1. PUROX Waste Test Results

Characteristic	Value
Chemical Oxygen Demand, mg/l	
Maximum	41,300
Minimum	18,400
Average (of 11 drums)	30,000
pH range	4.1-4.4
Biological Oxygen Demand, mg/l[(a)]	14,400
Volatile Acids, mg/l as acetic[(a)]	5,100

Heavy Metals[(a)]	Total	Dissolved
Cadmium, ppm	0.05	0.04
Chromium, ppm	0.26	0.10
Copper, ppm	0.09	0.07
Nickel, ppm	0.26	0.26
Lead, ppm	2.08	1.54
Zinc, ppm	45.6	27.50
Mercury, ppb	0.5	0.5

(a) Value given is for PUROX waste with a COD of 41,300 mg/l.

Union Carbide, it was discovered that the samples sent to the University of Iowa represented wastes which were only recycled through the gas scrubber once or twice. The waste characteristics in Table II-9 were from samples which were recycled several times and are therefore stronger.

Samples of the higher strength PUROX wastewater were taken to the University of Iowa Hygienic Laboratory for further analysis. A description of the analytical procedure used by the Hygienic Laboratory to characterize the PUROX waste is given in Appendix B. A 100 ml sample of the pyrolysis waste was subjected to an extraction and then analyzed by liquid chromatography methods. This separated the sample into eight fractions containing different classes of compounds. Table III-2 shows the results of the study. The data indicated that the organics in the waste were primarily in fraction number five which contains phenols, alcohols, and amines. However, there was a broad distribution of other chemical compounds present in the sample. The aldehydes and PAHs in the pyrolysis waste could cause some initial toxicity problems to unacclimated anaerobic bacteria.

A physical-chemical treatment study was conducted on the pyrolytic wastes at the Iowa State University at Ames, Iowa by Young (44). Samples of the higher strength (COD = 41,300 mg/l) PUROX waste were sent from the University of Iowa for use by Young in the Iowa State study. Some of the test results on the raw waste sample from this study are listed in Table III-3. It is significant to note that the waste contains a significant amount of total nitrogen (1200 mg/l), but very little ammonia nitrogen (7.4 mg/l). Levels of certain heavy metals, partic-

Table III-2. University of Iowa Hygienic Laboratory Analysis of PUROX Waste[1/].

Fraction #	Compound Type	Weight Residue in Samples (mg/100 ml)	% of Total
1	Aliphatic Hydrocarbons	0.873	5.7
2	Aromatic Hydrocarbons Polynuclear Aromatic Hydrocarbons Halides	3.959	2.7
3	Esters Ethers Nitro Compounds Epoxides	11.412	7.7
4	Phenols Ketones Aldehydes Phthalates	9.625	6.5
5	Phenols Alcohols Amines	110.346	74.5
6	Amides Sulfonates Aliphatic/Aromatic Acids	6.826	4.6
7	Sulfonates/Sulfonic Acids	3.409	2.3
8	Sulfonic Acids	1.695	1.1
	Total Mass Fractionated	148.145	

1/ Analysis conducted on strongest waste (COD = 41,300 mg/l) received from Union Carbide.

Table III-3. Characteristics of Untreated PUROX Pyrolysis Wastewater[1/].

Parameter	Union Carbide	Analytical Services Laboratory, ISU
Flow, gal/ton of refuse	80-100	-
Temperature, ^{o}F	90-110	-
pH	3.5-4.5	2.4-4.2
COD, mg/l	50,000-77,000	41,718 mg/l
BOD_5, mg/l	30,000-52,000	16,375 mg/l
TOC	-	12,625 mg/l
Total solids	-	18,680 mg/l
Suspended solids	-	2,115 mg/l
Volatile suspended solids	-	2,000 mg/l
Oil and grease, mg/l	500-1,000	-
Organics, weight %	-	-
Methanol	0.6-1.1	0.015
Ethanol	0.3-0.5	0.0035
Acetone	0.3-0.5	0.0015
Methyl ethyl ketone	0.06-0.1	0.0002
Acetic acid	0.5-0.8	0.522
Propionic acid	0.25-0.4	0.0575
Butyric acid	0.06-0.1	0.0635
Furfural	0.3-0.5	0.0065
Phenol	0.06-0.1	0.02
Benzene	0.03-0.06	0.0035
Other	0.2-0.38	-
Total	2.66-4.54	-

Table III-3. Continued.

Parameter	Union Carbide	Analytical Services Laboratory, ISU
Silver	-	0.01 mg/l
Arsenic	-	0.132 mg/l
Barium	-	5.1 mg/l
Calcium	-	440 mg/l
Cadmium	-	< 0.05 mg/l
Chromium	-	0.15 mg/l
Copper	-	0.02 mg/l
Chloride	-	1,079 mg/l
Iron	-	59.2 mg/l
Mercury	-	0.003 mg/l
Potassium	-	185 mg/l
Magnesium	-	46.0 mg/l
Manganese	-	62.8 mg/l
Sodium	-	445 mg/l
Nickel	-	<0.01 mg/l
Kjel-N	-	1,200 mg/l
NH_3-N	-	7.39 mg/l
$NO_2 + NO_3$ -N	-	0.39 mg/l
Lead	-	1.25 mg/l
PO_4 as phosphate	-	94.0 mg/l
Selenium	-	0.888 mg/l
SO_4 as sulfate	-	520 mg/l
Zinc	-	65.8 mg/l

1/ Analysis provided by Dr. J.C. Young, Iowa State University, Ames, IA.

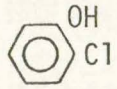
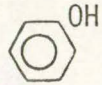
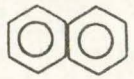
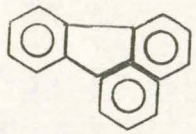
ulary zinc, were quite high. The salt cations including calcium, sodium, potassium, and magnesium were well below inhibitory concentrations for anaerobic bacteria.

The PUROX waste sample was also analyzed by gas chromatography/mass spectroscopy methods by Young at Iowa State University. The results indicate the presence of a wide variety of phenolic compounds as well as several types of polynuclear aromatics, as shown in Table III-4.

In appearance, the PUROX wastewater is a brown, rather opaque fluid with a distinct smoke-like odor.

Of major concern from a waste treatment standpoint is the very high organic content of the PUROX wastes, as reflected by the COD and total solids content, indicating a high oxygen demand. Also of concern are the relatively high heavy metals concentrations, expecially zinc, and the presence of a variety of polycyclic aromatics that are known to be inhibitory to biological systems and difficult to degrade.

Table III-4. Priority Pollutants Isolated in Raw PUROX Pyrolysis Wastewater[1/].

Priority pollutant	Phase in which isolated[2/]	Conc. (ppm)	Structure
o-chlorophenol	L-A	57	
phenol	L-A S-A	300 319	
naphthalene	L-B S-B	4.8 145	
acenaphthylene	L-B S-B	2.6 227	
flouranthene	L-B S-B	0.3 380	
bis-(2-ethylhexyl)phthalate	S-B	[3/]	$COOCH_2CH(C_2H_5)(CH_2)_3CH_3$ $COOCH_2CH(C_2H_5)(CH_2)_3CH_3$

1/ Analysis provided by Dr. J.C. Young, Iowa State University, Ames, Iowa.

2/ L-A = liquid fraction acid extract; S-A = solid fraction acid extract; L-B = liquid fraction base-neutral extract; S-B = solid fraction base-neutral extract.

3/ Compound isolated in solids fraction, however, concentration could not be determined because standard was not available.

CHAPTER IV

SUSPENDED GROWTH ANAEROBIC TREATMENT OF PYROLYSIS WASTEWATERS

1.0 INTRODUCTION

The suspended growth anaerobic treatment experiments (Track A of this project) were conducted in two phases.

The initial work (Phase I) involved the feeding of primary wastewater sludge and various small percentages of PUROX pyrolysis wastes on a batch-feed basis to the 5-liter, completely-mixed reactors. It was found that the PUROX wastes were extremely inhibitory to the anaerobic biological reactors. It was therefore concluded that the microorganisms would have to be acclimated to the PUROX wastes, if the wastes were to be accepted at all by the anaerobic reactors without inhibition.

Phase II of the suspended growth experiments involved the modification of the anaerobic reactors to enable the feeding of PUROX wastes on a continuous basis while continuing to feed primary sludge on a batch basis. Phase II involved studies at solids retention times (SRT) of 15 days and liquid retention times (LRT) as low as five days. The 5-day LRT experiments were intended to simulate the anaerobic contact mode of operation.

The maximum percentage of PUROX feed achieved during Phase II was 17 percent of total daily feed volume when operating at an SRT and LRT of 15 days. When operating at an SRT of 15 days and an LRT of five days, the PUROX pyrolysis waste was fed in an amount of 51 percent of total feed without inhibition. The reduction in COD of the PUROX wastes was approximately 70 percent during Phase II under equilibrium conditions.

Details on the procedures followed, results obtained, and conclusions arrived at as a result of the suspended growth experiments are presented in the remaining sections of this Chapter.

2.0 PROCEDURES

2.1 Bench-Scale Set Up

The bench-scale set up used during Phase II of the suspended growth experiments is shown in Figure IV-1. The set up was identical for Phase I with the exception of the peristaltic pump used for continuous feed of the pyrolysis wastes during Phase II. A total of three set ups of the design illustrated in Figure IV-1 were used throughout the suspended growth experiments.

The three bench-scale anaerobic reactors were made from three-eighths inch plexiglass with inside dimensions of 6-3/4" x 6-3/4" x 8". The units were calibrated to a liquid volume of five liters in 500 ml increments. A mixed liquor volume of 5.0 liters was maintained in each reactor throughout these experiments.

The top of each reactor was attached with metal screws. Threads were formed in previously drilled holes with an internal die. A rubber gasket coated with stopcock grease provided an air-tight seal.

Each top had four rigid plexiglass tubes fitted through previously drilled holes. The tubes were sealed to the top with the solvent trichloromethane. One tube was one-half-inch in outside diameter, and extended to the 3-liter mark from the bottom of the reactor. Externally, it was open to the air. This tube was centered in the top, and contained the mixer shaft. A second tube was three-eighths-inch in outside diameter, and did not penetrate the liquid surface. This tube was for the

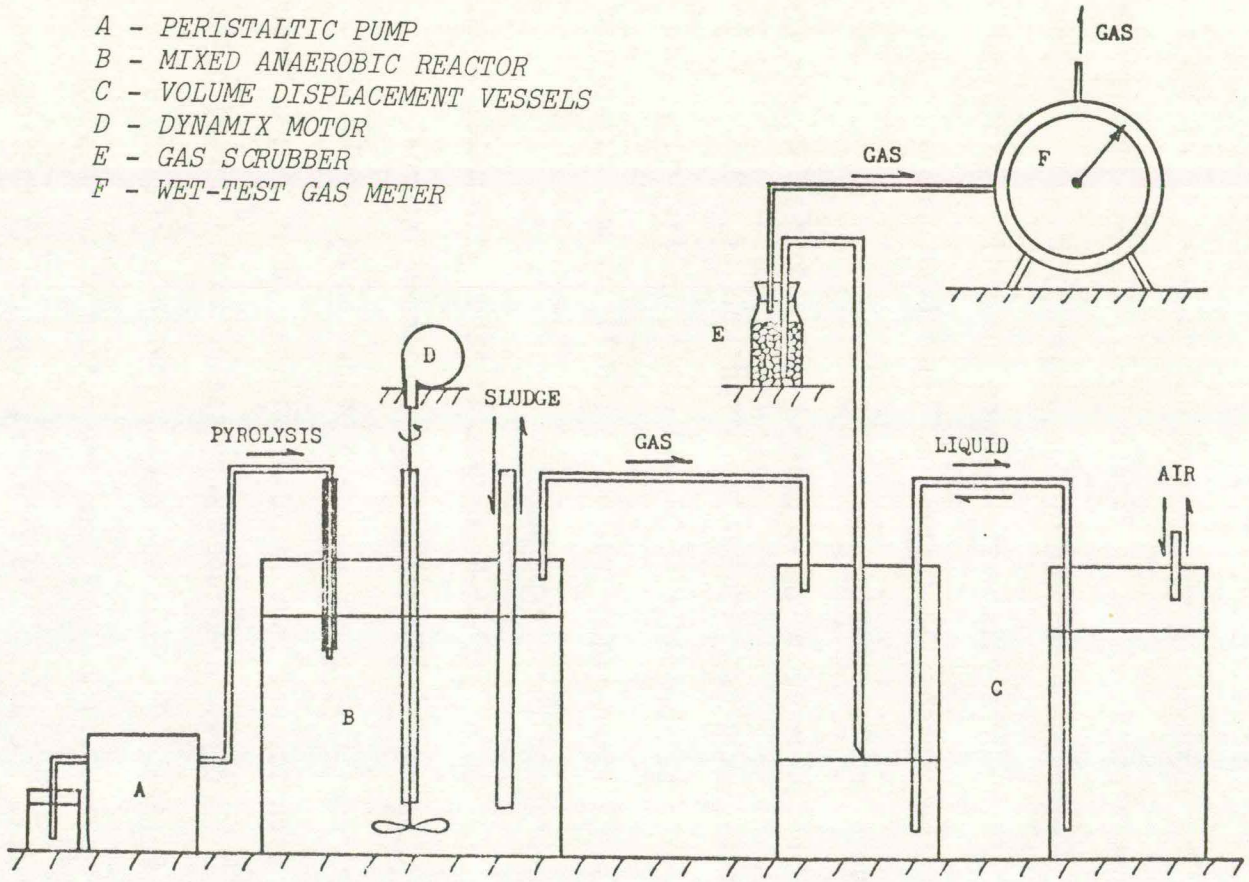


Figure IV-1. Schematic Diagram of Bench Scale Set-Up.

release of gas from the reactor. It was externally connected to the first liquid displacement column with three-eighths-inch inside diameter flexible Tygon tubing. The withdrawal of mixed liquor was accomplished through a third tube. This tube was five-eighths-inch in outside diameter, and extended to the 1-liter mark. Externally, it was open to the air. A fourth tube was used during Phase II for the continuous feed of pyrolysis waste. It was three-eighths-inch in outside diameter and extended to the 3-liter mark. Externally, it was open to the air.

Mixing was provided with two impellors on a shaft driven by a variable-speed, direct-drive Fisher Scientific Dyna Mix Electric Motor. A small impellor, one and one-half inches in diameter, was located at the 1-liter mark, and a larger impellor, four inches in diameter, was located at the 4-liter mark. The mixer shaft speed was adjusted with a motor control to a rotational velocity which provided complete, but not violent, mixing.

The three reactors were set in a Napco water bath. The water bath was filled with distilled water, and maintained a temperature at all times between $35^{o}C$ and $37^{o}C$.

A pair of interconnected volume displacement columns for each reactor maintained a pressure greater than atmospheric on the units and provided for the release of gas (Figure IV-1). Each column consisted of a six-inch outside diameter plexiglass cylinder, which was twelve inches long and one-fourth-inch thick. The top and bottom of each column was also made of one-quarter-inch plexiglass, and was attached to the cylinder with trichloromethane solvent.

The first column was partially filled with liquid, and contained a reactor gas atmosphere. Three, three-eighths-inch outside

diameter rigid plexiglass tubes were fitted through previously drilled holes in the top of the column and were sealed with trichloromethane solvent. One tube did not penetrate the liquid surface. It was connected externally to the gas release tube on one of the anaerobic reactors. This tube provided for the transfer of gas from the reactor to the column. A second tube had a V-notched end, and extended to within two and one-half inches of the bottom of the column. It was connected externally to the sulfide scrubber. This tube controlled the pressure on the reactor and provided for the release of gas from the column to the sulfide scrubber. A third tube extended to within one-half inch of the bottom of the column and penetrated the liquid surface at all times. It was connected externally to the second volume displacement column. This tube provided for the transfer of liquid between the two volume displacement columns. All external connections were made with three-eights-inch inside diameter flexible Tygon tubing.

The second volume displacement column was partially filled with liquid and contained an air atmosphere. Two, three-eighths-inch outside diameter rigid plexiglass tubes were fitted through previously drilled holes in the top of the column and sealed with trichloromethane solvent. One tube extended to within one-half inch of the bottom of the column, and penetrated the liquid surface at all times. It was connected externally to the first volume displacement column with three-eighths-inch inside diameter flexible Tygon tubing. This tube provided for the transfer of liquid between the two columns. A second tube did not penetrate the liquid surface and was not connected externally. This tube provided for the transfer of air into and out of the second column.

The combined volume of liquid in the two volume displacement columns was such that a pressure of about four and one-half inches of liquid was maintained on the digester. This pressure was the result of a differential liquid level between the two units of about four and one-half inches. As gas was produced in the reactors and transferred to the first column, liquid was transferred from the first column to the second column. At the same time, air was transferred out of the second column. This resulted in an increase in pressure in the reactor and the first column. When the increase in pressure was sufficient to force the liquid level in the first column below the V-notch at the bottom of the central tube, reactor gas was released from the first column to the sulfide scrubber. As the gas was released, liquid was transferred from the second column back to the first column. At the same time, air was transferred into the second column. This resulted in a decline in pressure in the reactor and the first column. When the decline in pressure was sufficient to allow the liquid level in the first column to rise above the V-notch at the bottom of the central tube, digester gas was again retained by the first column. $\pm$ 0.003 cubic gas released per cycle was approximately 0.003 cu.ft.

A liquid seal was maintained in the three tubes in the top of the digester which were externally open to the air. This prevented the introduction of air into the anaerobic reactors. The liquid level in these tubes was above the liquid level in the reactor due to the pressure maintained in the digester. Care was taken during withdrawal of mixed liquor from the digester to insure that this seal was not broken.

The liquid in the volume displacement columns consisted of a saturated sodium chloride solution, which had been acidified to pH 1, and colored red with methyl orange indicator. The salt and acid greatly reduced the solubility of carbon dioxide in the liquid. Methyl orange undergoes a color change from red to colorless at pH $\pm$ 4.5. As long as the liquid in the columns is red, the dissolution of carbon dioxide from the reactor gas in column one into the liquid, and subsequent release of carbon dioxide from the liquid to the air in column two, is minimal.

A sulfide scrubber was provided for each unit to remove hydrogen sulfide, which is corrosive, from the gas stream. The scrubber was placed just ahead of the gas meter to prevent damage to the meter. The sulfide scrubber consisted of a 1-liter bottle, filled with wood chips coated with a ferric oxide paste. The ferric oxide reacts with the sulfide in the reactor gas forming ferrous sulfide which is retained on the wood chips. A Number Six rubber stopper was placed in the top of the bottle, and provided an air-tight seal. Two three-eighths-inch outside diameter glass tubes were tightly fitted through previously drilled holes in the rubber stopper. One tube extended to the bottom of the scrubber, and was externally connected to the digester gas release tube on the first volume displacement column. This tube provided for the transfer of the reactor gas stream to the bottom of the sulfide scrubber. A second tube extended only partially into the scrubber, and was connected externally to the gas meter. This tube provided for the transfer of the hydrogen sulfide free gas stream from the sulfide scrubber to the gas meter. Both external connections were made with three-eights-inch inside diameter flexible Tygon tubing.

Three Precision Wet-Test Gas Meters were provided for the three reactors to measure gas production. Each meter had a range of 0 to 100 cubic feet, and was graduated to 0.001 cubic feet.

Pyrolysis feed to the reactors during Phase II was provided with a two-speed Monostat peristaltic cassette pump. The pump was capable of delivering flows as low as 1 ml per day, with the aid of a Dayton Time Switch on a 30-minute cycle. One-sixteenth-inch inside diameter by one-thirty-second-inch wall thickness, and three-thirty-second-inch inside diameter by one-thirty-second-inch wall thickness flexible Tygon tubes were used to deliver the pyrolysis waste to the digester. A graduated cylinder was used as a feed reservoir so that accurate measurements of the pyrolysis feed could be made and the pump calibration corrected as required.

During Phase II of the suspended growth experiments, the sludge feed and mixed liquor withdrawal tube (Figure IV-1) was modified to allow adjustment of the depth of penetration into the reactor liquid. This modification enabled the withdrawal of greater amounts of mixed liquor than had previously been possible without sucking air into the anaerobic reactors. To make this modification a two-inch diameter by one-fourth inch thick plexiglass disc was attached to the top of the reactors with metal screws. Threads were formed in previously drilled holes with an internal die. A one-half-inch-diameter hole was then drilled through the disc and through the top of the reactor, and a one-half inch outside diameter rigid plexiglass tube was inserted. A rubber O-ring placed between the disc and the top of the unit provided a gas-tight seal.

Another modification of the reactors during Phase II consisted of increasing the depth of penetration of the tubes containing the mixer shaft and the pyrolysis feed. This allowed a larger volume of mixed liquor to be withdrawn without lowering the liquid level in the reactor below the bottom of these tubes. Thus the liquid seal was maintained.

Two, 2-liter plastic graduated cylinders were used as settling columns to achieve solids separation for sludge recycle during the anaerobic contact (15 day SRT, 5-day LRT) experiments of Phase II.

2.2 Laboratory Analyses

2.21 Gas Production

Gas production was measured on a daily basis throughout the suspended growth experiments. Precision Wet-Test Gas Meters were used. The meter scale ranged from 0 to 100 cubic feet, and was graduated to 0.001 cubic feet. In addition to the daily increment in volume, the barometric pressure, gas temperature, and time interval between readings were also recorded. The volume of gas produced was then converted to, and expressed as, standard cubic feet per day (SCF/day) used the following equation:

$$\text{Gas, SCF/day} = G \times \frac{P}{(29.92)} \times \frac{273}{(273 + T)} \times \frac{(24)}{t}$$

Where: G = daily increment in volume, as indicated by gas meter;

P = Barometric pressure; inches of mercury

29.92 = inches of mercury (standard pressure);

273 = ^{o}Kelvin (standard temperature);

T = temperature, ^{o}Centigrade;

24 = hours per day;

t = number of hours between daily readings.

The gas meter has an accuracy of 0.2 percent. Gas production was recorded to the nearest 0.001 SCF/day.

2.22 pH

pH determinations were made routinely (generally, daily) during both phases of this research. A Corning Model 10 pH Meter was used. The meter had two scales: a standard scale, which ranged from 0 to 14, and which was graduated to 0.05 pH units; and an expanded scale, which ranged from 5.5 to 8.5, and which was graduated to 0.1 pH units. Measurements were recorded to the nearest 0.05 pH unit.

Dissolved carbon dioxide (CO_2) was present in the digester effluents at a concentration greater than the saturation concentration of CO_2 at laboratory temperature and pressure. To minimize the loss of CO_2 and corresponding increase in pH, measurements were made immediately following withdrawal of the sample from the digester. Agitation of the sample was minimized.

2.23 Alkalinity

Total alkalinity (Alk) measurements were made routinely (generally, every second or third day) during both phases of this research. Measurements were made as described in the Fourteenth Edition of Standard Methods (65): 50 ml of sample, 0.1 N sulfuric acid (H_2SO_4) titrant, and a pH 4.5 end-point were used.

Total alkalinity was calculated using the following equation:

$$Alk = \frac{(V_t) \times (N_t)}{(V_s)} \times (5000)$$

Solids were removed from the samples on which soluble COD determinations were made. This was accomplished by filtering the samples under 20 inches of mercury vacuum once through Whatman #41 filter paper, and then twice through Whatman #1 filter paper.

2.26 Solids

Solids determinations were made periodically during this research (generally every fourth or fifth day). Total solids (TS), total volatile solids (TVS), and total fixed solids (TFS) determinations were made on the raw sludge, the reactor effluents, and the settled supernatants. The following equation expresses the relationship between the aforementioned solids forms:

$$TS = TVS + TFS.$$

2.3 Operation of Units

2.31 Phase I

The first phase of this research involved the design and construction of the experimental laboratory set up, illustrated in Figure IV-1. Actual experimental work began on December 1, 1977, when the three anaerobic reactors were seeded with digesting sludge from the Iowa City, Iowa wastewater treatment plant. After seeding, primary domestic sludge from the Mount Vernon, Iowa wastewater treatment plant was used as a raw sludge feed to the reactors. Mount Vernon sludge is thought to be more typical of domestic wastewater sludge than is the Iowa City sludge. Typical characteristics of the Mount Vernon sludge are shown in Table IV-1.

Table IV-1. Characteristics of Mount Vernon, Iowa Primary Wastewater Sludge.

Characteristic	Value
Total Solids	6.6%
Volatile Solids	72.7% (of total)
Chemical Oxygen Demand	74,100 mg/l

Approximately the first two months of the experimental work were spent in achieving equilibrium conditions in the three reactors and checking for gas leaks, sufficiency of mixing in the reactors, and insuring proper temperature control at 35°C. Primary sludge feed was increased gradually to each of the three reactors during the early days. The units were brought to equilibrium at a daily sludge feed of 333 ml, providing a 15-day SRT and LRT. Sludge was fed on a batch basis.

The procedure for feeding the units involved first the withdrawal of approximately 500 ml of mixed liquor from each unit. This was accomplished by means of a vacuum pump connected to a side-arm suction flask which, in turn, was connected to the feed and withdrawal tube of the reactor. The volume of effluent withdrawn from the reactor is replaced with the reactor gas contained in the liquid displacement vessel connected to the reactor (Figure IV-1). This causes liquid to be transferred from the second displacement vessel to the first. The displacement process is reversed when the reactor volume is brought back to five liters with the raw sludge feed.

After the withdrawal of mixed liquor, the new daily feed was added with the aid of a funnel connected to the feed tube. After the feed was added, 333 ml of the effluent was set aside for analyses. The rest of the effluent (about 67 ml) was then used to flush the new feed completely through the feed tube and into the reactor.

2.32 Phase II

The experimental work of Phase II was conducted in two parts, designated Phase IIa and IIb in this report. Phase IIa consisted of operation of the anaerobic reactors on the basis of a 15 day SRT and 15 day LRT. Phase IIb consisted of operating the reactors on a 15 day SRT and five day LRT, simulating the anaerobic contact mode of operation. The temperature of operation was $35^{o}C$ throughout Phase II, as it was in Phase I.

On November 17, 1978, all three reactors were seeded with five liters of digesting sludge from the Mt. Vernon, Iowa anaerobic digesters. The primary sludge used for feeding the reactors was also obtained from the Mt. Vernon wastewater treatment plant, as in Phase I. However, shortly after the Phase II experiments began, the practice of recycling trickling filter sloughings to the primary clarifier was instigated at Mt. Vernon. The feed sludge was therefore a mixture of raw primary sludge and trickling filter humus.

During Phase IIa the solids retention time (SRT) and liquid retention time (LRT) were maintained at 15 days by withdrawing and wasting 1/15 (333 ml) of the completely mixed digester contents

once daily as was done in Phase I. This volume was replaced with an equivalent volume of raw sludge and pyrolysis waste.

Physically, this was accomplished by first removing ± 400 ml of mixed liquor from the digester with the aid of a vacuum pump and a sidearm suction flask. Of this, 333 ml was either wasted or set aside for laboratory analyses, and ± 67 ml was set aside to be used later. Raw sludge and pyrolysis waste in the amount of 333 ml was then added to the digester. The raw sludge was added on a batch basis with the aid of a funnel. The pyrolysis waste was added on a continuous basis, using a peristaltic pump. Finally, the raw sludge feed tube was flushed completely into the reactor with the ± 67 ml of digesting sludge previously set aside.

During Phase IIb units 2 and 3 were operated in the anaerobic contact mode at 35°C. The SRT and HRT were maintained at 15 days and 5 days, respectively, wasting 1/15 of the total volatile solids and 1/5 (1000 ml) of the liquid from the reactors once daily. This volume was replaced with 333 ml of raw sludge and pyrolysis waste, as in Phase IIa, and 667 ml of dilution water. The dilution water consisted of distilled water previously deoxygenated with 1 to 2 ml of raw sludge per 4 l of distilled water.

Physically, this was accomplished by removing ± 2000 ml of mixed liquor from the digester with the aid of a vacuum pump and a sidearm suction flask. Of this, ± 250 ml was wasted or set aside for laboratory analyses, ± 50 ml was set aside to be used later, and ± 1700 ml was placed in a 2000-ml graduated cylinder and allowed to settle in an incubator overnight at 15°C to 20°C. Raw sludge and pyrolysis waste

in the amount of 333 ml and dilution water in the amount of 667 ml were then added to the digester. The raw sludge and dilution water were added on a batch basis with the aid of a funnel. The pyrolysis waste was added on a continuous basis with the aid of a peristaltic pump. The graduated cylinder containing the previous day's digesting sludge was then removed from the incubator; ± 750 ml of relatively clear supernatant was withdrawn with the aid of a vacuum pump and sidearm suction flask, and was either wasted or set aside for laboratory analyses. The remaining ± 950 ml of subnatant, containing most of the solids, was added to the digester with the aid of a funnel. Finally, the feed tube was flushed with the ± 50 ml of digesting sludge previously set aside.

Thus, on any given day, the net effect was the displacement of ± 1950 ml of digesting sludge, with 333 ml of raw sludge and PUROX pyrolysis waste, 667 ml of dilution water, and ± 950 ml of the previous day's settled subnatant. This maintained the HRT at 5 days. By adjusting the relative amounts of digesting sludge (± 250 ml) and settled supernatant (± 750 ml) that were wasted, approximately 1/15 of the total volatile solids were removed daily to maintain the SRT at ± 15 days.

During Phase IIb, Unit No. 1 was operated at an SRT and LRT of 15 days, as in Phase IIa. This was done to provide a direct comparison of operation in the anaerobic contact mode to operation with equal SRT and LRT values.

3.0 RESULTS AND DISCUSSION

3.1 Phase I Results

When enough background data had been collected to insure

equilibrium conditions in the reactors, an attempt was made to feed PUROX pyrolysis wastes to one of the units. On February 7, 1978, Unit No. 3 was fed ten percent (33 ml) of PUROX wastes along with 90 percent (300 ml) of primary wastewater sludge. This resulted in severe inhibition of the reactor, as illustrated in Figure IV-2.

From Figure IV-2, it can be seen that in just one day the pH dropped 0.2 points (from 7.2 to 7.0), volatile acids rose from 120 mg/l to 1630 mg/l, and gas production dropped from 0.333 cu.ft . per day to 0.076 cu.ft. per day. The PUROX wastes feed rate was held constant at 33 ml/day for the next 25 days. Sodium bicarbonate was added several times over this period in an attempt to hold the pH above 6.5. By day 25 (February 24, 1978) the volatile acids had risen to 9,100 mg/l and gas production had declined to 0.050 cu.ft./day. By then it was obvious that Unit No. 3 was hopelessly "stuck" and would not recover. Feeding was therefore discontinued and 40 percent of the reactor contents was withdrawn and wasted. In the following days, effluent from Unit Nos. 1 and 2 was added to Unit No. 3 to speed its recovery.

With the negative results of the first attempt to feed PUROX wastes, it was decided to neutralize the pH of the wastes using sodium hydroxide. On February 28, 1978, the No. 2 unit was fed five percent (16 ml) of the pH neutralized PUROX waste and 95 percent (317 ml) of the primary wastewater sludge. This attempt also resulted in severe inhibition of Unit No. 2, as illustrated in Figure IV-3.

In just one day the pH of Unit 2 declined from 7.2 to 7.0, the volatile acids rose from 120 mg/l to 1,610 mg/l, and gas production dropped from 0.272 cu.ft./day to 0.086 cu.ft./day. The PUROX waste

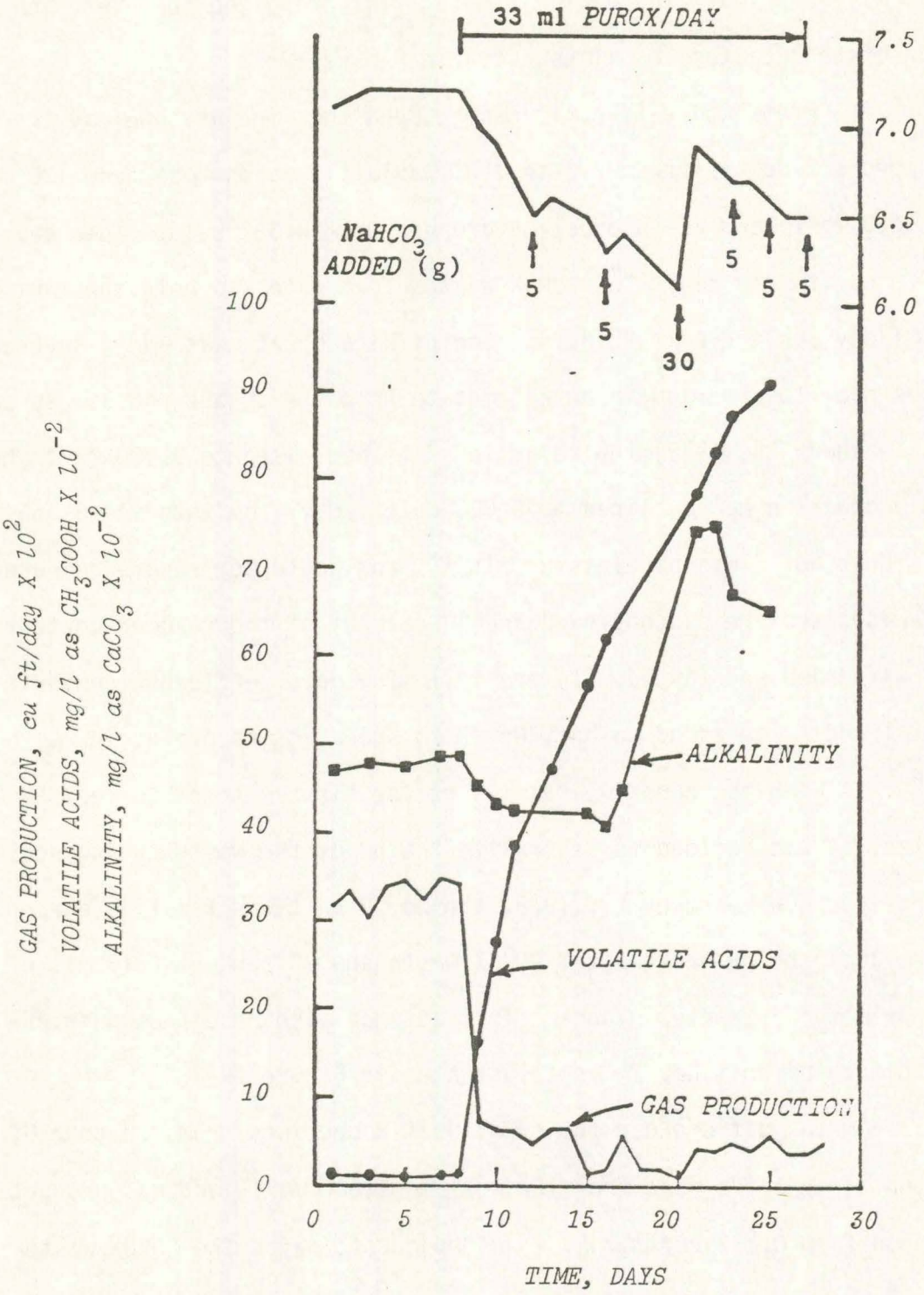


Figure IV-2. Effect of 10 Percent PUROX Pyrolysis Wastes Feed with No Pretreatment.

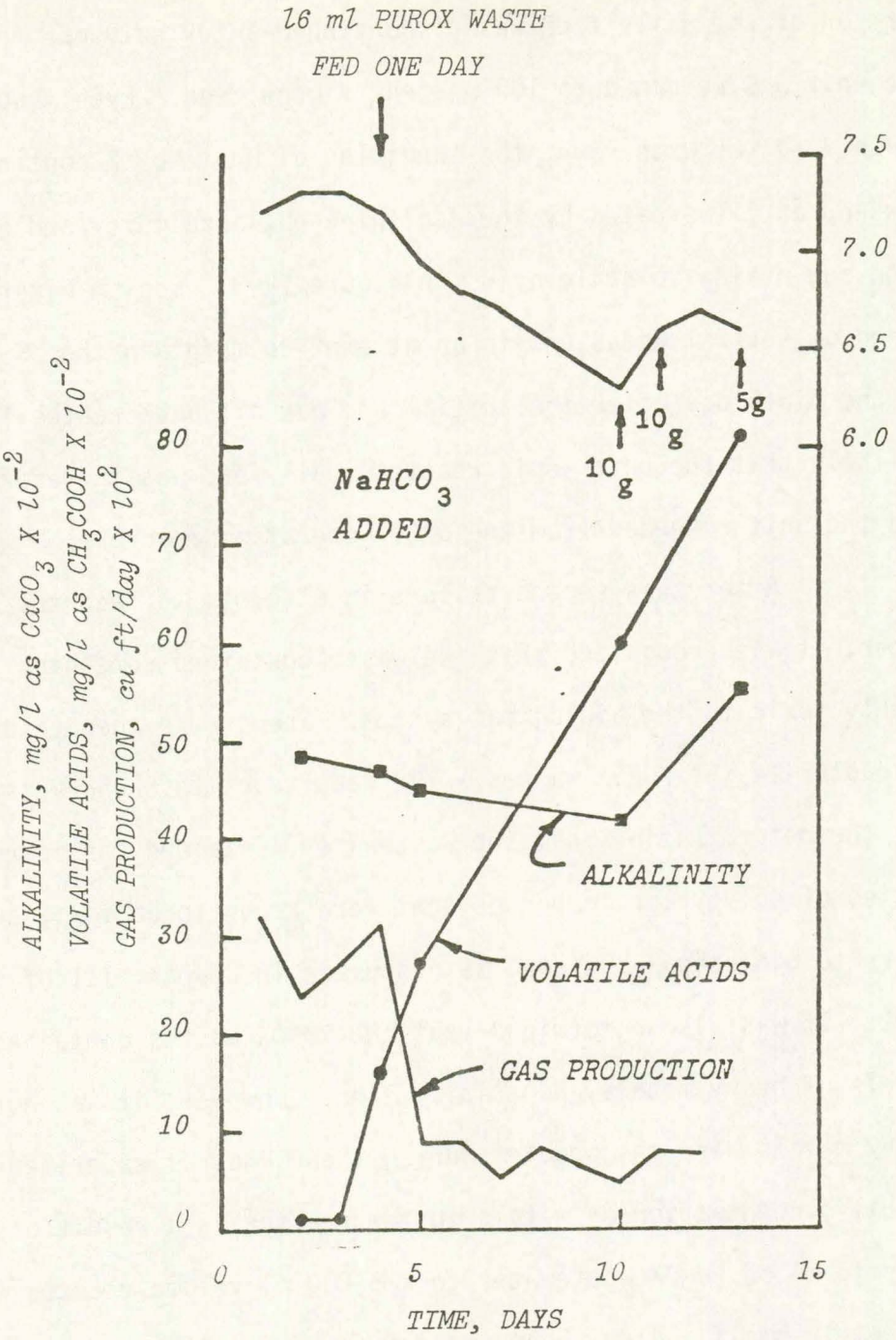


Figure IV-3. Effect of 5 Percent PUROX Pyrolysis Wastes Feed with pH Neutralization.

portion of the daily feed was discontinued after only one feeding and the unit was returned to 100 percent sludge feed. Even though the PUROX feed was withdrawn, the condition of Unit No. 2 continued to worsen, as illustrated by the declining pH, alkalinity and gas production and rising volatile acids in Figure IV-3. Sodium bicarbonate was added on several occasions in an attempt to maintain the pH above 6.5. By the ninth day after the initial one day of PUROX wastes feed it seemed unlikely that the unit would recover. All feed was therefore withdrawn and the unit reseeded from the other operating reactors.

After this second failure in attempts to feed the PUROX wastewater, it was recognized that the waste contained something that was highly toxic to the biological system. Steps were then taken to further characterize the PUROX wastes. The results of this characterization was the determination that the wastewater contained considerable quantities of polycyclic compounds that were known to be toxic and inhibitory to biological systems, as discussed in Chapter III of this report. It was also determined that the PUROX wastes contained high levels of heavy metals, especially zinc. However, it was not felt that heavy metals were the problem during these Phase I experiments. The actual concentration of metals in the reactor as a result of feeding only 16 ml of PUROX wastewater to a 5,000 ml volume reactor would be extremely small. Also, heavy metals are precipitated with sulfides in anaerobic reactors.

For the third attempt at treating the PUROX waste, it was decided to start two or the units on very small amounts of the waste. If the units accepted the waste without significant inhibition, the

amount of PUROX wastes being fed each day would be held constant for a few days. This was done in an attempt to acclimate the bacteria to the PUROX waste. When the unit appeared to have accepted the amount of PUROX wastes being fed, the amount was increased. In this phase, Units 1 and 2 were started at five ml/day and one ml/day of PUROX waste, respectively.

The results of Unit 1 are illustrated in Figure IV-4. In Figure IV-4, the arrows indicate the total milliliters of PUROX waste fed on that day. That amount was then continued until changed to a new daily total as indicated by the next arrow. The initial introduction of the PUROX waste (five ml/day on day 10, June 2, 1978), resulted in a slight inhibition of the digester. The pH declined from 7.1 to 7.0, the volatile acids increased from 1,354 mg/l to 1,766 mg/l, and gas production declined from 0.333 cf/day to 0.226 cf/day. Gas production declined 32.1 percent in one day compared to 72.7 percent and 68.4 percent in the first two attempts to feed PUROX wastes. In the next few days, the pH declined only an additional 0.1 point from 7.0 to 6.9. The volatile acids leveled off at 2,109 mg/l. Gas production increased from 0.226 cf/day to 0.267 cf/day. On day 19 (June 11, 1978), it was decided to increase the PUROX waste from five ml/day to ten ml/day (Figure IV-4). This resulted in further inhibition to Unit 1. Because of this, the PUROX feed was reduced to eight ml/day. At day 25 (June 17, 1978), it was decided to feed the unit one half the daily feed twice a day. This was done to keep the concentration of PUROX waste in the unit at any one time to a minimum. The twice a day feeding was continued from day 25 (June 17, 1978) to day 51 (July

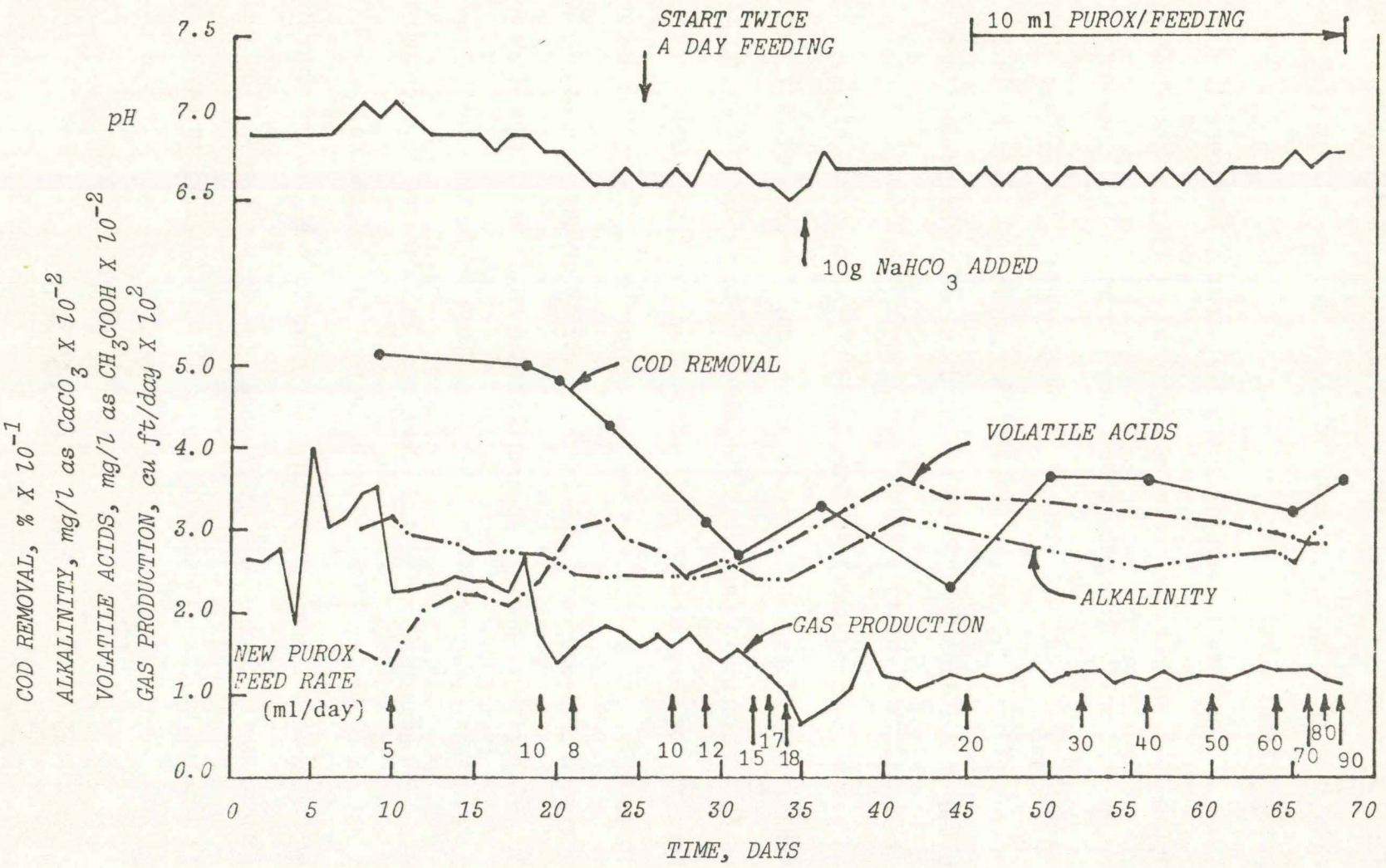


Figure IV-4. Unit No. 1 Results.

13, 1978). During this time, the PUROX feed was slowly increased from four ml/feeding (8 ml/day) to ten ml/feeding (20 ml/day). Additional decline in the condition of the reactor occurred. On day 35 (June 27, 1978), the pH was 6.6 and gas production was at a low of 0.066 cf/day. Ten grams of sodium bicarbonate were added to the unit. The condition of the reactor improved over the next few days and then stabilized somewhat after day 40 (July 2, 1978). From day 52 (July 14, 1978) to the conclusion of this experimental period (July 30, 1978), the maximum amount of PUROX waste fed at any one time was held at ten ml. The amount of PUROX fed per day was then increased by increasing the number of ten ml feedings per day. For example, on day 52 (July 14, 1978), the PUROX waste was increased from 20 ml/day (2 - 10 ml feedings/day) to 30 ml/day (3 - 10 ml feedings/day). During this period, no further change in the condition of the reactor took place. The pH stayed between 6.6 and 6.8. Volatile acids declined from 3,200 mg/l to 2,850 mg/l. Gas production held fairly constant at around 0.20 cf/day. COD removal held at approximately 35 percent. By the end of this experiment, the condition of the reactor was stable as shown in Figure IV-4. On day 68 (July 30, 1978), the influent and effluent COD's were 58,550 mg/l and 37,500 mg/l, respectively. Using the accepted figure of 5.62 cubic feet of methane per pound of COD stabilized, methane production was 0.087 cf/day. Total gas production for that day was 0.114 cf/day; therefore, the methane content was 76.2 percent of the total gas.

The results for Unit No. 2 are illustrated in Figure IV-5. In Figure IV-5, as in Figure IV-4, the arrows indicated the total

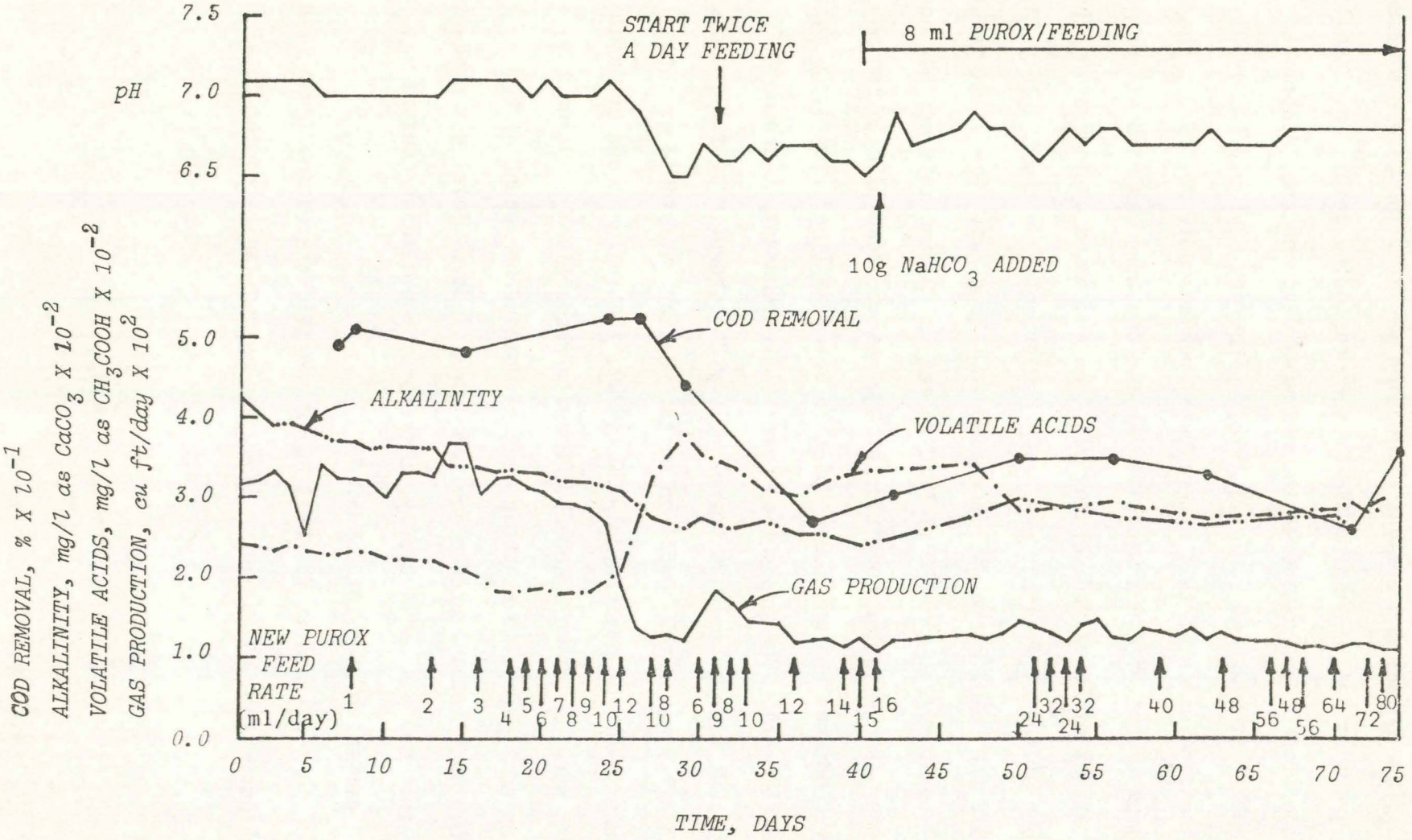


Figure IV-5. Unit No. 2 Results.

milliliters of PUROX waste fed on a given day. That amount was then continued until changed to a new daily total as indicated by the next arrow. The initial introduction of the PUROX waste (1 ml/day on day 8, May 25, 1978) had little effect on the reactor. From day 8 (May 25, 1978) to day 24 (June 10, 1978) the PUROX feed was increased from one ml/day to ten ml/day. Increases were made in one ml increments. During this period, no change in the condition of the reactor occurred. On day 25 (June 11, 1978), the PUROX feed was increased by two ml from ten ml/day to 12 ml/day. This resulted in a 44.4 percent decrease in gas production (0.270 cf/day to 0.150 cf/day), as shown in Figure IV-5. The amount of PUROX fed per day was decreased over the next few days in an attempt to reduce the inhibition. Starting on day 31 (June 17, 1978), the primary sludge and PUROX were fed twice a day. The twice a day feeding was continued from day 31 to day 50 (July 6, 1978). During this time, the PUROX feed was increased from four ml/feeding (8 ml/day) to eight ml/feeding (16 ml/day). The condition of the reactor appeared to stabilize after day 36 (June 22, 1978) with the exception of the pH which declined to 6.5 on day 40. Ten grams of sodium bicarbonate were added to the reactor and the pH eventually leveled off around 6.8. From day 51 (July 7, 1978) to the conclusion of this experiment (July 30, 1978), the maximum amount of PUROX wastes fed at any one time was held at eight ml. The amount of PUROX fed per day was then increased by increasing the number of eight ml feedings per day. For example, on day 51 (July 7, 1978), the PUROX waste was increased from 16 ml/day (2 - 8 ml feedings/day) to 24 ml/day (3 - 8 ml feedings/day). During this time, the condition of the reactor held fairly

constant as shown in Figure IV-5. The pH stayed between 6.7 and 6.8. The volatile acids stayed around 2,900 mg/l. Gas production stayed fairly constant at around 0.125 cf/day. COD removal averaged about 32.5 percent. On the last day of the experiment, (day 74, July 30, 1978), the influent and effluent CODs, were 58,550 mg/l and 37,500 mg/l, respectively. From these figures, the methane production was calculated to be 0.087 cf/day. The total gas production was 0.114 cf/day so the methane content was 76.1 percent of the total gas.

At the conclusion of these simulated continuous-feed experiments, samples of the three reactors were taken. Unit No. 1 was being fed 90 ml of PUROX per day, Unit No. 2 was being fed 80 ml of PUROX per day, and Unit No. 3 was a control (no PUROX fed). These samples plus a sample of the raw PUROX waste were taken to the University of Iowa Hygienic Laboratory. Tests were run to identify the organic compounds present in each sample. A description of the analytical procedure is given in the Appendix B. The classes of organic compounds represented in each fraction are listed in Table IV-2. The results are given in Table IV-3.

Unit No. 1 was fed a total of 1,379 ml of the PUROX waste during the experiment illustrated by Figure IV-4. Due to the daily withdrawal of one-fifteenth of the total reactor volume, the amount of PUROX in the unit at the end of the experiment was about 640 ml in the five liter unit. Therefore, the 100 ml sample of Unit No. 1, analyzed for organics, would have contained approximately 13 ml of volume that originated as PUROX waste and 87 ml of volume that originated as primary sludge. These figures were used to estimate the organics in Unit No. 1

Table IV-2. Classes of Organic Compounds Eluting in Each Liquid Chromatography Fraction

Fraction #	Compound Type
1	Aliphatic Hydrocarbons
2	Aromatic Hydrocarbons Polynuclear Aromatic Hydrocarbons Halides
3	Esters Ethers Nitro compounds Epoxides
4	Phenols Ketones Aldehydes Phthalates
5	Phenols Alcohols Amines
6	Amides Sulfonates Aliphatic/Aromatic acids
7	Sulfonates/Sulfonic acids
8	Sulfonic acids

Table IV-3. Residue in Fraction (Normalized)*

Fraction No.	Weight Residue in Samples (mg/100 ml)			
	Raw PUROX Waste	Unit 1 90 ml PUROX/day	Unit 2 80 ml PUROX/day	Unit 3 control No PUROX
1	0.873	13.412	4.951	0.694
2	3.959	3.451	1.212	0.862
3	11.412	2.412	1.221	0.211
4	9.625	5.437	3.354	0.506
5	110.346	1.057	0.801	0.059
6	6.826	47.864	26.425	3.031
7	3.409	8.813	4.455	96.722
8	1.695	1.891	0.986	137.065

* 100 ml samples used for Raw PUROX Waste. 85 ml samples used for Units 1-3. Values for Units 1-3 normalized to 100 ml.

assuming the same degree of removal of the primary sludge in Unit No. 1 as in the control (Unit No. 3).

The estimation process is shown in Table IV-4. In Table IV-4, columns B and D are the organics found in the PUROX waste and Unit No. 3 (the control), respectively. Column C represents the organics present in a 13 ml sample of PUROX waste. Column E represents the organics present in an 87 ml sample of digested primary sludge. Columns C and E are added to give column F, which is the estimate of organics present in Unit No. 1. This column is compared to column G, which lists the organics found in Unit No. 1. Most of the organics found in Unit No. 1 were close to or less than the estimated values with the exception of fractions one and six.

Unit No. 2 was fed a total of 1,514 ml of PUROX wastes. Due to dilution, approximately 690 ml of PUROX wastes remained in the five liter unit at the end of the experiment. Therefore, a 100 ml sample from Unit No. 2 would contain about 14 ml of PUROX wastes. The same procedure that was used for estimation of organics in Unit No. 1 was used for Unit No. 2. This is shown in Table IV-5. Comparison of columns F and G in Table IV-5 shows that fractions one and six were again higher in Unit No. 2 than estimated.

At the conclusion of Phase I, one final experiment was run using Unit No. 3 which had served as the control. On day 11 (July 31, 1978) the unit was introduced to the PUROX waste by feeding three ml of the waste ten times a day (30 ml PUROX/day). The results of this experiment were to be compared with the first experiment when 33 ml of PUROX wastes was fed on a slug basis. This was to compare continuous

Table IV-4. Estimated Organics in Unit No. 1

A Fraction No.	B PUROX mg/100 ml	C PUROX mg/13 ml	D Unit 3 mg/100 ml	E Unit 3 mg/87 ml	F C + E	G Unit 1 mg/100 ml
1	0.873	0.112	0.694	0.605	0.717	13.412
2	3.959	0.510	0.862	0.751	1.261	3.451
3	11.412	1.469	0.211	0.184	1.653	2.412
4	9.625	1.239	0.506	0.441	1.680	5.437
5	110.346	14.207	0.059	0.051	14.258	1.057
6	6.826	0.879	3.031	2.641	3.520	47.864
7	3.409	0.439	96.722	84.269	84.708	8.813
8	1.695	0.218	137.065	117.418	117.636	1.891
Totals	148.145	19.073	239.150	206.360	225.433	84.337

Table IV-5. Estimated organics in Unit No. 2

A Fraction No.	B PUROX mg/100 ml	C PUROX mg/14 ml	D Unit 3 mg/100 ml	E Unit 3 mg/86 ml	F C + E	G Unit 1 mg/100 ml
1	0.873	0.121	0.694	0.598	0.719	4.951
2	3.959	0.547	0.862	0.743	1.290	1.212
3	11.412	1.577	0.211	0.182	1.759	1.221
4	9.625	1.330	0.506	0.436	1.766	3.354
5	110.343	15.251	0.059	0.048	15.299	0.801
6	6.826	0.943	3.031	2.612	3.555	26.425
7	3.409	0.471	96.722	83.354	83.825	4.455
8	1.695	0.234	137.065	118.121	118.355	0.986
Totals	148.145	20.474	239.150	206.094	226.568	43.405

feeding with once-a-day batch feeding without acclimation. The results of this experiment are illustrated in Figure IV-6. On day one the pH dropped from 7.1 to 6.9, volatile acids increased from 360 mg/l to 1,303 mg/l, and gas production decreased from 0.239 cf/day to 0.087 cf/day or 63.6 percent. After the first day, the inhibition continued but appeared to be slowing down.

3.2 Phase I Discussion

The threshold limit for introduction of the PUROX waste to unacclimated bacteria is five milliliters in a five liter reactor volume (1 ml/l). This amount did exhibit some inhibition but the reactor was able to recover to a degree. Some acclimation by the bacteria to the PUROX waste occurred in both of the simulated continuous feed experiments. Acclimation was achieved by introducing the PUROX feed at or below the threshold limit mentioned above. The process of acclimation was very slow. Any increases in the PUROX feed rate have to be small and implemented slowly during the early stages of acclimation. Once the bacteria are acclimated to the PUROX waste, degradation of the PUROX wastes occurs to some degree. Evidence of the acclimation and degradation is the fact that during the continuous feed experiments, both Unit 1 and 2 were fed PUROX wastes at a much higher rate (80 ml/day and 90 ml/day) than in the slug feed experiments (33 ml/day and 16 ml/day) where severe inhibition caused reactor failure. In the continuous feed experiments, Units 1 and 2 were fed 1,379 ml and 1,514 ml, respectively, of the PUROX waste. This compares to 33 ml and 16 ml of PUROX wastes fed in the initial experiments.

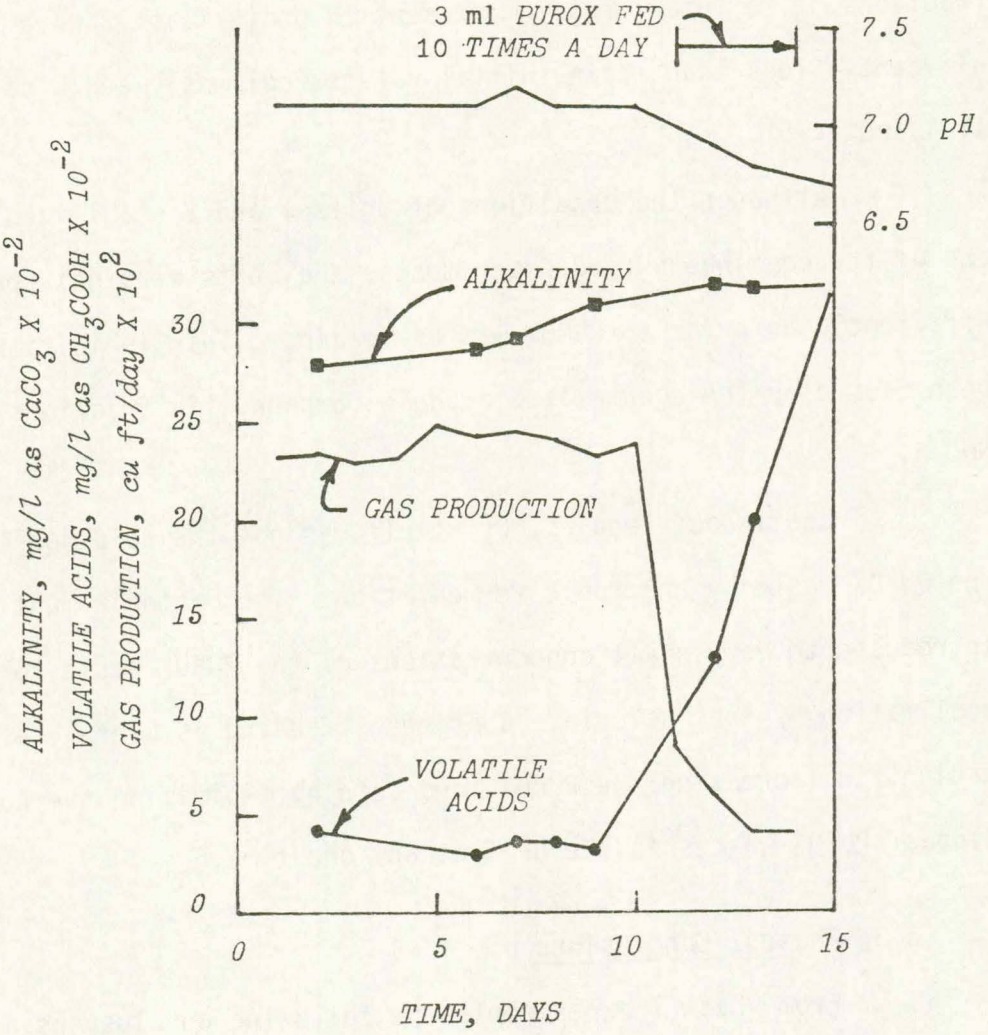


Figure IV-6. 3 ml pH Neutralized PUROX Fed 10 Times a Day.

The organic analysis (Tables IV-4 and IV-5) shows that most of the organic fractions are being degraded to some degree. The exceptions in both units are fractions no. 1 and no. 6. It could be that the bacteria require a longer period of acclimation to the organics in these fractions. The total organics present in Units 1 and 2 were both significantly less than their initial values (columns F and G of Tables IV-4 and IV-5).

Although the conditions of Units 1 and 2 stabilized toward the end of the continuous feed experiments, the units were not operating as efficiently as prior to PUROX wastes feeding. This inhibition may have been caused by the accumulated organic compounds in fractions No. 1 and No. 6.

Continuous feeding, by itself, is not the solution to treating the PUROX waste by anaerobic fermentation. The bacteria must first be introduced to very small concentrations of the PUROX waste to allow acclimation by the bacteria. Continuous feeding is useful, after acclimation, in increasing the PUROX feed rate by minimizing the concentration of PUROX wastes in the unit at any one time.

3.3 Phase I Conclusions

From Phase I experiments the following conclusions are evident:

1) Five milliliters in the five liter anaerobic reactors was the threshold limit for the introduction of PUROX waste to unacclimated bacteria without inhibition.

2) Acclimation of the anaerobic bacteria to the PUROX waste is possible.

3) Acclimated bacteria are able to degrade the PUROX waste to some degree.

4) Continuous feeding, by itself, is not the total solution to treating the PUROX waste. The bacteria need to be acclimated to the wastes.

3.4 Phase II Results

3.41 Phase IIa

Phase IIa involved the acclimation of a completely mixed anaerobic biological system to the PUROX wastes. The SRT, LRT, and temperature were maintained at 15 days, 15 days, and 35°C, respectively.

Phase IIa can be divided into six time periods on the basis of the rate of PUROX waste feed to Unit No. 1. These six time periods are: (1) start-up, (2) initial pyrolysis feed, (3) increasing pyrolysis feed, (4) constant pyrolysis feed, (5) decreasing pyrolysis feed, and (6) discontinued pyrolysis feed. In each period, the rate of pyrolysis feed was dictated by reactor response. Units No. 2 and 3 were maintained as controls throughout Phase IIa and were fed only raw sludge (333 ml/day).

The time period from November 17, 1978, to January 5, 1979, constituted start-up. It consisted of 50 days, or approximately three turnovers (SRTs) of the reactor volume. During this period, only raw sludge (333 ml) was fed to Unit No. 1. December 29, 1978, was arbitrarily designated as day zero of Phase IIa.

On day 7, the last day of the start-up period, the digesters were being fed 0.12 pounds of volatile solids per cubic foot of volume (lb VSa/f^3). By this time all three reactors were achieving similar results in terms of volatile solids destruction and gas production. Volatile solids reductions in Units 1, 2, and 3 were 48,8%, 51.8% and 48.9%, respectively. Gas production from Units 1, 2, and 3 was averaging 21.0, 20.9 and 21.8 standard cu.ft. per pound of volatile solids

destroyed (SCF/lb VSD), respectively. Thus all three units were operating normally and were considered to be in equilibrium.

Days 8 through 16 constituted the period of initial pyrolysis feed. During this period, 6 to 7 ml/day of pyrolysis waste and 326 to 327 ml/day of raw sludge were fed to Unit No. 1. Based on the findings of Phase I, it was decided to introduce the pyrolysis waste on a continuous-feed basis.

Table IV-6 shows the volume of PUROX pyrolysis wastes added to, wasted from, and remaining in Unit No. 1 from day 7 through day 90 of Phase IIa. The PUROX wastes feed varied from an initial daily value of 7 ml on day 7 to a high of 110 ml on day 64. Since the total volume of wastes added daily is constant (333 ml. of sludge and PUROX wastes), but the fraction of the total feed that is PUROX wastes increases, the percentage of the reactor volume occupied by PUROX wastes lags behind the actual percentage of PUROX wastes in the daily feed. Thus on day 22, for example, 14 ml of PUROX wastes was added to the reactor. This is 4.2 percent of the total feed volume of 333 ml. But 1.15 of the 79.3 ml of PUROX feed already in the reactor from previous days was removed. This amounts to 5.3 ml wasted, as shown on day 22 in Table IV-6. After feeding on day 22, the percentage of the reactor contents attributable to PUROX wastes is 1.8 and the PUROX wastes is diluted by a factor of 56.8 (5000/88). The data in Table IV-6 are also illustrated in Figure IV-7. Unit No. 1 was inhibited slightly by the initial 7 ml of PUROX wastes feed on day 7. This was reflected by a slight increase in the volatile acids concentration in the reactor and a slight decrease in gas production. On day 10, the volatile acids con-

Table IV-6. Pyrolysis Waste Added and Remaining, Unit No. 1

Day	PUROX Pyrolysis Wastes					
	Added		Wasted	Remaining		
	% of Feed	ml	ml	ml	% of Volume	Dilution
7	0	0	0	0	0	
8	2.1	7	0	7	0.1	714.3
9	1.8	6	0.5	12.5	0.2	398.9
10	1.8	6	0.8	17.7	0.4	282.5
11	1.8	6	1.2	22.5	0.4	222.0
12	1.8	6	1.5	27.0	0.5	185.1
13	1.8	6	1.8	31.2	0.6	160.2
14	1.8	6	2.1	35.1	0.7	142.3
15	2.1	7	2.3	39.8	0.8	125.6
16	2.2	7.5	2.6	44.6	0.9	112.0
17	2.9	9.7	3.0	51.4	1.0	97.4
18	2.9	9.7	3.4	57.6	1.2	86.8
19	2.9	9.7	3.8	63.5	1.3	78.7
20	3.4	11.2	4.2	70.5	1.4	71.0
21	4.0	13.5	4.7	79.3	1.6	63.1
22	4.2	14	5.3	88.0	1.8	56.8
23	4.9	16.2	5.9	98.3	2.0	50.9
24	5.3	17.7	6.6	109.5	2.2	45.7
25	6.0	20	7.3	122.2	2.4	40.9
26	6.7	22.2	8.1	136.2	2.7	36.7
27	6.5	21.7	9.1	148.8	3.0	33.6
28	6.6	22	9.9	160.9	3.2	31.1
29	7.4	24.5	10.7	174.7	3.5	28.6
30	8.0	26.5	11.6	189.5	3.8	26.4
31	4.8	16	12.6	192.9	3.9	25.9
32	8.6	28.5	12.9	208.6	4.2	24.0
33	8.9	29.5	13.9	224.1	4.5	22.3
34	8.6	28.5	14.9	237.7	4.8	21.0
35	9.2	30.5	15.8	252.4	5.0	19.8
36	8.6	28.5	16.8	264.0	5.3	18.9
37	9.3	31	17.6	277.4	5.6	18.0
38	9.8	32.5	18.5	291.4	5.8	17.3
39	10.7	33.5	19.4	307.5	6.2	16.3
40	11.6	38.5	20.5	325.5	6.5	15.4
41	12.3	41	21.7	344.8	6.9	14.5
42	12.3	41	23.0	362.8	7.3	13.8
43	14.1	47	24.2	385.6	7.7	13.0
44	14.1	47	25.7	406.9	8.1	12.3
45	15.0	50	27.1	429.8	8.6	11.6
46	15.9	53	28.6	454.1	9.1	11.0

Day 0 = 12/29/78

Table IV-6. Continued.

Day	PUROX Pyrolysis Wastes					
	Added		Wasted	Remaining		
	% of Feed	ml	ml	ml	% of Volume	Dilution
47	17.4	58	30.3	481.9	9.6	10.4
48	17.7	59	32.1	508.7	10.2	9.8
49	18.9	63	33.9	537.8	10.8	9.3
50	19.5	65	35.8	567.0	11.3	8.8
51	23.3	77.5	37.8	606.7	12.1	8.2
52	25.5	85	40.4	651.2	13.0	7.7
53	24.6	82	43.4	689.8	13.8	7.2
54	24.6	82	46.0	725.8	14.5	6.9
55	22.5	75	48.4	752.4	15.0	6.6
56	24.3	81	50.2	783.3	15.7	6.4
57	25.5	85	52.2	816.0	16.3	6.1
58	27.0	90	54.4	851.6	17.0	5.9
59	29.1	97	56.8	891.9	17.8	5.6
60	31.2	104	59.5	936.4	18.7	5.3
61	31.8	106	62.4	980.0	19.6	5.1
62	28.8	96	65.3	1010.7	20.2	4.9
63	30.6	102	67.4	1045.3	20.9	4.8
64	33.0	110	69.7	1085.6	21.7	4.6
65	33.0	110	72.4	1123.2	22.5	4.4
66	31.8	106	74.9	1154.3	23.1	4.3
67	32.4	108	77.0	1185.4	23.7	4.2
68	32.4	108	79.0	1214.4	24.3	4.1
69	31.8	107	81.0	1239.4	24.8	4.0
70	32.1	105	82.6	1263.8	25.3	4.0
71	31.5	92	84.2	1284.5	25.7	3.9
72	27.6	94	85.6	1290.9	25.8	3.9
73	28.2	93	86.1	1298.8	26.0	3.8
74	27.9	95	86.6	1305.2	26.1	3.8
75	28.5	83.2+	87.0	1313.2	26.3	3.8
76	22.8	86 *	99.3	1297.1	25.9	3.8
77	23.4	87 *	99.4	1283.8	25.7	3.9
78	23.7	87 *	98.3	1272.4	25.4	3.9
79	23.7	86 *	97.5	1262.0	25.2	4.0
80	23.4	86 *	96.7	1251.3	25.0	4.0
81	23.4	86 *	95.8	1241.4	24.8	4.0
82	23.4	86 *	95.1	1232.4	24.6	4.1
83	23.4	86	94.4	1224.0	24.5	4.1
84	0	0	0	1224.0	24.5	4.1
85	0	0	0	1224.0	24.5	4.1
86	0	0	62.4	1161.6	23.2	4.3
87	0	0	59.2	1102.3	22.0	4.5

TABLE IV-6. Continued.

Day	PUROX Pyrolysis Wastes					
	Added		Wasted	Remaining		
	% of Feed	ml	ml	ml	% of Volume	Dilution
88	0	0	56.2	1046.1	20.9	4.8
89	0	0	53.4	992.8	19.9	5.0
90	0	0	0	992.8	19.9	5.0

Day 90 = 3/29/79

\+ Includes 7.2 ml in the 45 ml of composite effluent from days 51 to 60 added as seed.

* Includes 8 ml in the 50 ml of composite effluent from days 51 to 60 added as seed.

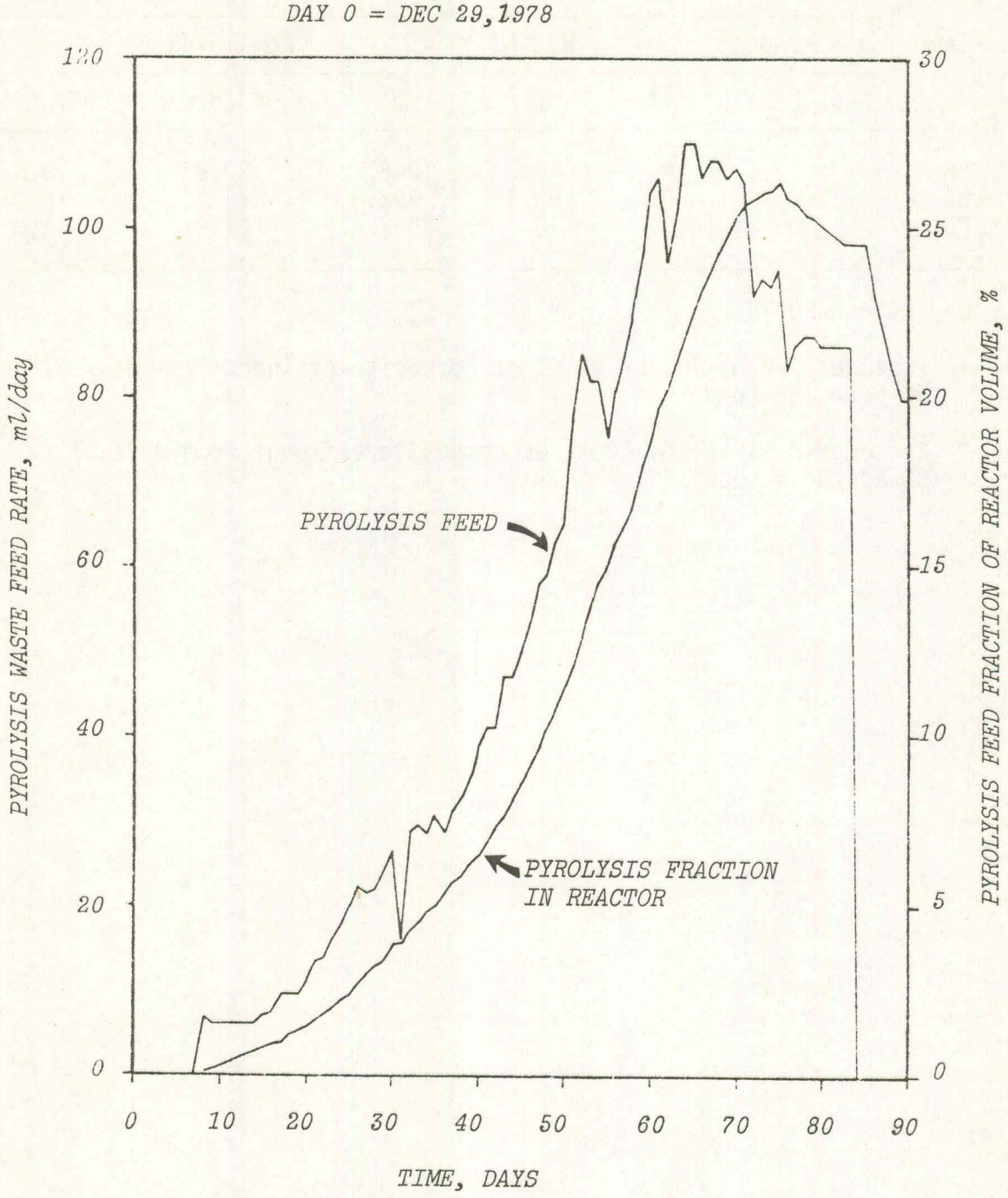


Figure IV-7. Pyrolysis Feed and Pyrolysis Fraction of Digester Volume vrs. Time, Phase I.

centration in Unit 1 was 608 mg/l, as compared to 206 mg/l on day 7, and gas production had decreased by 14.7 percent. However, by day 16, the volatile acids and gas production had returned to normal, and all three units were again operating similarly. Therefore, it was decided to begin increasing the rate of pyrolysis feed to Unit No. 1.

Days 17 through 64 constituted the period of increasing PUROX pyrolysis feed. During this period, the rate of pyrolysis feed to Unit 1 was gradually increased from 7.5 ml/day to 110 ml/day, in the manner indicated by Table IV-4 and Figure IV-8. The raw sludge feed was correspondingly reduced from 326 to 223 ml/day. This was accomplished in 48 days. On any given day during this period, the combined volume of raw sludge and pyrolysis waste fed to the digester was always 333 ml.

From Table IV-6 it can be seen that on day 64, 1085.6 ml of the volume of Unit 1 had been added as pyrolysis waste and the remaining 3914.4 ml (5000 - 1085.6) had been added as sludge. The pyrolysis waste in Unit 1 was, in effect, diluted by a factor 4.6:1, and constituted 21.7 percent of the reactor volume.

The data indicate that from day 17 through day 55, when the pyrolysis feed was $\pm$ 80 ml/day, the microorganisms in Unit 1 were undergoing acclimation and were apparently responding well to the pyrolysis feed. During this period of time, the volatile acids, alkalinity, and pH of all three units remained virtually the same. The total gas production in Unit 1 decreased gradually with respect to the total gas production in Units 2 and 3. This is illustrated in Figure IV-9. However, this relative decline in total gas production was to

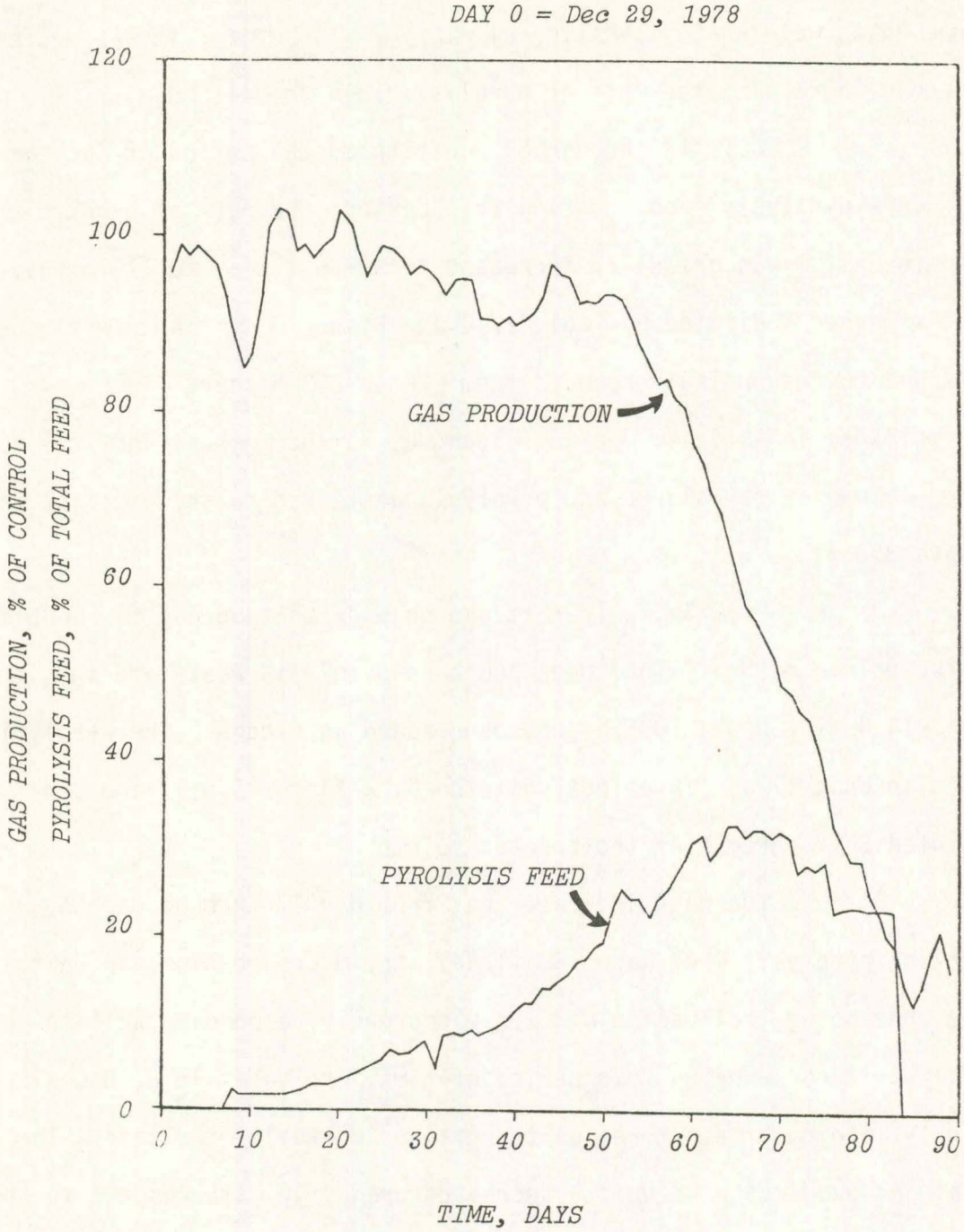


Figure IV-8. Gas Production as Per Cent of Control and Pyrolysis Feed as Per Cent of Total vrs. Time for Unit #1, Phase I.

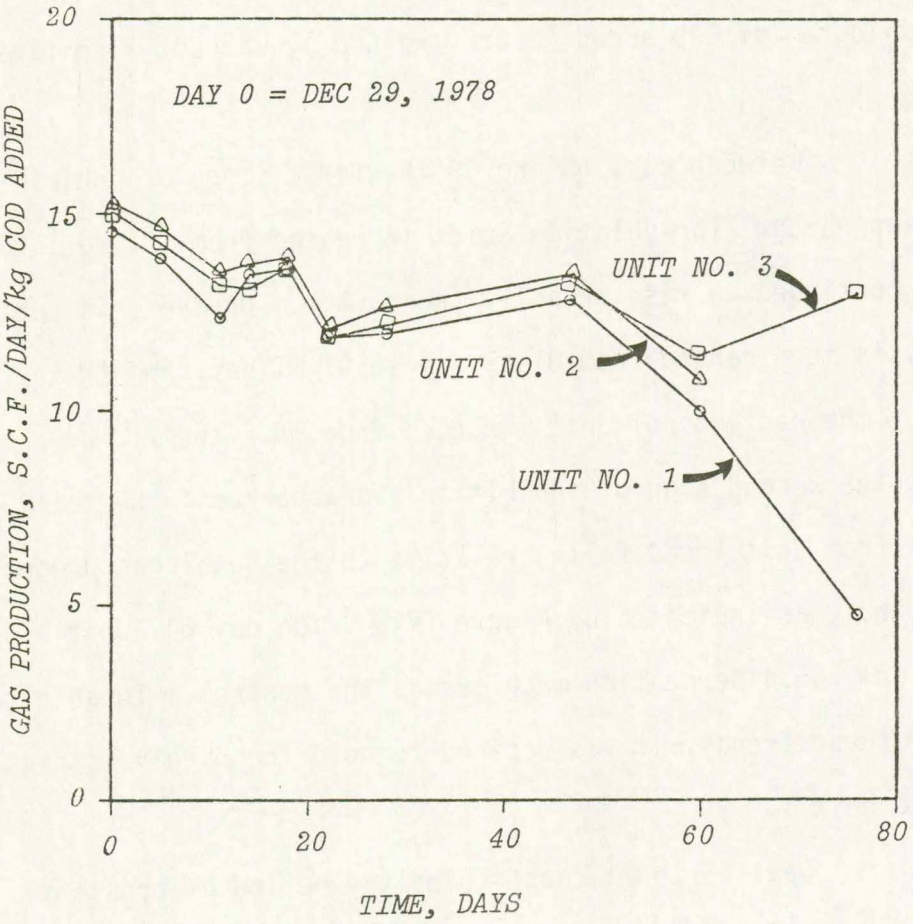


Figure IV-9. Gas Production per Kilogram of COD added vrs. Time, Phase I.

be expected, as the chemical oxygen demand (COD) of the raw sludge exceeded the COD of the pyrolysis waste. Therefore, the total COD added daily to Unit 1 gradually decreased with respect to the total COD added daily to Units 2 and 3. Figure IV-9 indicates that the difference in gas production between the three units, when expressed as standard cubic feet per kilogram of COD added (S.C.F./kg COD_a), was not significant through day 55.

Between days 56 and 59 the first signs of inhibition in Unit 1 appeared. The volatile acids increased from 197 mg/l to 351 mg/l, and continued to rise steadily thereafter. During this period, the pyrolysis feed ranged from 81 ml/day to 97 ml/day, and the pyrolysis fraction of the contents of Unit 1 ranged from 15.7 to 17.8 percent. By day 64, the second sign of inhibition had appeared. The total gas production from Unit 1 had fallen relative to the total gas production in the control, as indicated by Figure IV-9 . On day 64, Unit 1 was producing only 65.5 percent as much gas as the control. In an attempt to reverse these trends, it was decided to hold the pyrolysis feed constant to Unit 1.

Days 65 to 71 constituted the period of constant pyrolysis feed. During this period, 105 to 110 ml/day of pyrolysis waste and 221 to 225 ml/day of raw sludge were fed to Unit 1. The volatile acids continued to rise, and the total gas production continued to fall relative to the control. During this period, two other indicators of the impending failure appeared. The pH in Unit 1 fell from 7.25 to 7.0, and the alkalinity declined relative to the alkalinity in the control.

By day 71, Unit 1 was well into failure. It was therefore decided to determine whether or not the reactor would respond to a series of cutbacks in the rate of pyrolysis feed.

Day 72 through day 83 constituted the period of decreasing pyrolysis feed. During this period, the pyrolysis feed was first decreased to ± 93 ml/day, and then to ± 78 ml/day. The raw sludge feed was correspondingly increasing to 240 ml/day and then to 55 ml/day.

The first decrease to ± 93 ml/day on day 72 held the pyrolysis fraction of the volume of Unit 1 constant at ± 26 percent. The second decrease, to ± 78 ml/day on day 76, reduced the pyrolysis fraction to 24.5 percent on day 83. This was still well above the 15.0 to 17.0 percent pyrolysis fraction at which inhibition began. On day 76, the practice of adding the composited effluent from days 51 through 60 to Unit 1 was instigated. This was an attempt to provide the digester with needed enzymes. Alkalinity in the form of sodium bicarbonate ($NaHCO_3$) was also added to provide for pH control.

In spite of these efforts, Unit 1 continued toward complete failure. On day 81, the pH fell to 6.1. On day 82, the volatile acids had risen to 6636 mg/l, and the total alkalinity was 4860 mg/l. This meant that the bicarbonate alkalinity was only 160 mg/l. Salts of the volatile acids accounted for the rest of the total alkalinity measured. By day 84, Unit 1 was producing only 14.8 percent as much total gas as the control. Figure IV-9 indicates that gas production, expressed as S.C.F./kg COD_a, had also fallen drastically by this time. Thus, it was decided to discontinue PUROX pyrolysis feed to Unit 1.

3.42 Phase IIb

Phase IIb involved the acclimation of both a completely mixed anaerobic biological system (as in Phase IIa) and an anaerobic contact biological system to PUROX pyrolysis gas scrubber waste. The SRT, LRT, and temperature for the complete mix system were maintained at 15 days, 15 days, and 35^{o}C (as in Phase IIa). The SRT, LRT, and temperature for the contact system were maintained at 15 days, 5 days and 35^{o}C, respectively.

Phase IIb can be divided into four time periods on the basis of the rate of pyrolysis feed to Units 1 and 2. These four time periods are: (1) start-up, (2) initial pyrolysis feed, (3) increasing pyrolysis feed, and (4) equilibrium pyrolysis feed. In each period, the rate of pyrolysis feed was dictated by the reactor's response. Unit 1 was operated in the conventional mode, and Units 2 and 3 were operated in the contact mode. Unit 3 was maintained as a control and was fed only raw sludge (333 ml) throughout Phase IIb.

The time period from March 30, 1979, to June 7, 1979, constituted start-up. It consisted of the conversion of Units 2 and 3 to the anaerobic contact mode, and the reseeding and complete recovery of Unit 1. This period spanned 70 days, or apprixmately 4-1/2 SRTs. During this period, only raw sludge (333 ml) was fed to Units 1 and 2. May 30, 1979, was arbitrarily designated as day 0 of Phase IIb.

On day 3, the alkalinity in Units 1, 2, and 3 was 5220 mg/l, 2290 mg/l, and 2250 mg/l, respectively, as calcium carbonate. The pH was 7.3, 6.75, and 6.75. The lower pH and alkalinity in Units 2 and 3 were the result of the higher rate of washout associated with the

lower LRT of the anaerobic contact mode of operation. The pH in Units 2 and 3 was at the lower end of the normal operating range and approching the level at which the methane formers are inhibited. Therefore, it was decided to artificially raise the pH in these units prior to the introduction of the pyrolysis waste. Alkalinity, in the form of sodium bicarbonate ($NaHCO_3$), was added on days 5 and 6 to Units 2 and 3 for this purpose.

On day 7, the last day of the start-up period, Units 1, 2, and 3 were achieving volatile solids reductions of 49.2, 61.1 and 59.5 percent, respectively. Gas production was averaging 20.1, 16.4, and 16.5 standard cubic feet per pound of volatile solids destroyed from Units 1, 2 and 3, respectively.

As shown in Table IV-7, Unit 1 was operating in much the same manner as the three units of Phase IIa, as would be expected. The high alkalinity and low volatile acids condition provided Unit 1 with a large buffer capacity against failure from inhibition. Therefore, it was decided that Unit 1 was ready for acclimation to the pyrolysis waste.

It can also be seen from Table IV-7, that Units 2 and 3 were operating very similarly, although quite differently from Unit 1. The volatile acids concentration, alkalinity, and pH in Units 2 and 3 were significantly less than the volatile acids concentration, alkalinity, and pH in Unit 1. Because of this, the buffer capacity of Units 2 and 3 was also less than the buffer capacity of Unit 1. Total gas production from Units 2 and 3 was essentially the same as the total gas production from Unit 1. Therefore, it was decided that Unit 2 was also

Table IV-7. Actual Operating Conditions on Day 7 of Phase IIb

Parameter	Unit 1	Unit 2	Unit 3
Solids Retention Time (days)	15	15	15
Liquid Retention Time (days)	15	5	5
Temperatire (^{o}C)	35	35	35
Volatile Solids Loading (lb VS added/day)	0.11	0.11	0.11
Volatile Solids Reduction (%)	49.2	61.1	59.5
Gas Production (S.C.F./lb VS destroyed)	20.1	16.4	16.5
Volatile Acids (mg/l as CH_3COOH)	86	34	43
Alkalinity (mg/l as $CaCO_3$)	5650	3380 (2290)*	3490 (2250)*
pH	7.25	7.0 (6.75)*	7.0 (6.75)*

* Value on Day 3 prior to $NaHCO_3$ addition on days 5 and 6.

ready for acclimation to the pyrolysis waste. Unit 3 was the control, as mentioned earlier.

Days 8 through 14 constituted the period of initial pyrolysis feed, as shown in Table IV-8. During this period, ± 2 ml/day of pyrolysis waste and 331 ml/day of raw sludge were fed to Units 1 and 2. As in Phase IIa, the pyrolysis waste was introduced on a continuous basis. The ± 2 ml/day of initial pyrolysis feed was less than the initial ± 6 ml/day of pyrolysis feed used in Phase IIa, due to the lower buffer capacity in Unit 2.

As shown in Table IV-8, on day 14, 11.3 ml of the volume of Unit 1 had been added as pyrolysis waste, and the remaining 4989.7 ml had been added as raw sludge. The pyrolysis waste in Unit 1 was, in effect, diluted 441.2:1, and the pyrolysis waste constituted 0.2 percent of the digester volume. It can also be seen that on day 14, 7.8 ml of the volume of Unit 2 had been added as pyrolysis waste, and the remaining 4992.2 ml had been added as raw sludge and dilution water. The pyrolysis waste in Unit 2 was, in effect, diluted 640.4:1, and constituted 0.2 percent of the digester volume. The lower volume of pyrolysis waste in Unit 2 is the result of the higher rate of washout, due to the lower LRT.

Units 1 and 2 experienced only very slight inhibition, if any, during the initial acclimation period. The first indication of inhibition, volatile acids, remained at essentially at a constant level in all three units during this period. The pH and alkalinity in Units 2 and 3 decreased over this period. However, this was expected since both units had been artificially raised with $NaHCO_3$ prior to the intro-

Table IV-8. Pyrolysis Fraction of Digester Volume, Phase II

Day	Unit	Pyrolysis					
		Added		Wasted	Remaining		
		% of Feed	ml	ml	ml	% of Volume	Dilution
7	1	0	0	0	0	0	
	2	0	0	0	0	0	
8	1	0.6	1.9	0	1.9	0.1	2631.6
	2	0.6	1.9	0	1.9	0.1	2631.6
9	1	0.6	2.1	0.1	3.9	0.1	1290.9
	2	0.6	2.1	0.4	3.6	0.1	1381.2
10	1	0.6	2.0	0.3	5.6	0.1	890.4
	2	0.6	2.0	0.7	4.9	0.1	1021.2
11	1	0.5	1.8	0.4	7.0	0.1	710.2
	2	0.5	1.8	1.0	5.7	0.1	874.6
12	1	0.6	2.0	0.5	8.6	0.2	583.3
	2	0.6	2.0	1.1	6.6	0.1	760.6
13	1	0.6	2.0	0.6	10.0	0.2	500.0
	2	0.6	2.0	1.3	7.2	0.1	688.8
14	1	0.6	2.0	0.7	11.3	0.2	441.2
	2	0.6	2.0	1.4	7.8	0.2	640.4
15	1	1.2	3.9	0.8	14.5	0.3	345.4
	2	1.2	3.9	1.6	10.1	0.2	492.8
16	1	1.1	3.8	1.0	17.3	0.4	288.8
	2	1.1	3.8	2.0	11.9	0.2	419.6
17	1	1.7	5.6	1.2	21.8	0.4	229.8
	2	1.7	5.6	2.4	15.1	0.3	330.4
18	1	1.6	5.5	1.5	25.8	0.5	193.7
	2	1.6	5.5	3.0	17.6	0.4	284.0
19	1	1.8	5.9	1.7	30.0	0.6	166.7
	2	1.8	5.9	3.5	20.0	0.4	250.2
20	1	1.6	5.4	2.0	33.4	0.7	149.8
	2	1.6	5.4	4.0	21.4	0.4	233.8
21	1	1.6	5.2	2.2	36.4	0.7	137.5
	2	1.6	5.2	4.3	22.3	0.4	224.1
22	1	1.6	5.4	2.4	39.3	0.8	127.1
	2	0.7	5.4	4.5	20.2	0.4	246.9
23	1	2.2	7.4	2.6	44.1	0.9	113.3
	2	2.2	7.4	4.0	23.6	0.5	211.9
24	1	2.3	7.7	2.9	48.9	1.0	102.3
	2	2.3	7.7	4.7	26.6	0.5	188.1
25	1	2.7	9.1	3.3	54.7	1.1	91.4
	2	2.7	9.1	5.3	30.4	0.6	164.7
26	1	2.8	9.3	3.6	60.4	1.2	82.8
	2	2.8	9.3	6.1	33.6	0.7	148.8
27	1	2.9	9.7	4.0	66.0	1.3	75.7
	2	2.9	9.7	6.4	36.8	0.7	135.7

Day 0 = 5/30/79

Table IV-8. Continued.

Day	Unit	Pyrolysis					
		Added		Wasted	Remaining		
		% of Feed	ml	ml	ml	% of Volume	Dilution
28	1	3.3	11.0	4.4	72.6	1.4	68.8
	2	3.3	11.0	7.4	40.5	0.8	123.5
29	1	3.4	11.4	4.8	79.2	1.6	63.1
	2	3.4	11.4	8.1	43.8	0.9	114.2
30	1	4.1	13.6	5.3	87.5	1.8	57.1
	2	4.1	13.6	8.8	48.6	1.0	102.8
31	1	3.9	13.0	5.8	94.7	1.9	52.8
	2	3.9	13.0	9.7	51.9	1.0	96.3
32	1	4.6	15.2	6.3	103.6	2.1	48.3
	2	4.6	15.2	10.4	56.7	1.1	88.2
33	1	4.7	15.6	6.9	112.3	2.2	44.5
	2	4.7	15.6	11.3	61.0	1.2	82.0
34	1	5.2	17.5	7.5	122.3	2.4	40.9
	2	5.2	17.5	12.2	66.3	1.3	75.4
35	1	5.0	16.5	8.2	130.6	2.6	38.3
	2	5.0	16.5	13.3	69.5	1.4	71.9
36	1	5.6	18.6	8.7	140.5	2.8	35.6
	2	5.6	18.6	13.9	74.2	1.5	67.4
37	1	5.4	17.9	15.0	143.4	2.9	34.9
	2	5.4	17.9	14.8	77.3	1.6	64.7
38	1	7.8	26	9.6	159.8	3.2	31.3
	2	7.8	26	15.5	87.8	1.8	56.9
39	1	7.2	24	10.7	173.2	3.5	28.9
	2	7.2	24	17.6	94.3	1.9	53.0
40	1	8.7	29	11.6	190.6	3.8	26.2
	2	8.7	29	18.9	104.4	2.1	47.9
41	1	8.1	27	12.7	204.9	4.1	24.4
	2	8.1	27	20.9	110.5	2.2	45.2
42	1	8.6	28.5	13.7	219.8	4.4	22.8
	2	8.6	28.5	22.1	116.9	2.3	42.8
43	1	9.0	30	14.6	235.1	4.7	21.3
	2	9.0	30	23.4	123.5	2.5	40.5
44	1	8.7	29	15.7	248.4	5.0	20.1
	2	8.7	29	24.7	127.8	2.6	39.1
45	1	9.0	30	16.6	261.8	5.2	19.1
	2	9.0	30	25.6	132.3	2.6	37.8
46	1	9.3	31	17.5	275.4	5.5	18.2
	2	9.3	31	26.4	136.8	2.7	36.6
47	1	10.8	36	18.4	293.0	5.9	17.1
	2	10.8	36	27.4	145.4	2.9	34.4
48	1	11.1	37	19.5	310.5	6.2	16.1
	2	11.1	37	29.1	153.4	3.1	32.6
49	1	10.8	36	20.7	325.8	6.5	15.4
	2	10.8	36	30.7	158.7	3.2	31.5

Table IV-8. Continued.

Day	Unit	Pyrolysis					
		Added		Wasted	Remaining		
		% of Feed	ml	ml	ml	% of Volume	Dilution
50	1	11.4	38	21.7	342.1	6.8	14.6
	2	11.4	38	21.7	165.0	3.3	30.3
51	1	12.0	40	22.8	359.3	7.2	13.9
	2	12.0	40	33.0	172.0	3.4	29.1
52	1	12.9	43	24.0	378.3	7.6	13.2
	2	12.9	43	34.0	180.6	3.6	27.7
53	1	13.5	45	25.2	398.1	8.0	12.6
	2	13.5	45	36.1	189.4	3.8	26.4
54	1	9.9	33	26.5	404.6	8.1	12.4
	2	9.9	33	37.9	184.6	3.7	27.1
55	1	14.4	48	27.0	425.6	8.5	11.8
	2	14.4	48	36.9	195.6	3.9	25.6
56	1	13.8	46	28.4	443.2	8.9	11.3
	2	13.8	46	39.1	202.5	4.0	24.7
57	1	15.3	51	29.6	464.7	9.3	10.8
	2	15.3	51	40.5	213.0	4.3	23.5
58	1	15.3	51	31.0	484.7	9.7	10.3
	2	15.3	51	42.6	221.4	4.4	22.6
59	1	15.0	50	32.3	502.1	10.0	10.0
	2	15.0	50	44.3	227.1	4.5	22.0
60	1	15.6	52	33.5	520.9	10.4	9.6
	2	15.6	52	45.4	233.7	4.7	21.4
61	1	16.8	56	34.7	542.2	10.8	9.2
	2	16.8	56	46.7	243.0	4.9	20.6
62	1	16.5	55	36.1	561.0	11.2	8.9
	2	16.5	55	48.6	249.4	5.0	20.0
63	1	18.0	60	37.4	583.6	11.7	8.6
	2	18.0	60	49.9	259.5	5.2	19.3
64	1	19.2	64	38.9	608.7	12.2	8.2
	2	19.2	64	51.9	271.6	5.4	18.4
65	1	20.7	69	40.6	637.1	12.7	7.8
	2	20.7	69	54.3	286.3	5.7	17.5
66	1	21.3	71	42.5	665.6	13.3	7.5
	2	21.3	71	57.3	300.0	6.0	16.7
67	1	24.0	80	44.1	701.3	14.0	7.1
	2	24.0	80	60.0	320.0	6.4	15.6
68	1	25.2	84	46.8	738.5	14.8	6.8
	2	25.2	84	64.0	340.0	6.8	14.7
69	1	26.7	89	49.2	778.3	15.6	6.4
	2	26.7	89	68.0	361.0	7.2	13.8
70	1	27.0	90	51.9	816.4	16.3	6.1
	2	27.0	90	72.2	378.8	7.6	13.2
71	1	27.3	91	54.4	853.0	17.1	5.9
	2	27.3	91	75.8	394.0	7.9	12.7

Table IV-8. Continued.

Day	Unit	Pyrolysis					
		Added		Wasted	Remaining		
		% of Feed	ml	ml	ml	% of Volume	Dilution
72	1	29.7	99	56.9	895.1	17.9	5.6
	2	29.7	99	78.8	414.2	8.3	12.1
73	1	30.3	101	59.7	936.4	18.7	5.3
	2	30.3	101	82.8	432.4	8.6	11.6
74	1	32.1	107	62.4	981.0	19.6	5.1
	2	32.1	107	86.5	452.9	9.1	11.0
75	1	33.3	111	65.4	1026.6	20.5	4.9
	2	33.3	111	90.6	473.3	9.5	10.6
76	1	28.2	94	68.4	1052.2	21.0	4.8
	2	28.2	94	94.7	472.7	9.4	10.6
77	1	30.0	100	70.1	1082.0	21.6	4.6
	2	28.8	96	94.5	474.1	9.5	10.6
78	1	33.3	111	72.1	1120.9	22.4	4.5
	2	33.3	111	94.8	490.3	9.8	10.2
79	1	36.6	122	74.7	1168.2	23.4	4.3
	2	36.6	122	98.1	514.2	10.3	9.7
80	1	38.1	127	77.9	1217.3	24.4	4.1
	2	38.1	127	102.8	438.4	10.8	9.3
81	1	2.1	7	81.2	1143.1	22.9	4.4
	2	39.6	132	107.7	562.7	11.2	8.9
82	1	5.1	17	76.2	1083.9	21.7	4.6
	2	42.6	142	112.5	592.2	11.8	8.4
83	1	15.0	50	72.3	1061.7	21.2	4.7
	2	41.4	138	118.4	611.7	12.2	8.1
84	1	23.1	77	70.8	1067.9	21.4	4.7
	2	44.7	149	122.3	638.4	12.8	7.8
85	1	22.5	75	71.2	1071.7	21.4	4.7
	2	47.2	157	127.7	667.7	13.4	7.5
86	1	21.6	72	71.4	1072.2	21.4	4.7
	2	48.6	162	133.5	696.2	13.9	7.2
87	1	21.3	71	71.5	1071.8	21.4	4.7
	2	49.8	166	139.2	722.9	14.5	6.9
88	1	13.2	44	71.4	1044.3	20.9	4.8
	2	48.6	162	144.6	740.4	14.8	6.8
89	1	21.6	72	69.6	1046.7	20.9	4.8
	2	47.1	157	148.1	749.3	15.0	6.7
90	1	21.3	71	69.8	1047.9	21.0	4.8
	2	49.5	165	149.8	764.4	15.3	6.5
91	1	5.7	19	69.9	997.0	19.9	5.0
	2	52.8	176	152.9	787.5	15.8	6.3
92	1	18.9	63	66.5	993.6	19.9	5.0
	2	52.2	174	157.5	804.0	16.1	6.2

Table IV-8. Continued.

Day	Unit	Pyrolysis					
		Added		Wasted	Remaining		
		% of Feed	ml	ml	ml	% of Volume	Dilution
93	1	19.5	65	66.2	992.3	19.9	5.0
	2	54.0	180	160.8	823.2	16.5	6.1
94	1	20.1	67	66.2	993.2	19.9	5.0
	2	55.8	186	164.6	844.6	16.9	5.9
95	1	19.5	65	66.2	992.0	19.8	5.0
	2	55.6	185	168.9	860.7	17.2	5.8

Day 95 = 9/2/79

duction of the pyrolysis waste. Therefore, it was decided to begin increasing the rate of PUROX pyrolysis feed to Units 1 and 2, as shown in Figure IV-10.

Days 15 through 80 constitute the period of increasing pyrolysis feed to Unit 1. During this period, the rate of pyrolysis feed was gradually increased from 2 ml/day to 127 ml/day (Table IV-8). The raw sludge feed was correspondingly reduced from 331 ml/day to 206 mg/day. This was accomplished in 66 days, as opposed to 35 days for the same increase in pyrolysis feed in Phase IIa. On any given day during this period, the combined volume of raw sludge and pyrolysis waste fed to Unit 1 was 333 ml.

During the period from day 15 through 80, Unit 1 appeared to be undergoing acclimation and was responding well to the pyrolysis waste. The pH and alkalinity declined gradually, and on day 80 were 7.1 and 5120 mg/l, as calcium carbonate, as compared to 7.3 and 5490 mg/l, as calcium carbonate, on day 15. The volatile acids concentration remained essentially constant, and was below 300 mg/l through day 78. The total gas production fell gradually through this period, both in absolute terms and relative to Unit 3 (the control).

The decline in total gas production was partially the result of the fact that the COD of the raw sludge exceeded the COD of the pyrolysis waste. Therefore, the total COD added daily to Unit 1 fell gradually with respect to the total COD added daily to Unit 3. Figure IV-11 indicates that the difference in gas production between Units 1 and 3, when expressed in terms of standard cubic feet per kilogram of COD added (S.C.F./kg COD_a), was small. The rate of pyrolysis

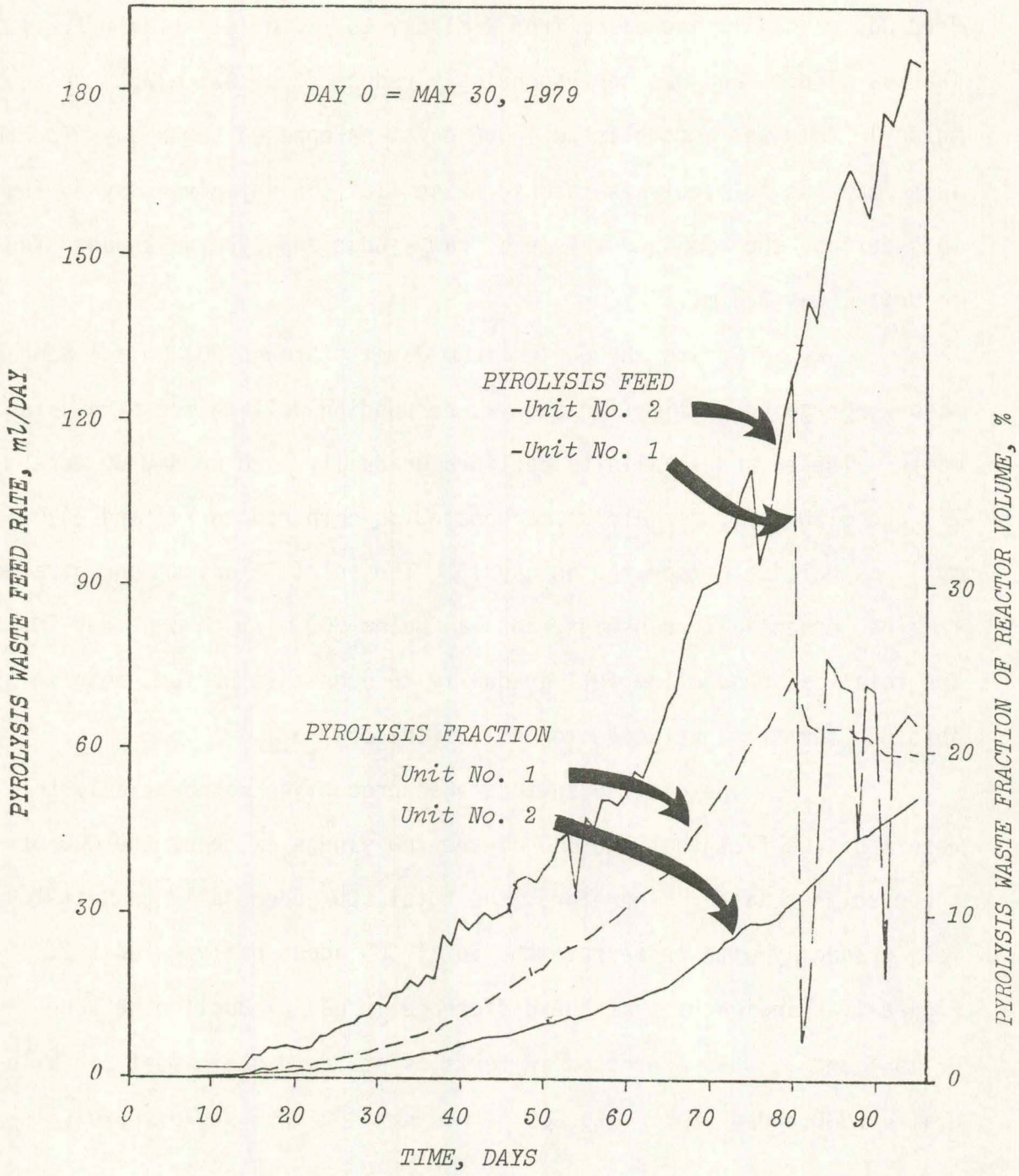


Figure IV-10. Pyrolysis Feed and Pyrolysis Fraction of Digester Volume vrs. Time, Phase II.

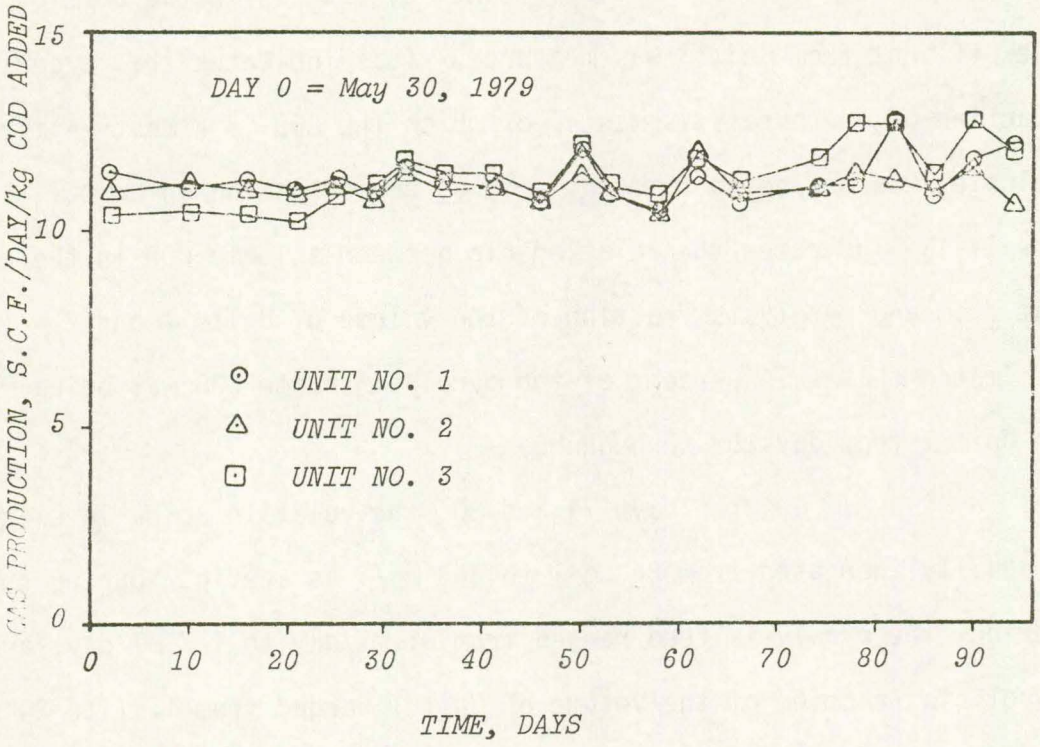


Figure IV-11. Gas Production per Kilogram of COD added vrs. Time, Phase II.

feed to Unit 1 and the gas production, as a percent of the control (Unit 3) is shown in Figure IV-12.

The soluble COD in the effluent from Unit 1 increased from an initial background level of 500 mg/l to 2583 mg/l on day 80. During the same period, no significant increase in the soluble COD in the effluent from Unit 3 was measured. This indicates that a certain fraction of the pyrolysis waste, of which the COD is almost entirely soluble, was not being removed, and was concentrating in Unit 1. Figure IV-13illustrates the relationship between soluble COD in the effluent from and pyrolysis fraction of the volume of Units 1 and 2. It is estimated that $\pm$ 76 percent of the pyrolysis waste COD was being removed in Unit 1 from days 53 through 80.

Between days 71 and 80, the volatile acids in Unit 1 gradually increased from 86 mg/l to 368 mg/l as acetic. During this period, the pyrolysis feed ranged from 91 ml/day to 127 ml/day, and the pyrolysis fraction of the volume of Unit 1 ranged from 17.1 to 24.0 percent. Although this increase in volatile acids was only slightly larger than the temporary increases experienced previously (around days 20, 41, and 59), it was decided to decrease the rate of pyrolysis feed to Unit 1. This was to ensure that this increase was only temporary, and to avoid the type of failure experienced in Phase IIa.

Days 15 through 95 constituted the period of increasing pyrolysis feed to Unit 2 as shown in Table IV-8 and Figure IV-10 During this period, the rate of pyrolysis feed to Unit 2 was gradually increased from 2 ml/day to 186 ml/day. The raw sludge was correspondingly reduced from 331 ml/day to 142 ml/day. This was accomplished in

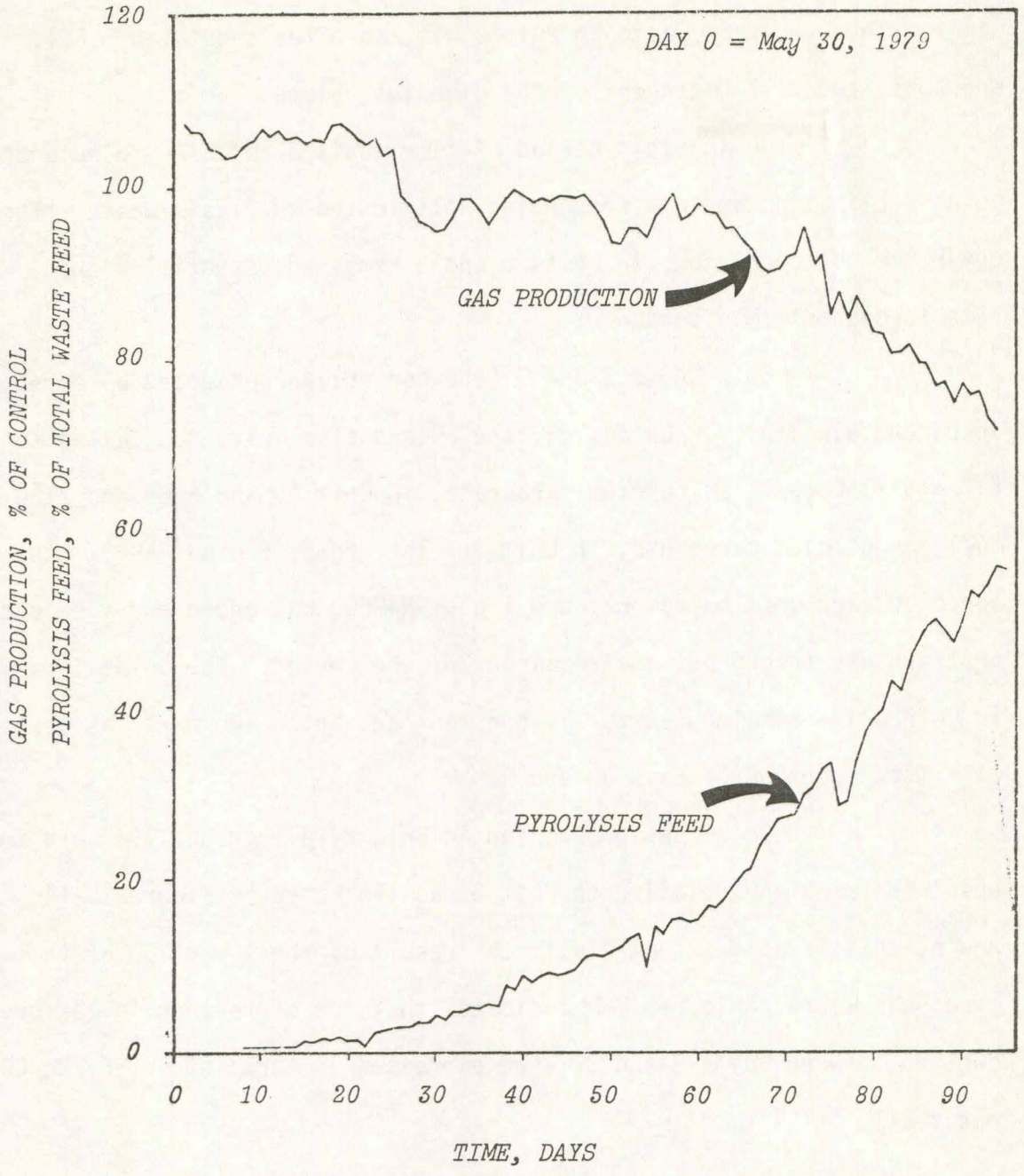


Figure IV-14. Gas Production as Per Cent of Control and Pyrolysis Feed as Per Cent of Total vrs. Time for Unit #2, Phase II.

81 days. On any given day during this period, the combined volume of raw sludge and pyrolysis waste fed to Unit 2 was 333 ml/day.

Referring to Table IV-9, it can be seen that on day 95, 860.7 ml of the volume of Digester 2 had been added as pyrolysis waste, and the remaining 4139.3 ml had been added as raw sludge and dilution water. The pyrolysis waste in Unit 2 was, in effect, diluted 5.8:1, and constituted 17.2 percent of the digester volume.

During this period of time, Unit 2 appeared to be undergoing acclimation and was responding well to the pyrolysis waste. The environmental conditions in Units 2 and 3 remained essentially the same throughout this period.

Both Units 2 and 3 (the control) experienced a decrease in pH and alkalinity. On day 61, the pH and alkalinity had fallen to 6.7 and 2130 mg/l, as calcium carbonate, in Unit 2, and 6.65 and 2100 mg/l, as calcium carbonate, in Unit 3. Therefore, 5 g of $NaHCO_3$ was added to each unit on day 62, and 1 g of $NaHCO_3$ was added every second or third day throughout the remainder of the period. The volatile acids in both Units remained virtually constant and below 100 mg/l, as acetic, with the exception of days 90 and 95.

Total gas production in Unit 2 fell gradually, both in absolute terms and relative to Unit 3, as indicated by Figure IV-14. Again, this is at least partially the result of the lower COD of the pyrolysis waste. Figure IV-11 indicates that the difference in gas production between Units 2 and 3, when expressed in terms of S.C.F./kg COD_a, was small.

The soluble COD in the effluent from Unit 2 increased from an initial background level of $\pm$ 250 mg/l to 2458 mg/l on day 94.

During the same period, no significant increase in the soluble COD in the effluent from Unit 3 (the control) was measured. This indicates that a certain fraction of the pyrolysis waste, of which the COD is almost entirely soluble, was not being removed, and was concentrating in Unit 2. Figure IV-13 illustrates the relationship between soluble COD in the effluent from and pyrolysis fraction of the volume of Unit 2. It is estimated that ± 68 percent of the pyrolysis waste COD was being removed from days 66 through 94.

The first signs of possible inhibition in Unit 2 occurred on days 90 and 95, when the volatile acids concentration in the reactor reached minor peaks of 163 mg/l and 137 mg/l, as acetic. Between days 90 and 95, the pyrolysis feed ranged from 165 ml/day to 186 ml/day, and the pyrolysis fraction of the volume of Unit 2 ranged from 15.3 percent to 17.2 percent.

3.5 Phase II Discussion

The completely mixed anaerobic biological system of Phase IIa was slightly inhibited by the initial introduction of pyrolysis waste at a continuous rate of ± 6 ml/day (1.8 percent of the total feed, and 0.12 percent of the reactor volume). However, the system quickly recovered from this inhibition and did not show further signs of inhibition until the continuous rate of pyrolysis feed had been increased to ± 90 ml/day (27.0 percent of the total feed). This rate of pyrolysis feed was reached 51 days after the initial introduction of pyrolysis wastes into the reactor. At the time the inhibition occurred, the fraction of the reactor volume that originated as pyrolysis wastes was 17 percent.

The system continued to fail as the rate of PUROX pyrolysis wastes feed was increased to and held constant at 106 ml/day (31.8 percent of the total feed). During this period, the pyrolysis fraction of the reactor volume increased to 25.7 percent, well above the 17 percent where inhibition first occurred. Decreases in the rate of pyrolysis feed to 92 ml/day (27.6 percent of the total feed) and 78 ml/day (23.4 percent of the total feed) still did not save the reactor. Complete failure resulted.

The completely mixed anaerobic biological system of Phase IIb did not show signs of inhibition following the initial introduction of PUROX pyrolysis waste at a rate of $\pm$ 2 ml/day (0.6 percent of the total feed). The first signs of inhibition did not occur until the rate of pyrolysis feed had been increased to $\pm$ 111 ml/day (33.3 percent of the total feed). This rate was reached 68 days after the beginning of pyrolysis feed. At the time the inhibition occurred, the pyrolysis fraction of the reactor volume was 22 percent. Prior to inhibition, the digester was achieving a $\pm$ 76 percent reduction of the COD in the PUROX pyrolysis wastes.

The system responded favorably to a decrease in the rate of pyrolysis feed, which reduced the pyrolysis fraction of the reactor volume to 19.9 percent, well below the 22 percent at which the inhibition occurred. The reactor appeared well on its way to complete recovery when the rate of pyrolysis feed to the unit was maintained at 65 ml/day (19.5 percent of the total feed). This rate of feed maintained the pyrolysis fraction in the reactor volume at $\pm$ 20 percent.

The anaerobic contact biological system of Phase IIb did not show signs of inhibition following the initial introduction of pyrolysis waste at a continuous rate of ± 2 ml/day (0.6 percent of the total feed). The first signs of inhibition occurred during the final days of Phase IIb when the rate of PUROX pyrolysis feed had been increased to 186 ml/day (55.9 percent of the total feed). This rate of pyrolysis feed was reached 88 days after the initial introduction of the pyrolysis waste. At the time the first signs of inhibition occurred, the pyrolysis fraction of the reactor volume was 17 percent. Prior to this time, the digester was achieving a ± 68 percent reduction in the COD of the PUROX pyrolysis wastes.

The system appeared capable of operating at a rate of pyrolysis feed which would result in a fraction of the reactor volume occupied by pyrolysis wastes of 17 percent. This translates into a pyrolysis feed of 170 ml/day (51.0 percent of the total feed) in the anaerobic contact system used in this research.

Each anaerobic biological system fed pyrolysis waste in this research appeared capable of acclimating to a rate of pyrolysis feed which led to a pyrolysis fraction in the reactor volume of ± 17 percent. In the process, the reactors of Phase IIb appeared to be removing ± 70 percent of the pyrolysis waste COD. Beyond this level of pyrolysis feed, it appeared that the fraction of the pyrolysis waste COD that was not being removed reached a concentration which produced inhibition in the reactor. The pyrolysis waste COD which passed through the reactor was of sufficient quantity to require further treatment by some other means.

3.6 Phase II Conclusions

Based on the suspended growth experiments of Phase II, the following conclusions are warranted:

1) The PUROX pyrolysis gas scrubber wastes are treatable with an anaerobic biological system.

2) The pyrolysis gas scrubber waste must be diluted, preferably with some readily degradable waste such as primary sludge, prior to anaerobic biological treatment.

3) By operating in the anaerobic contact mode, thus reducing the liquid retention time while maintaining the necessary minimum solids retention time and thereby diluting the PUROX pyrolysis wastes, a larger percent of the total waste feed can be pyrolysis waste.

4) An anaerobic biological system cannot, by itself, remove all of the organic constituents of the waste. Thus further treatment prior to discharge is required.

4.0 PRACTICAL CONSIDERATIONS

Based on the findings of this research, it appears that an anaerobic biological system operating at 35^{o}C and a SRT of 15 days can be successful in the treatment PUROX pyrolysis wastes. However, the pyrolysis wastes feed would have to be limited to a rate that would result in a fraction of the reactor volume attributable to pyrolysis wastes of not more than 17 percent. For a system operated at a 15-day LRT, this translates into a pyrolysis feed of 17 percent of the total feed. For a system operating at a LRT of 5 days, this translates into a pyrolysis feed of 51 percent of the total feed, but would require approximately a three-fold dilution (51/17) of the combined raw sludge and pyrolysis wastes.

This research indicates that such an anaerobic system can be acclimated to the pyrolysis waste in a period of two months. The

initial rate of pyrolysis feed should be less than 1.5 percent of the total feed. Pyrolysis waste COD removals of approximately 70 percent can be achieved by such a system, based on the removals obtained in this research. Neutralization of the pyrolysis waste prior to treatment appears to be a necessity, and pH control during treatment may be required.

Caution should be used in applying these results to other pyrolysis wastes. The COD of the PUROX pyrolysis wastes used in this research was well below the typical COD range furnished by Union Carbide, as indicated by Table II-9. The bench scale reactors used in this research were under much tighter control than would be expected in a full-scale system. Also, the raw sludge used in this research produced a high-alkalinity, low-volatile-acids condition in the reactor, which provided good buffering against pH reductions. Nothing is known of the potential toxic or carcinogenic effects of the fraction of the pyrolysis waste COD left in the treated effluent. Further research will be needed to identify these refractory organics and to investigate methods of removal of the remaining organics.

Table V-3. Heavy Metals and Methods of Removal from the Low-Strength PUROX Waste.

Sample	Zinc (mg/l)		Lead (mg/l)	
	Total	Dissolved	Total	Dissolved
Untreated	15.0	15.0	1.62	1.10
Filtered	15.3	14.7	1.60	1.10
Activated Carbon (5 mg/l) 30 min. contact then filtered	14.0	14.0	1.05	0.69
Raise pH to 11.5	11.43	7.0	0.50	--
Na_2S (4 gram/l)	0.13	--	0.10	--

The selection of the lower strength pyrolysis wastewater had a significant effect upon the relative success of the anaerobic filter experiments as compared with the initial suspended growth experiments. Dilution of a toxic material is one of the simplest methods of controlling the inhibitory effects that certain compounds display in anaerobic systems. By selecting the most dilute strength PUROX waste sample for this phase of the project, the anaerobic filters were able to tolerate a higher percentage of pyrolysis waste in the daily feed, as will be shown later.

2.3 Loadings

It was decided that the hydraulic loading applied to the filters would remain constant throughout the project. Variations in organic loadings during the start-up of the filters were accomplished by changing the COD strength of the feed. In an examination of such factors

as filter volume, paristaltic pumping capacity, pyrolysis wastewater COD, and typical filter loadings, it was decided to feed each unit five liters of substrate per day. This would provide a rather long hydraulic detention time for an anaerobic filter (approximately six days).

The paristaltic pump was unable to operate at such a low feed rate continuously so a small appliance timer was used to control the pump. A daily feeding cycle consisted of eight separate pumping periods. Each period was 30 minutes long and the eight periods were evenly spaced over the 24 hour cycle. Approximately 90% of the daily feed was pumped automatically by this timed pump cycle. The last 10% was pumped under visual inspection prior to the make-up of the feed for the next day. This procedure ensured that the total feed volume was delivered to the units each day without any air being pumped into the filters by mistake.

Young and McCarty (22) operated an anaerobic filter on a synthetic waste with COD removals of 79% at a loading of 1.70 Kg COD/day/m^3. This level of COD removal was accomplished with a relatively low strength waste (1500 mg/l COD) using a hydraulic retention time of only nine hours. The operating temperature was only 25^{o}C (22). The research reported in this chapter used a higher temperature (35^{o}C), a longer detention time (about six days), and a much higher strength waste (13,600 mg/l COD). This resulted in a 96% removal of COD on synthetic wastes at a slightly higher organic loading of 1.80 Kg COD?day/m^3. This loading was determined by trial operation during the start-up phase rather than by a predetermined value.

2.4 Procedure

The filters were initially filled with digester supernate from the Iowa City wastewater plant to provide the necessary biological seed. Synthetic substrate was then introduced on a daily basis at a feed COD of 6,550 mg/l. The organic loading was gradually increased during this start-up phase (Days 1 to 87) by increasing the COD concentration in the synthetic feed. Equilibrium within the filters was established during the later stages of the start-up period at a loading of 1.80 Kg COD/day/m^3 (feed strength of 13,600 mg/l COD). The data observed at equilibrium was recorded and became the baseline for comparing later operation when the PUROX pyrolysis wastewater was introduced into the feed.

The PUROX wastewater was gradually introduced into the synthetic feed from day 87 to day 148. This introduction of the pyrolysis waste was done in 5% increments (based upon the COD of the filter influent). If inhibition of the anaerobic filters was noticed (by a decrease in daily gas production) the PUROX content of the feed was held constant. If gas production within the filters returned to normal, the PUROX content in the feed would be again increased gradually in 5% increments. Using this procedure, threshold toxicity concentrations for the anaerobic treatment of the pyrolysis wastewater could be determined. Also, acclimation of the anaerobic bacteria to the PUROX wastewater could be observed. By measuring the COD in the effluent, the anaerobic decomposition of the PUROX waste could be evaluated.

2.5 Data Collection

Analytical tests were run from various sample locations on the anaerobic filters and recorded for data evaluation. Performance

of the filters was measured by daily gas production and COD removal efficiency. The environmental control parameters were the pH, volatile acid concentrations, alkalinity and temperature. The data collected included:

1) Daily gas production from each filter unit.
2) COD (chemical oxygen demand) in the influent, effluent, and PUROX wastewater.
3) The pH of the influent, effluent, within the filters, and of the PUROX wastewater.
4) Volatile acid concentrations within the filters.
5) Alkalinity of the influent and effluent.
6) Temperature of the heating water reservoir and the filter water jackets.

2.6 Analytical Techniques

2.61 Gas Production

The daily gas production of each unit was measured volumetrically by Precision Scientific wet-test gas meters. These values were recorded at laboratory conditions and the fluctuations in air temperature and pressure could create a 3% variation. Correction to standard temperature and pressure (STP) would decrease the measured gas volumes by about 9%

2.62 COD

The chemical oxygen demand of the PUROX wastewater, the anaerobic filter influent and effluent was determined by the method described in part 508 of Standard Methods (65).

2.63 pH

The pH of the PUROX wastewater, filter influent, effluent and within the reactor was measured with a Beckman Zeromatic II pH meter. The samples were continuously stirred with a rotary magnetic mixer to assure good liquid contact with the pH probe. The pH meter was standardized with a pH 7 buffer solution prior to each measurement.

2.64 Volatile Acids Concentration

The volatile acids within the filters were determined by a distillation method described in part 504C of Standard Methods (65).

2.65 Alkalinity

The alkalinity of the filter influent and effluent was determined by a potentiometric titration using the Beckman Zeromatic II pH meter. The procedure is described in part 403 of Standard Methods (65).

2.66 Temperature

The temperature of the heating water reservoir and the filter water jackets was measured with mercury thermometers.

3.0 RESULTS AND DISCUSSION

3.1 Start-Up Phase

The purpose of the start up period was to establish steady-state conditions in the reactors and to provide a baseline of performance data for later comparison with operation when the PUROX waste was being fed to the units. The pyrolysis wastewater is acidic and contains such toxins as heavy metals, phenols, PAHs, and aldehydes. Therefore it was necessary to establish operation on the easily degradable synthetic feed

in such a manner that the filters were not strained with respect to pH or organic loadings. The objectives were to operate the units with very high levels of COD removal and at pH levels on the slightly alkaline side of optimal. Final baseline data were established with an effluent pH of about 7.8 and a COD removal efficiency of approximately 96%.

During the first 37 days of operation the Similac-based feed was supplemented with a protein extract (Bacto peptone). The purpose of this was to increase the protein content of the feed in an attempt to keep solids production down and to provide additional buffering for the system. Most of the alkalinity buffer in sewage sludge digesters comes from protein deaminization and subsequent reaction of the ammonia with carbon dioxide and water to form ammonium bicarbonate (18). The addition of peptone to the feed provided an additional 1,000 to 1,400 mg/l of alkalinity to the system. This is shown by comparing data of influent and effluent alkalinities during days 1 through 37.

The organic loadings applied to the filters were gradually increased during the initial stages of start-up. This was accomplished by increasing the feed strength while keeping the daily feed volume constant at five liters per unit. The decision to increase the loading to the filters was based on a leveling off in gas production and the maintenance of favorable pH conditions in the effluent. Variations in loadings were therefore determined by evaluation of data and by personal judgement rather than by adherance to a predetermined schedule.

On day 25 of operation the daily feed was accidently made without Similac. The one day drop in organic loading to the filters

resulted in lowered gas production for days 25 through 27, as shown in Figure V-2.

Performance of the units on the peptone supplemented feed substrate was so good that on day 27 the buffer addition of sodium bicarbonate was lowered from five to four grams per liter. The effect of this was minimal because loadings were increased at this time, providing additional protein for the formation of ammonium bicarbonate. Effluent pH ran as high as 8.0 and alkalinities exceeded 5,000 mg/l during the period of lowered buffer additions to the feed.

On day 38 of operation it was decided to eliminate Bacto peptone from the feed solution and run the filters on Similac liquid concentrate and primary wastewater effluent. This decision was made because of the high cost of Bacto peptone and other suitable protein extracts. Also it was thought that the sulfur compounds in the peptone were responsible for excessive hydrogen sulfide production, causing the gas scrubbers to need media replacement after only 23 days of operation. During the remainder of start-up (days 38 through 86) the units were fed Similac liquid concentrate, primary effluent, and five grams per liter of added sodium bicarbonate. The buffer addition was increased to compensate for the reduced level of protein in the feed. The organic loading was also increased at this time to 2.60 Kg COD/day/m^3. This corresponded to a feed COD of 19,600 mg/l. It was hoped that operation of the columns would be such that the feed strength would be similar to that of the selected pyrolysis wastewater. However, the switch to a largely carbohydrate feed resulted in dramatically increased levels of solids production in the filters and the loading was

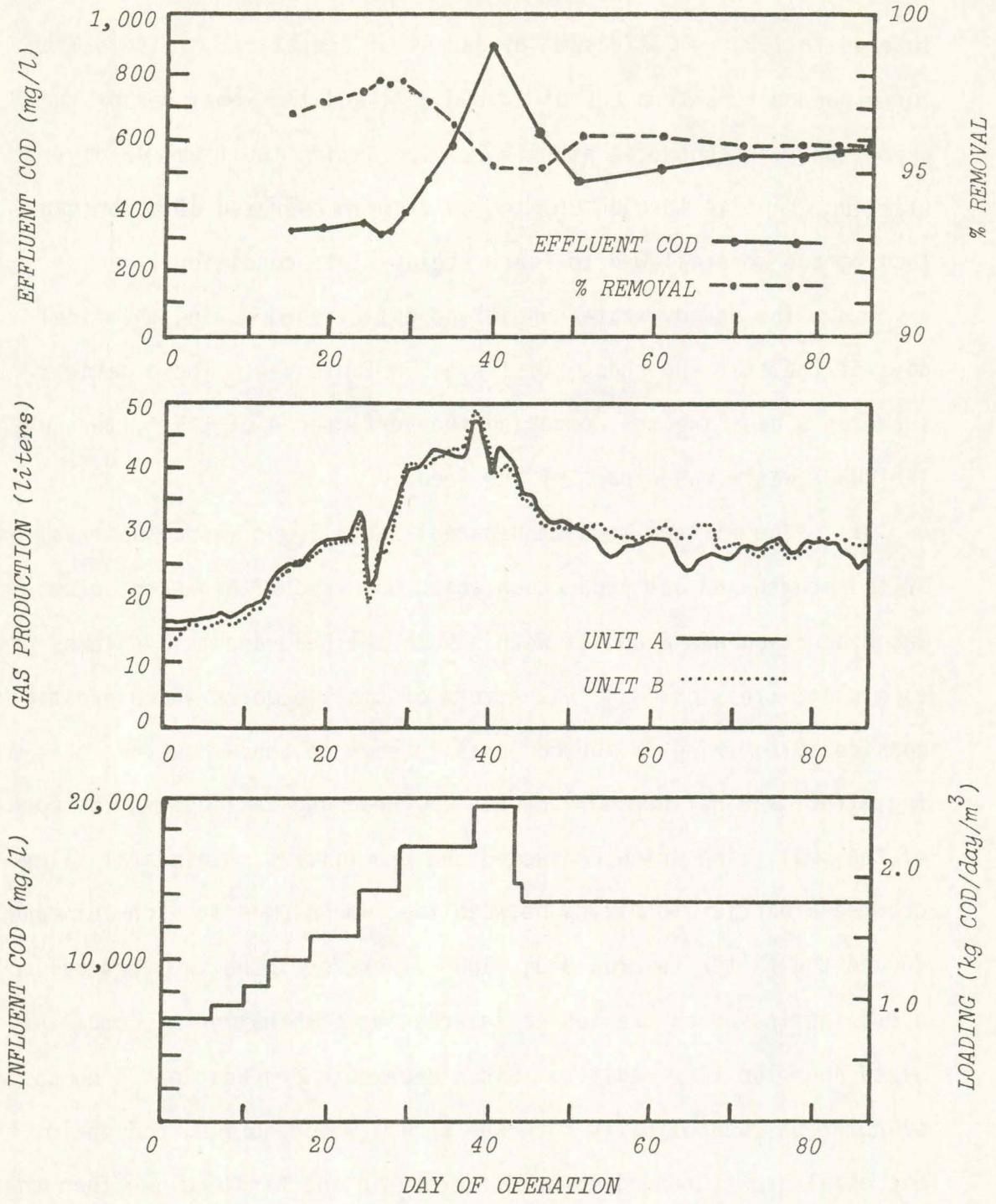


Figure V-2. Phase I Results.

lowered to 1.80 Kg COD/day/m^3 by day 44 of operation. This loading corresponded to a feed COD of 13,600 mg/l and the remainder of the experiment was conducted at this level. During the final 42 days of start-up (days 44 through 86) the units were operated at a constant loading and were allowed to reach steady-state conditions.

The steady-state conditions established during the final days of the start-up phase are listed in Table V-4. These data will serve as a baseline for comparing the performance of the filters when the PUROX waste was a part of the feed.

The filters were transparent and allowed visual observation of the growth and gas production which occurred within each column. Gas production was abundant within both the head and tail columns of each unit. This gas was in the form of small bubbles which created considerable mixing of the contents in each column. However, this mixing effect was not present between the head and tail columns because of the small line which connected the two filters. This small line created a barrier to mixing between the two columns in each unit and forced the filter towards plug flow. Therefore, the two vertical columns operating in series created an interesting combination of completely mixed and plug flow regimes. Since anaerobic degradation is composed of numerous catabolically diverse species which form a food chain, the microbial growth tended to be different in the first column than that found in the second. The front columns had a thicker microbial film attached to the media. It was light grey in color and frothy in appearance. Build-up of excess solids was much more prevalent in the first columns and required more frequent removal. The second columns had a

Table V-4. Phase I Steady-State Conditions

Daily Feed:	
Composition	350 ml Similac liquid concentrate 9.65 liters primary wastewater effluent 50 grams sodium bicarbonate
	Total 10 liters (5 liters to each unit)
COD, mg/l	13,600 ± 3%
Alkalinity, mg/l as $CaCO_3$	3,300 ± 1.5%
pH	7.8 ± 0.2%
Effluent:	
COD, mg/l	500 ± 5%
Alkalinity, mg/l as $CaCO_3$	3,600 ± 3%
pH	7.9 ± 0.2
Gas Production:	
Quantity, liters/day	28.0 ± 7% (each unit)
liters/gram COD destroyed	0.43
Estimated CH_4 content (calculated from 0.35 liters/ gram COD destroyed)	81%
COD Removal Efficiency:	96%

much thinner microbial film which was black in color. Excess solids production was much less than in the first columns. These differences in cellular yields would be expected because of the lower ATP yields achieved by acetogenic and methanogenic bacteria. After the project was terminated the baskets holding the plastic media were lifted out of the filters. The changes in liquid height in the columns was recorded and these results are listed in Table V-5.

Table V-5. Void Volume Measurement of Unit A.[(a)]

Column	Initial Liquid Height	Final Liquid Height	Void Volume
First	123 cm	79 cm	72%
Second	123 cm	103 cm	84%

(a) Void volume is devined as the liquid volume in the filter divided by the total volume.

The void volumes indicate that the microbial film in the head column was significantly thicker than that found in the tail column. The hydraulic detention time within the two column filter would be approximately six days (based upon the feed volume of five liters per day).

3.2 PUROX Waste Feed

By May 24, 1978 (day 87) the units had established steady-state conditions and the PUROX gas scrubber wastewater was intorduced into the daily feed. The objectives were to gradually increase the percentage of PUROX waste in the feed and to note at what concentration inhibition to microbial activity occurred. It was decided to intro-

duce the PUROX waste to the feed in increments of five percent. The units were operating with an influent COD of 13,600 mg/l but the lowest strength PUROX waste available had a COD of 18,400 mg/l. Therefore, additions of PUROX waste to the daily feed which represented 5% of the total COD was only 3.7% addition by volume. Similarly, when the filters reached PUROX levels of 45% of the daily feed COD, the volumetric addition was only 33.3%.

During the first two days of PUROX waste feeding (days 87 and 88) the filters were run with the usual Similac-based feed except for a 5% substitution of PUROX waste. This 5% was measured on a COD basis and represented an addition of 370 ml of PUROX waste to the daily feed volume of ten liters (5 liters for each column pair). No significant inhibition of gas production was noted so the percentage of PUROX waste in the feed was increased to the 10% on day 89. Even though gas production was not significantly affected by this level of PUROX waste, the effluent COD had begun to rise with values over 1,000 mg/l after only a few days, as shown in Figure V-3.

On day 91 the percentage of PUROX wastes in the feed was raised to 15% and two days later to 20%. It was at these levels that inhibition was first noticed. Gas production in Unit A had dropped sharply from 25.5 liters on day 91 to 17.3 liters by day 94. This 32% drop in gas production in Unit A did not occur in Unit B where gas production remained quite steady. For the next eleven days (93 through 103) the units were fed 20% PUROX waste (based on COD) and the gas production in Unit A gradually returned to its previous level. However, effluent CODs continued to rise during this period, reaching a peak of 2,630 mg/l

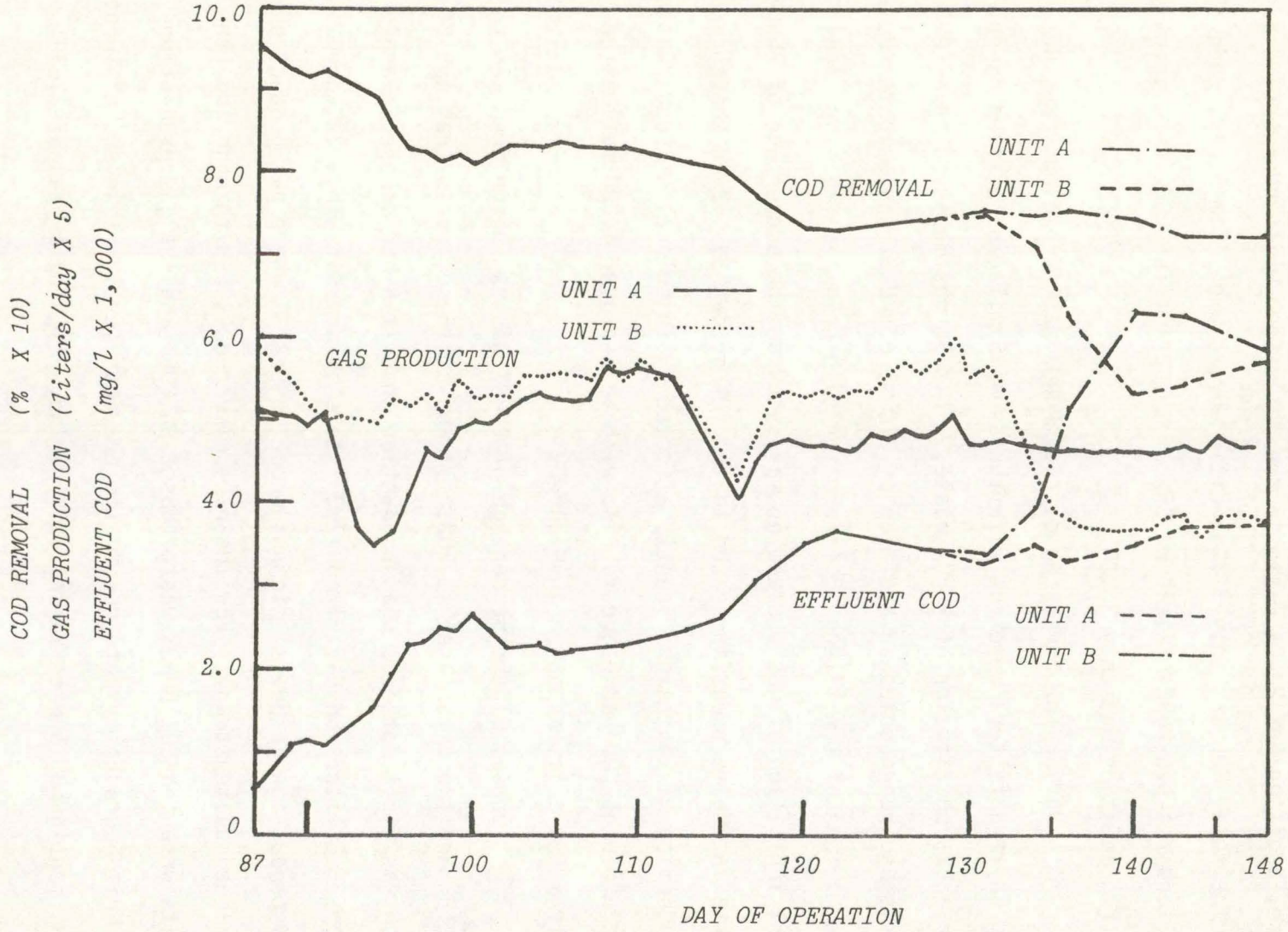


Figure V-3. Phase II Results.

by day 100. There was a gradual decline in effluent CODs after they peaked on day 100 as the units appeared to be accepting the PUROX waste at this 20% level. However, the decline was minor and the effluent CODs of 2,300 mg/l represented an increase of over 1,700 mg/l compared with the effluent data established during start-up. After Unit A had regained its gas production the PUROX content of the feed was increased to 25% on day 104. During the next five days there were no noticable changes in gas production or effluent CODs. On day 109 the PUROX content was again increased to 30% of the feed COD.

By this time it became apparent that the level of excess solids production within the columns was much lower with PUROX waste in the feed than that observed during the start-up phase. The removal of accumulated solids from the filters was only necessary every five or six days. This was in contrast to removal every other day during the latter stages of start-up.

Operation of the units at 30% PUROX levels (22.2% by volume) was going quite well but equipment malfunctions on day 114 caused a temporary setback. One of the heaters that supplied warm water to the units for temperature control at 35^{o}C had become stuck in the "on" position and raised the temperature of the filters to 48^{o}C. The heating system was immediately drained and refilled with cooler water. The faulty heater was removed from the heating water reservoir and subsequent operation was accomplished with the use of only one heater for temperature control. During days 114 to 116 there were also problems with the pump timer and it is possible that air was pumped into the system by mistake. This timer was replaced on day 116 of operation and it

caused no further problems during the remainder of the experiment. By day 117 accurate data for gas production was available and it showed that the thermal shock and possible air pump into the filters had caused some inhibition to the microbes. However, gas production was only down 18% and recovery of the units took only ten days with PUROX levels held at 30% of the feed COD. Unit B recovered more completely and in less time than Unit A. Furthermore, it was Unit A that suffered a drop in gas production at PUROX levels of 20% while Unit B appeared unharmed. The reason for these differences in the performance of the units is not clear. However, later operation at higher PUROX levels showed a reversal of this trend, as it was Unit B that showed inhibition while Unit A appeared unharmed.

By day 127 the units had apparently recovered from the environmental shock caused by the equipment malfunctions and the PUROX content of the daily feed was raised to 35% of the total COD. No decreases in gas production were noted at this time but Unit B was producing more gas than Unit A. Because of this difference in gas production, it was decided that separate monitoring of the effluents from each unit was necessary. Previous effluent monitoring had been accomplished using a mix of the two effluents. After day 131 the effluents were collected and tested separately. Effluent CODs for day 131 showed agreement between Unit A and Unit B with values near 3,300 mg/l. This represented an increase of COD in the effluent of over 2,700 mg/l compared to operation during start-up. Since the PUROX contribution to the feed at this time was about 4,750 mg/l COD, it showed that at least 30% of the Pyrolysis waste's COD was being degraded anaerobically.

On day 131 the PUROX content of the feed was raised to 40% of the total COD. No real decline in gas production was noted during the following three days, except there was a gradual decrease in gas from Unit B. On day 134 the PUROX content in the feed was raised to 45% of the total COD. This was accomplished by adding 3,330 ml PUROX to the daily feed volume of 10 liters. This was the highest level of PUROX waste added to the feed during this project. This increase caused the gas production in Unit B to drop sharply from 28.1 liters on day 131 to 18.3 liters by day 139. This 35% drop in gas production in Unit B did not occur in Unit A where gas production remained constant at approximately 23.5 liters per day. Effluent CODs in Unit A rose slightly during this time and approached 3,800 mg/l. Since the COD contributed by the PUROX waste in the influent was about 6,100 mg/l, it showed at least 38% of the pyrolysis waste's COD was being degraded anaerobically in Unit A at the end of the PUROX waste feed experiments. However, in Unit B, where the gas production dropped significantly at PUROX additions of 45%, the effluent COD rose past 6,300 mg/l by day 140 and remained above 5,800 mg/l on day 148. Therefore, it appeared that very little degradation of the PUROX waste was occurring in Unit B once it had become inhibited.

The volatile acids data within the columns during the final stages showed some interesting differences between the two units (Table V-6). On day 121, when both units were operating with PUROX waste representing 30% of the feed COD, there was a substantial reduction in volatile acid concentrations between the two columns in each unit. However, as the PUROX waste content in the feed increased, the

Table V-6. Volatile Acid Concentrations and pH Within the Filters

Day of Operation	% Purox in Feed (based on COD)	Sample Location							
		A 13		A 23		B 13		B 23	
		pH	Volatile Acids mg/l as Acetic	pH	Volatile Acids mg/l as Acetic	pH	Volatile Acids mg/l as Acetic	pH	Volatile Acids mg/l as Acetic
117	30%	6.2	3420	7.0	905	6.2	3385	7.0	----
121	30%	6.2	3405	6.9	1060	6.2	3385	6.9	1130
127	35%	6.3	3575	7.0	1045	6.3	3350	7.0	905
129	35%	6.2	3590	7.0	890	6.3	3470	7.0	870
137	45%	6.1	3470	7.1	840	6.3	3230	6.9	2070
140	45%	6.2	3440	7.1	855	6.3	3370	6.9	2290
143	45%	6.2	3385	7.1	870	6.3	3350	7.0	2240
148	45%	6.3	3440	7.1	905	6.3	3540	7.1	1830

volatile acid concentrations in the second column of Unit B rose sharply. Data for Unit A during this period remained constant. These data indicate that it was the volatile acid utilizing bacteria in Unit B that were more sensitive to the PUROX waste. As they became inhibited, they could no longer remove the substrates that were supplied by the acid forming bacteria. This caused a drop in gas production and a rise in effluent COD to occur in Unit B during the end of these experiments (Figure V-3).

The measured volatile acids concentrations within the first columns never exceeded 3,600 mg/l, as acetic (equivalent to 3,000 mg/l as $CaCO_3$). Since effluent alkalinities were around 3,300 mg/l, as $CaCO_3$, it would appear that adequate pH buffer was supplied to the filters. The pH data shown in Table V-6 supports this assumption because values were near neutrality in the second columns of both units. Furthermore, the pH data for the effluent of the filters were around 7.9 for Unit A and 7.5 for Unit B. During the final day of these experiments (day 148) the volatile acids concentration, as acetic, in the effluent of Unit A was 720 mg/l while Unit B had 1,950 mg/l of these acids. This would explain the differences in effluent pH between the two filters.

3.3 Discussion

Unit A was initially inhibited when PUROX waste concentrations reached 14.8% of the feed volume (20% of the feed COD). Unit B was not affected at this concentration. However, after an acclimation period of over forty days, Unit B showed a more severe inhibition when the PUROX waste concentrations reached 33.3% of the feed volume (45%

of the feed COD). Unit A was not affected at this concentration. The reasons for these differences in the performance of the two filters is not clear. It does suggest, however, that the inhibitory concentrations noted were threshold values.

From the suspended growth experiments it was concluded that the threshold concentration of PUROX wastewater feed to unacclimated anaerobic bacteria was about 0.1% on a volumetric basis. However, this was for batch fed, completely mixed, suspended growth reactors and a much higher strength pyrolysis waste (COD of 41,300 mg/l) was used (COD of 41,300 mg/l vs. 18,400 mg/l). Since the reactor type, feeding method, start-up substrate, and PUROX waste sample used in the suspended growth experiments were different than that used in these anaerobic filter experiments, a direct comparison of results is not possible. However, several common conclusions can be made from the data of the two projects:

1) The PUROX wastewater is quite toxic to unacclimated anaerobic bacterial populations.

2) Acclimation to the waste and a degree of degradation is possible.

3) Inhibition is characterized by a rise in volatile acids and a decline in gas production, indicating that the acid utilizing bacteria (the methanogens and/or the acetogens) are more sensitive to the toxic effects of the PUROX waste.

The differences in the inhibitory concentrations that were found in the suspended growth experiments, when compared with this study, can not be totally explained by the differences in the PUROX wastes used in the two experiments. The COD of the pyrolysis wastes used were 41,300 mg/l in the suspended growth experiments and 18,400 mg/l in

these anaerobic filter experiments. This is only about a two-fold difference in COD strength. The inhibitory concentrations for unacclimated anaerobic bacteria differed by a factor of almost 150. Therefore, it would appear that a continuously fed anaerobic filter has some advantageous over a batch-fed, completely mixed reactor when treating toxic materials. A greater tolerance to PUROX waste additions in the completely mixed reactors were noted when feeding schedules were more frequent or continuous. By removing toxic materials through decomposition reactions, the bacteria could be subjected to higher levels of pyrolysis waste additions. With an anaerobic filter (an essentially plug flow reactor) the toxic materials can be degraded by more tolerant species prior to contact with the sensitive species (the methanogens and/or acetogens).

Comparison of the performance of Unit A during the end of the PUROX waste feeding experiments with the steady-state conditions established during start-up shows the effect that the PUROX waste had on the filter. The effluent COD rose from 550 mg/l to almost 3,800 mg/l. The COD removal efficiency correspondingly dropped from 96% to 72%. The daily gas production dropped from 28.0 liters to 23.5 liters, representing a 16% decrease. However, gas production increased, based upon the actual amount of COD destroyed. During start-up, gas productivity was around 0.43 liters per gram COD destroyed (6.9 cu. ft./lb) while at the end of the PUROX waste feeding period this value approached 0.45 liters/gram (7.7 cu. ft./lb). This would increase the estimated CO_2 content of the digester gas from 19% during start-up to 27% during PUROX feeding. As stated previously, at least 38% of the COD in the pyrolysis

waste was being degraded anaerobically. Union Carbide determined that the BOD/COD ratio was approximately 2/3 for the pyrolysis wastewater (Table II-9). However, the five-day BOD of the PUROX waste with a COD of 41,300 mg/l was only 14,400 mg/l. It would appear that a substantial portion of the biodegradable organics present in the PUROX waste are capable of being degraded by an anaerobic filter. However, the significant presence of organics in the effluent indicates that anaerobic treatment alone would not provide adequate treatment of the pyrolysis wastewater.

The results of these anaerobic filter studies have answered several questions about the anaerobic treatability of pyrolysis wastewaters from the Union Carbide PUROX process. The waste contains toxic materials that cause severe inhibition to unacclimated anaerobic bacteria. These toxics seem to affect the volatile acid utilizing bacteria the most, causing failures to be typified by lower gas production, higher effluent COD, and an increase in the volatile acid concentrations within the reactor. Once the anaerobic bacteria become acclimated to the wastes, higher concentrations can be tolerated until a new toxic threshold is reached. A significant percentage of the biodegradable portion of the organic material in the pyrolysis waste is amenable to anaerobic decomposition. However, there is a percentage of COD in the waste which appears to be refractory under anaerobic conditions.

An anaerobic filter process could provide a cost effective approach to the partial removal of organics from the pyrolysis wastewater. Operation of an anaerobic pretreatment process would require dilution of the waste to control the effects of toxic materials. Since anaerobic

filters are more adaptable to treating dilute waste streams than conventional digestion systems, they would appear to be a preferred design for anaerobic pretreatment processes. A plug flow reactor appears to posses some advantages over completely mixed digesters when decomposing toxic materials. The inhibitory materials are subjected to potential microbial decomposition prior to contact with the more sensitive volatile acid utilizing bacterial species. Therefore, higher concentrations of the toxic compounds can often be tolerated in the influent of a plug flow reactor.

Using an anaerobic filter as a pretreatment process for the PUROX waste would probably require secondary treatment systems. Aerobic processes would provide additional removal of organics from the pretreatment pyrolysis waste as well as adsorption of PAH compounds by the activated sludge. On-site aerobic treatment systems could consider the recycling of dewatered sludge into the combustion zone of the oxygen refuse converter as a possible means of sludge disposal. The costs of an aerobic treatment facility could be greatly reduced by pretreating the pyrolysis waste anaerobically. The total cost of an anaerobic-aerobic facility would probably be less than that of an aerobic treatment process alone. This is due to the low cost removal of organics that could be provided by an anaerobic filter. The gas scrubbing system in the PUROX process could be operated to provide as low a strength waste as possible since dilution would be required for biological treatment anyway.

Additional research of the anaerobic treatability of the PUROX wastewater would be required before the reliability of their use as

pretreatment processes could be ensured. Longer acclimation periods and hydraulic detention times should be studied to see if additional degradation of the pyrolysis waste is possible. Filter operation on dilute PUROX waste as the sole carbon source is also needed to evaluate if supplemental nutrient additions are required. The control of toxic materials by other methods than dilution should also be studied. If the toxic compounds can be identified and removed or inactivated, treatment of higher strength pyrolysis wastes could be evaluated.

4.0 CONCLUSIONS

Based on the results of the experiments on the treatment of PUROX pyrolysis wastewaters with anaerobic filters, the following conclusions are evident:

1) The introduction of PUROX wastewaters to unacclimated anaerobic bacteria results in inhibition of the process. Using a relatively low strength pyrolysis waste (COD of 18,400 mg/l) an anaerobic filter process first observed inhibition when the influent contained 15% PUROX waste (by volume).

2) Acclimation of the anaerobic bacteria to the PUROX waste is possible. This allows higher concentrations of the waste to be tolerated by the bacteria. Pyrolysis waste representing as much as 33% of the feed volume can be treated by an anaerobic filter.

3) A substantial portion of the organic material present in the PUROX waste can be degraded under anaerobic conditions. Removals of at least 38% of the pyrolysis waste COD were observed with a low strength PUROX waste when overall COD removal was at 72%

4) The materials which exhibited toxicity to the anaerobic bacteria appear to affect the volatile acid utilizing populations to a greater extent than the acid forming microorganisms. This observation is consistent with typical inhibtion of anaerobic digestion processes.

5) A percentage of the COD present in the PUROX waste appears to be refractory under anaerobic conditions. This indicates that anaerobic processes alone would not provide adequate treatment of the pyrolysis waste.

CHAPTER VI

ACTIVATED CARBON TREATMENT OF PYROLYSIS WASTEWATERS

1.0 INTRODUCTION

The liquid wastes from the scrubbing of product gases from the pyrolysis of municipal refuse in the PUROX process are toxic and extremely high in organic pollutants, as discussed previously in this report. As indicated in Chapters IV and V, anaerobic biological processes are effective in the removal of organics from the pyrolysis wastes up to about 70 percent, on a COD basis. Anaerobic treatment by itself, however, is not sufficient for complete treatment.

The purpose of this research was to explore the application of activated carbon to the treatment of the raw PUROX wastes and to investigate the feasibility and effectiveness of using a combination of activated carbon and the anaerobic biological process to treat the pyrolysis wastes. The suspended growth anaerobic studies discussed in Chapter IV (Phase II) were going on at the same time that these carbon studies were being conducted. Thus effluent from the anaerobic reactors was available for treatment with carbon.

The carbon experiments involved the development of adsorption isotherms for the raw PUROX wastes followed by laboratory-scale carbon column tests to reflect the performance of carbon columns in COD removal and to enable an economic analysis of the application of carbon columns to treating the PUROX pyrolysis wastes.

Isotherms were also run on the effluent from an anaerobic reactor being fed PUROX pyrolysis wastes. This was done to determine the feasi-

bility of using carbon adsorption as a polishing step for the effluent from the anaerobic biological treatment systems.

2.0 TECHNICAL BACKGROUND

2.1 Activated Carbon

Activated carbon is manufactured in a two-stage process from a variety of carbonaceous materials including wood, coal, lignite, bone, sawdust and nutshells. The first stage involves the dehydration and carbonization of the raw materials. This is accomplished by slow heating at 600^{o}C in the absence of air. This removes all water and converts the organic matter to elemental carbon while driving off the non-carbon portion.

Activation of the carbon is accomplished by the use of stream or carbon dioxide (CO_2) as an activating agent. The hot steam, at a temperature of 750^{o} to 950^{o}C, passes through the carbon burning off tar deposits. This frees the pore openings while enlarging and expanding the pore network. Activation enhances the adsorptive characteristics of the carbon by increasing the surface area to weight ratio. Typical values range around 1,000 square meters per gram (M^2/gm). This large ratio is the result of the porous structure of carbon formed by the heat in the activation process.

The pore network consists of macropores (>1,000 A) and micropores (10 to 1,000 A). The macropores do not add appreciably to the surface area of the carbon, but allow passage to the interior micropores. Pore size distribution determines what molecules are capable of entering the carbon particle to be adsorbed. Large molecules can block off the openings of the micropores. However, irregular shapes and constant

molecular movement usually allow small molecules to penetrate into the interior pores.

2.2 Adsorption

2.21 Basic Mechanisms

The adsorption process is one in which matter is extracted from one phase and concentrated on the surface of another. This process occurs at gas-solid, solid-solid, gas-liquid, liquid-liquid, and liquid-solid interfaces. Adsorption with solids like activated carbon occur at the liquid-solid interface and are heavily dependent on the surface area of the solid. Adsorption is therefore termed a surface phenomenon. Activated carbon is capable of removing soluble organic material from liquid wastewater by the process of adsorption.

Adsorption onto activated carbon is thought to be a combination of two basic mechanisms: physiosorption and chemisorption (68). Both methods involve the contaminant molecules in the liquid waste stream becoming attached to the surface of the carbon. This results when the attractive forces at the solid surface (adsorbent) overwhelm the kinetic energy at the liquid contaminant molecules (adsorbate) (68).

The driving force behind this phenomenen is a result of, or a combination of: (1) the low solubility of a certain adsorbate in the wastewater; and (2) a high affinity of a particular adsorbate in the wastewater for activated carbon (69).

Physisorption occurs as the result of energy differences and/or electrical attractive forces (Van der Waal's forces). The adsorbate molecules become physically attached to the adsorbent

molecules. Physisorption can be multi-layered in that the molecular layers form on top of each other. The number of layers is proportional to the concentration of adsorbate in the wastewater. The reversibility of physisorption is related to the strength of the attractive forces present.

Chemisorption occurs as the result of covalent bonding between the adsorbate molecule and the adsorbent. Unlike physisorption, chemisorption is one layer thick and irreversible because energy is required to form the new chemical compound at the surface of the adsorbent. Energy would be necessary to reverse the process (68).

Adsorption is possible only in pores that can be entered, so the physical characteristics of the carbon and the molecular size of the adsorbate are important in adsorption mechanics. The most efficient adsorption takes place when the carbon pores are just large enough to admit the adsorbate molecule. The smaller the pores with respect to the molecule, the greater the force of atraction.

Activated carbon is ideal in its ability to remove contaminants from wastewater, not only because of its large surface area but also because of its preference for organic compounds.

There are two major forms of activated carbon, powdered and granular. Powdered particles are those smaller in size than the openings of U.S. Sieve Series No. 50 while granular particles are the ones that are larger than that sieve size. The adsorptive rate is influenced by particle size but the adsorptive capacity is related to total surface area. Reducing particle size does not significantly affect the surface area to weight ratio.

2.22 Adsorption Rate

The rate of adsorption on activated carbon is governed by the adsorption reaction kinetics. There are essentially three steps in the adsorption of molecules by carbon:

1. The transport of the solute through a surface film to the exterior of the carbon.
2. Diffusion of the solute into and through the pore spaces of the carbon.
3. Adsorption of the solute onto the surfaces of the carbon.

It is thought that step no. 2 is the rate limiting step in the adsorption process (69).

The total amount of solute adsorbed per gram of carbon is closely tied to the surface area of the carbon. Indirectly, molecular shape and pore distribution determine the adsorptive capacity. Major factors affeting adsorption include:

1. Physical and chemical traits of the adsorbate, i.e. molecular size and polarity.
2. Physical and chemical traits of the adsorbent, i.e. pore size, distribution and surface area.
3. Concentration of the adsorbate in solution.
4. Characteristics of the wastewater, i.e., pH and temperature.
5. Length of time in the system.

2.23 Adsorption Capacity

The total surface area of activated carbon will give one idea of adsorption capacity. The surface area is measured by the Brunave-Emmett-Teller (BET) method (68). The area distribution into pores of various diameters is measured by determining the quantity of

nitrogen desorbed at intermediate pressures. The adsorptive capacity of carbon can also be measured reasonably well by simple capacity tests such as the iodine and molasses numbers. These tests involve the ability of carbon to adsorb low molecular weight substances and color bodies, respectively, and are valuable in evaluating the carbon capacity. However, the test does not measure the ability of carbon to adsorb the wastewater of interest. This ability is established through the use of adsorption isotherms (70). An adsorption isotherm is the relationship under constant conditions between the amount of substance adsorbed and its concentration in the surrounding solution. Generally, straight line plots of the amount of adsorbate adsorbed per unit weight of carbon versus the concentration of adsorbate remaining in solution may be obtained by making use of the following empirical Freundlich equation:

$$x/m = kc^{\frac{1}{n}}$$

where,

x = amount of adsorbate adsorbed

w = weight of carbon

x/m = quantity adsorbed by a unit weight of carbon

k = empirical constant

c = equilibrium concentration of adsorbate in solution after adsorption

n = empirical constant

A typical isotherm test curve developed from the above equation is shown in Figure VI-1, where COD represents the amount of adsorbate adsorbed (x).

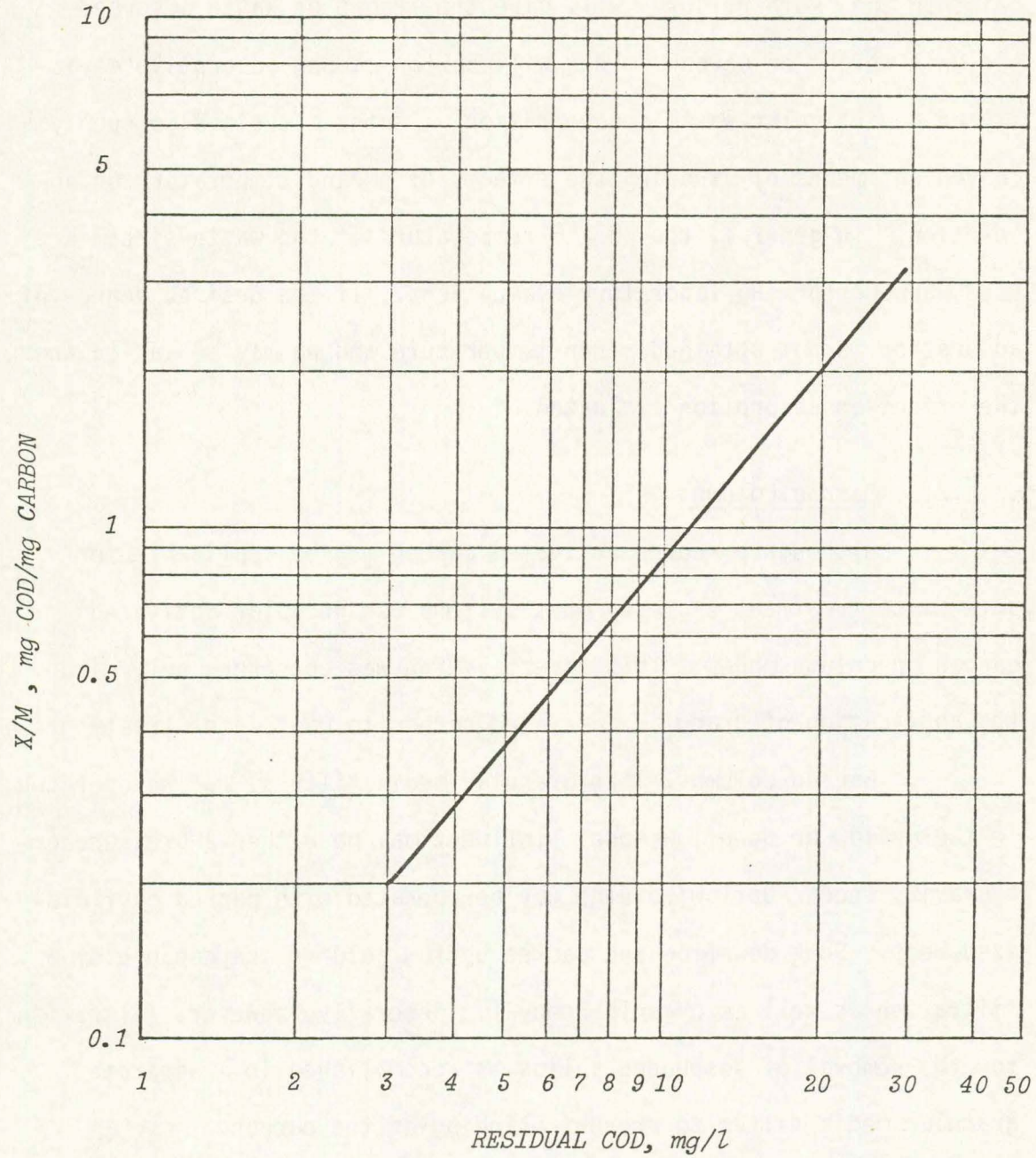


Figure VI-1. Typical Freundlich Isotherm Plot.

From the isotherm test curve, the capacity of a particular carbon for an adsorbate can be determined. A reading at any point on the isotherm curve will give the amount of waste adsorbed per unit weight of carbon. This will be the carbon adsorptive capacity at a particular waste concentration. Isotherm tests also supply a convenient means of studying the effects of pH and temperature on adsorption. In general, the pH and temperature of the waste stream are used when performing laboratory evaluations. If the desired degree of adsorption is not obtained, then temperature and pH may be varied and the effect on adsorption evaluated.

2.3 Carbon Columns

Although powdered activated carbon may be applicable for some waste treatment systems, most systems use granular activated carbon in column modes. This investigation was concerned only with the application of granular activated carbon to wastewater treatment.

Carbon columns, like granular media filters, may be operated in the upflow or downflow mode. Influent may be either a pressure or a gravity feed. Upflow columns may be operated with packed or fluidized beds. Some downflow and packed upflow columns are capable of filtration as well as organic removal. Generally, however, filtration for the removal of suspended solids is accomplished in a separate granular media filter to prevent blinding of the carbon.

Carbon selection and design of columns for specific applications is best achieved by laboratory tests. Isotherm tests, as described earlier, provide information on the possibility of granular carbon treatment. Pilot column studies are conducted to obtain dynamic

operational data which is necessary in design of full-scale plants. The most prudent method of testing and design procedures is the Bohart-Adams or bed depth versus service time (BDST) analysis (71).

As water flows through a carbon column, the organic contaminants are gradually removed and the liquid is purified as it moves through the column. There is no distinct line formed between the purified effluent and the raw feed. Instead, a transition zone is established where the impurity content is high at the back of the zone and low at the front of the zone. This zone is the active layer in the column where most adsorption takes place. As the back of the zone becomes saturated, new incoming impurities are passed forward and the transition zone moves forward in the direction of the flow. The zone moves forward with only a gradual increase in impurities in the effluent until the zone reaches the discharge point of the column. At this time, the impurity concentration increases rapidly until it is equal to the feed concentration.

This forward movement of the zone is reflected in a breakthrough curve. This curve is obtained by passing the wastewater through a column and then plotting the concentration of the adsorbed substance in the effluent versus the volume of water treated (or time) as illustrated in Figure VI-2.

The breakthrough curve depicts the variation of impurity concentration over time at a specific point in the column. Ideally, as the zone passes a certain point, the breakthrough curve at that point will show a change in concentration from near zero to that of the feed.

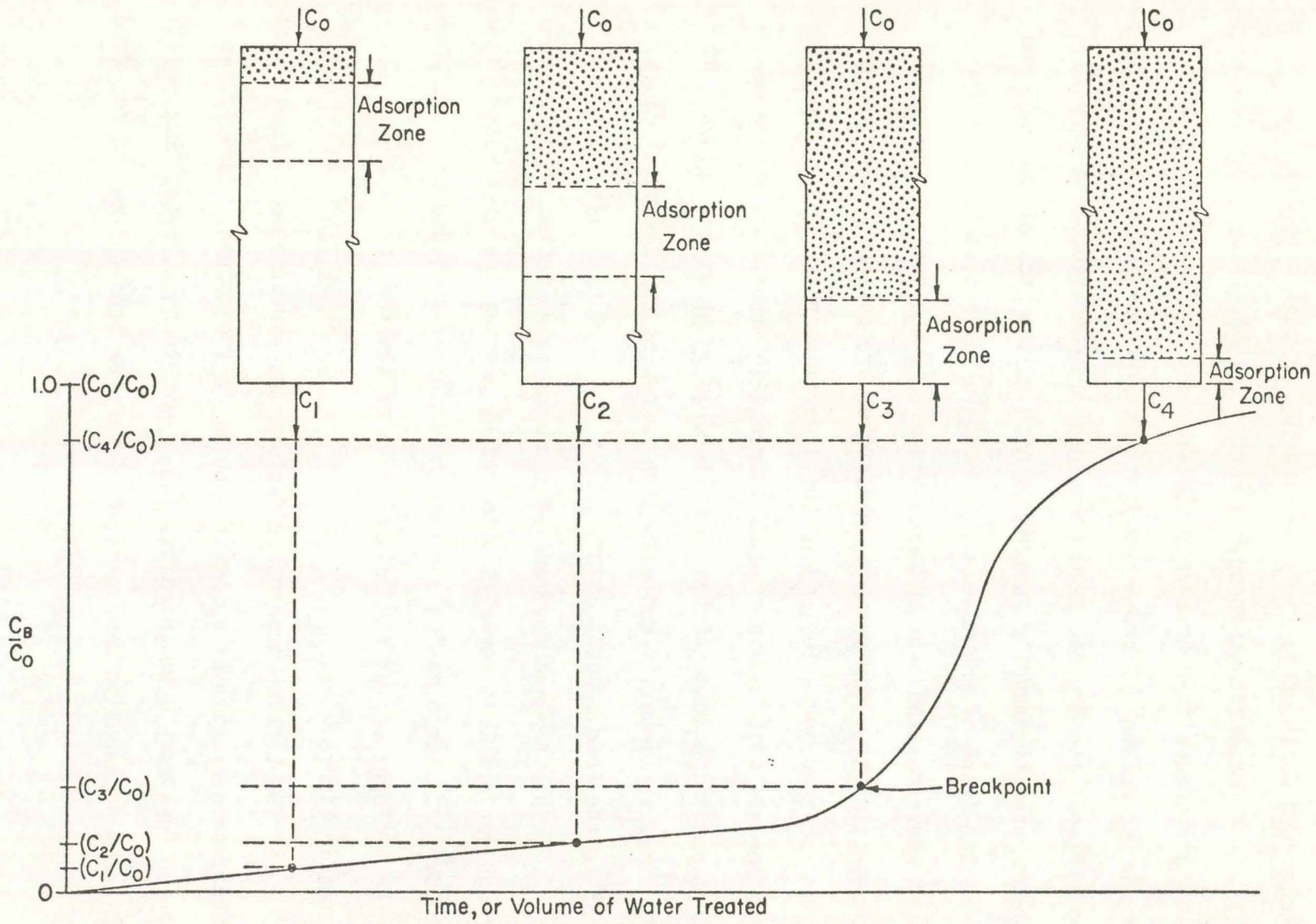


Figure VI-2. Representation of Adsorption Zone and Breakthrough Curve.

2.4 Design Considerations

For design considerations, the breakthrough curves are often presented in bed depth versus service time diagrams. Data points are obtained by choosing various ratios of concentration of organics in the effluent to the concentration in raw waste (C_B/C_0) and then picking the corresponding time from the proper breakthrough curve of the desired bed depth as illustrated in Figure VI-3 for a 90% breakthrough.

According to the Bohart-Adams analysis, as described by Adams and Eckenfelder (71), the service time to reach the breakpoint concentration from a continuous flow carbon column may be evaluated using the following relationship:

$$t = [N_0/(C_0V)]\,[(D) - (V/(KN_0)]\ \ (\ln C_0/C_B - 1)$$

where:

t = column service time to breakpoint concentration (hrs.)

V = linear flow rate through column (ft.hr.)

D = depth of carbon bed (ft.)

D_0 = critical depth of carbon bed (ft.)

K = carbon rate constant (cu. ft./lb.-hr.)

N_0 = carbon adsorptive capacity (lbs./cu. ft.)

C_0 = influent solute concentration (lbs./cu. ft.)

C_B = allowable effluent concentration (lbs./cu. ft.)

The theoretical depth of carbon that is just deep enough to prevent effluent breakthrough at time zero is referred to as the critical bed depth. This depth is obtained by setting the above equation equal to zero and solving for D_0 as follows (68):

$$D_0 = [V \ln (C_0 - C_B/C_B)]/KN_0$$

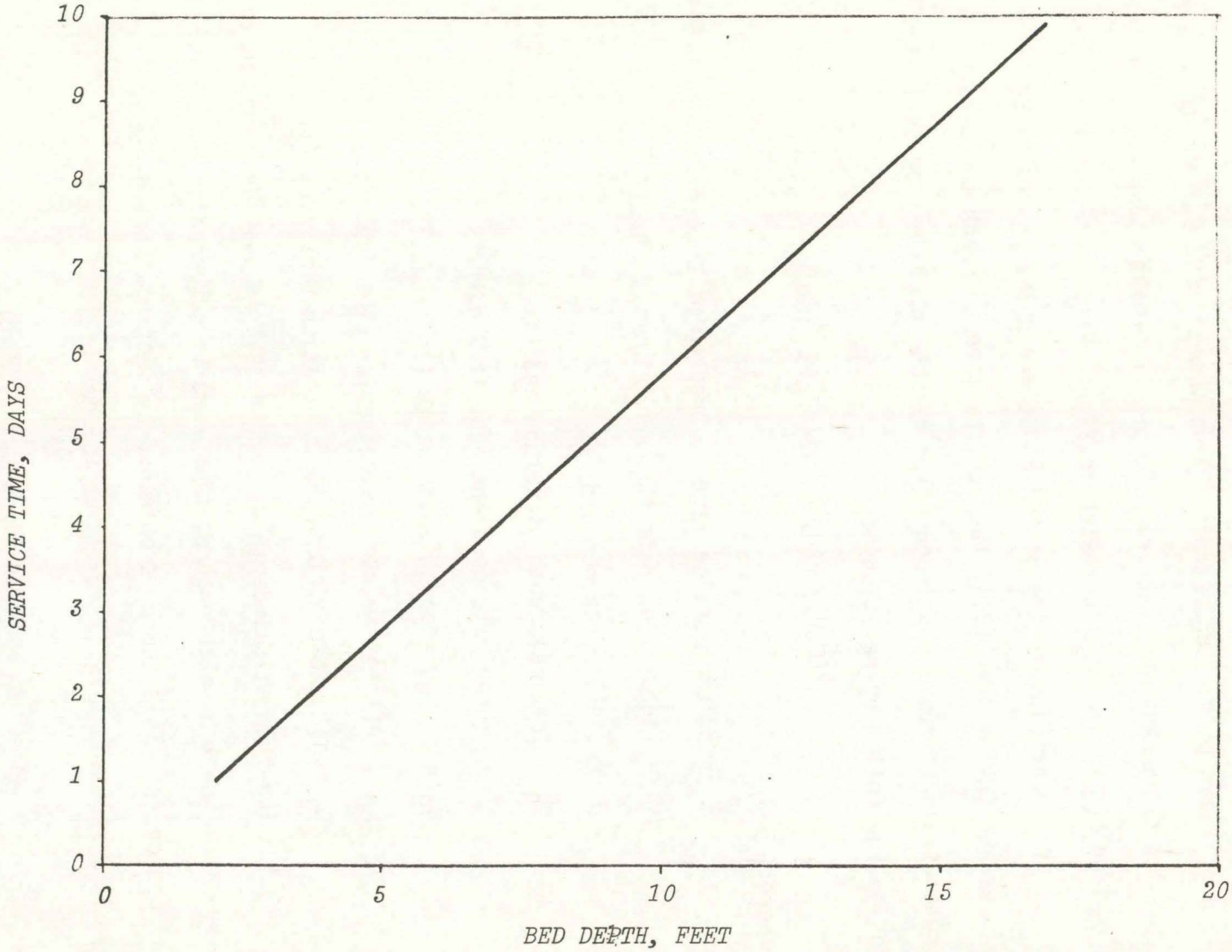


Figure VI-3. Typical Bed Depth - Service Time Curve.

The adsorptive capacity of the system (N_0) and the carbon rate constant (K) may be determined from the slope and intercept of the bed depth versus service time plots. In mathematical form, the following equations may be used to derive numerical values for N_0 and K (72, 73):

$$N_0 = \text{slope } (C_0 V)$$

$$K = \ln \frac{(C_0/C_B - 1)}{C_0 \text{ (intercept)}}$$

The procedure for obtaining design data from continuous flow columns is as follows:

1. Data is collected on the removal of solute by passing a known concentration of wastewater through a known mass of activated carbon. It is best to use at least three different loading rates, each applied to three different carbon bed depths.

2. For every bed depth and flow rate combination, the through-put waste volume and service time (t) to break-through concentration is determined.

3. Bed depth versus service time diagrams are plotted for each surface loading rate. The slope and intercept for each are then calculated to determine the N_0 and K values for each loading rate.

4. The critical depth (D_0) for each loading rate is then determined.

5. The relationship between flow rate, K, N_0, and D_0 is then illustrated.

6. A loading rate is then selected and the filter designed.

General design considerations suggest that:

1. The empty bed contact time $\frac{\text{(volume of empty contactor)}}{\text{(flow rate into contactor)}}$ should be in the range of 10 to 50 minutes.

2. The hydraulic loading should be in the range of 2 to 10 gpm/sq.ft.

3. The ratio of column depth to diameter, or aspect ratio, should be in the range of 4:1 to 10:1.

4. Backwash expansion of downflow units should be in the range of 10 to 50%

5. Surface wash for solids should be approximately 5 to 12 gpm/sq. ft. for 10 to 12 minutes.

6. The total bed depth in all contactors should be in the range of 10 to 30 feet.

Once breakthrough is reached in the effluent, several choices must be considered to once again meet effluent criteria. The carbon may be thrown away and replaced by new carbon or it may be reactivated or regenerated in such a way as to return it to near its original adsorptive capacity. The cost of carbon is usually such that the use of carbon would be prohibitive without regeneration. The most common method of carbon regeneration is a three-step thermal process consisting of: (1) drying at 212^{o}F., (2) pyrolysis of adsorbates at 212 to 1,500^{o}F. and (3) activating by oxidation of carbon residues from decomposed adsorbates at temperatures greater than 1,500^{o}F. All three steps can be carried out in a direct fired multiple hearth furnace.

After regeneration, the carbon is quenched in a water bath and washed of carbon fines. It is then returned to the adsorbers. Each thermal regeneration cycle takes about 30 minutes. During the regeneration cycle, the carbon losses can be up to about 10% of the original weight. Makeup carbon must therefore be added.

3.0 PROCEDURES

3.1 General

All scrubber wastes used in this research came from one of the 55-gallon drums of wastes originally obtained from Union Carbide's

pilot PUROX plant at South Charleston, West Virginia. This was done to insure that the waste was uniform, enabling a proper comparison of results. The waste in this particular drum had a chemical oxygen demand of 25,000 mg/l and a pH of 4.3.

The granular activated carbon used in all laboratory procedures was Nuchar WV-H. The calculated effective size and uniformity coefficient along with other characteristics are included in Table VI-1. These data have been furnished by Westvaco.

The parameter used for measuring organic removal effectiveness was the chemical oxygen demand (COD test).

All tests were conducted at the Philip F. Morgan Research Laboratory at the University of Iowa and in accordance with Standard Methods for the Examination of Water and Wastewater (65).

Table VI-1. Activated Carbon Characteristics.

Characteristic	Value
Effective size	0.55 mm
Uniformity coefficient	1.78
Apparent Density	30 lbs/cu. ft
Hardness number	90
Ash (%)	8
Moisture Content (%)	2
Surface area	1000 M^2/g

3.2 Laboratory Procedures

3.21 Isotherms

Data for the isotherm plots were obtained by adding known weights of pulverized Nuchar Carbon to 100 ml volumes of the PUROX pyrolysis. The carbon-waste mixture was then agitated for 45 minutes to ensure that equilibrium had been reached. After the carbon was removed by filtration, the residual organic content was determined using the COD test. From the COD tests, all data necessary to plot the isotherms were obtained.

Contact time and carbon dosage were determined through preliminary experimentation at carbon dosages of 5,000, 10,000, 20,000 40,000 and 60,000 mg/l of PUROX waste.

A study of the relationship between pH of the waste and adsorption was accomplished by the addition of NaOH to the samples. In addition to the original pH of 4.3, pH values of 5.5, 7.0, 8.5 and 10.0 were evaluated.

Isotherm runs on the anaerobic digester effluent were at carbon dosages of 200, 500, 1,000, 5,000 and 10,000 mg/l of effluent. No attempt at pH or temperature adjustment of the effluent was made.

The anaerobic effluent was from a continuous-feed, complete mix 5-liter reactor that was being fed a combination of primary sludge and pyrolysis wastes to provide a 15-day detention time. The daily feed was 17 percent PUROX waste and 83 percent primary sludge by volume. The digester had been conditioned to this level of feed, but higher levels of pyrolysis feed per day were toxic to the digestion system.

The experimental procedure used for the isotherms was as follows:

1) The granular carbon was washed with distilled water to eliminate the fine material and then oven dried for several hours at 100°C.

2) The granular carbon was pulverized with a mortar and pestle so that the powdered carbon would pass through a 140-mesh sieve and then oven dried at 100°C. for 24 hours.

3) The pH of the waste was adjusted as necessary and then filtered to remove suspended material.

4) The desired weight of carbon was added to each 250-ml screwtop Erlenmeyer flask along with 100-ml of sample. Each flask, along with a control flask sample, was placed on a mechanical shaker table and agitated for 45 minutes.

5) The contents of each flask and the control blank was filtered to remove the carbon and any fines generated during agitation.

6) The COD of the filtrates was then determined.

7) The residual COD concentration in solution (C) was obtained from the filtrate analyses. The amount of COD adsorbed on the carbon (x) was found by subtracting the value of C from that of C_o, the original COD of the waste. The amount adsorbed per unit weight of carbon is then determined by dividing x by m.

8) The COD concentration, C, was then plotted on the horizontal axis versus x/m on the vertical axis on log-log paper. Figure VI-1 is an illustration of the plotted data.

3.22 Column Runs

All laboratory scale column tests were conducted in five feet long columns of one-inch diameter plexiglass. The columns were operated in the downflow mode with a gravity feed. Tests requiring deeper bed depths were conducted by hooking several columns together into a series operation as illustrated in Figure VI-4.

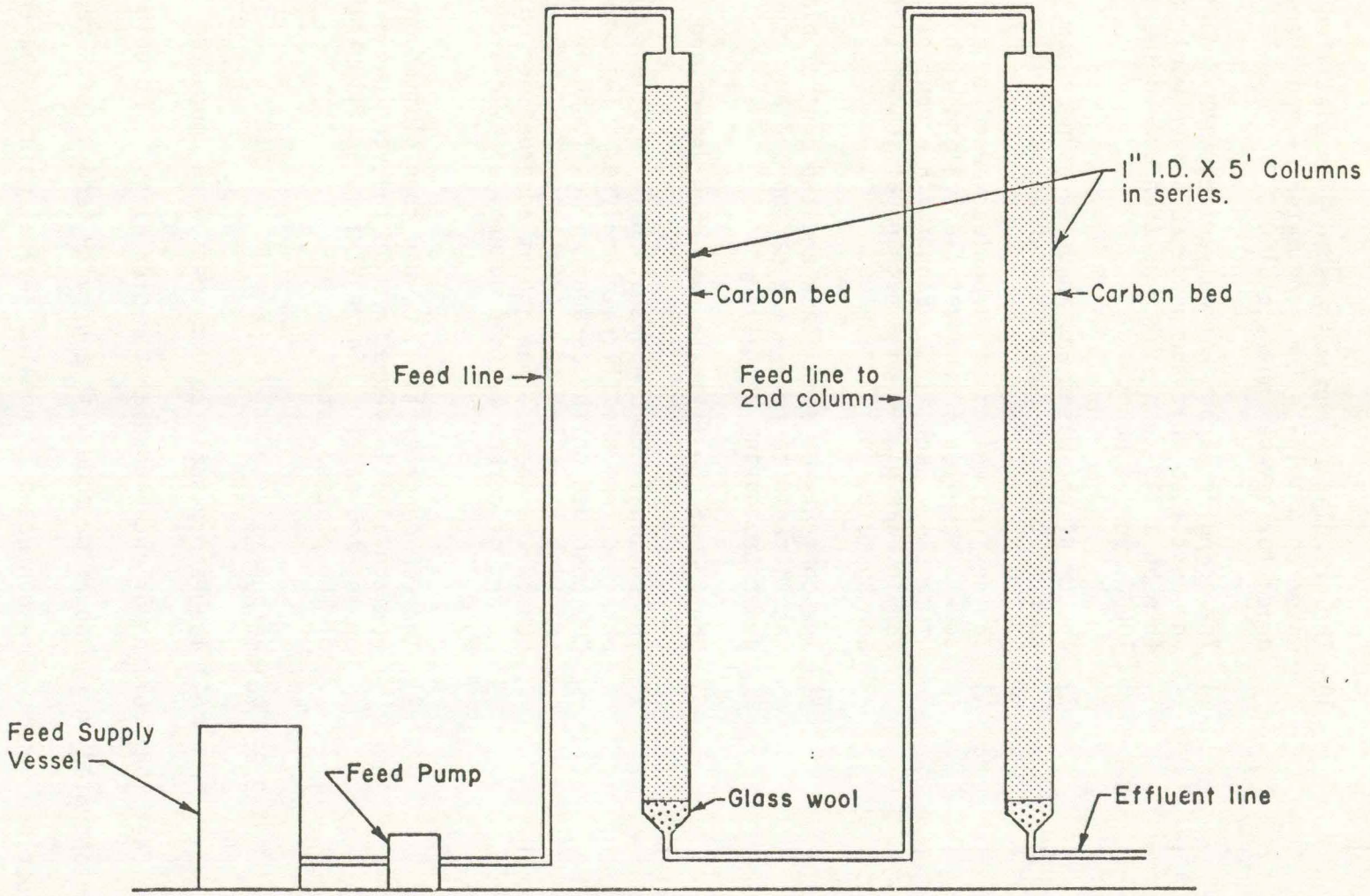


Figure VI-4. Laboratory Carbon Column Set-Up.

The end of the columns were tapered and stuffed with glass wool to prevent carbon loss. A constant head was kept on each column to insure complete submersion of the carbon.

Scrubber wastes were fed to the front column by the use of a Cole-Palmer peristaltic pump that had been calibrated to deliver feed at the desired loading rate.

All granular carbon was washed of fines with distilled water and then oven dryed at 100^{o}C for 24 hours. After the carbon was packed to the desired depth, the column was backwashed with distilled water and agitated in order to eliminate air pockets.

After pumping was started, equilibrium was achieved by effluent rate control. Rate control enabled a constant head to be established on the columns.

Samples for the breakthrough curve analysis were obtainable only at the effluent point. The time table for sampling was established through preliminary experimentation and observation of curve trends. All breakthrough curves were run using the COD test. No attempt to regenerate or reuse carbon was made.

The ranges of loading rates and bed depths were established through the use of common design guidelines and observed ability to effectively control the flow rate and sampling accuracy.

As an attempt to correlate differences in adsorptive capacity due to pH in an isotherm and in a dynamic column test, a column using scrubber waste neutralized to pH 7.0 was also conducted.

4.0 RESULTS AND DISCUSSION

4.1 Isotherms and x/m Values

The results of the PUROX waste isotherm tests indicate that a high degree of COD removal is achievable by carbon adsorption. This is illustrated in Figures VI-5 through VI-9. The adsorption capacities (x/m values) at a typical waste concentration of 25,000 mg/l of COD, range from 0.76 at pH = 7 to 1.86 at pH = 8.5 as shown in Table VI-2. These values indicate that the PUROX waste is highly adsorbable on activated carbon.

It can be observed that all the isotherms, Figures VI-5 through VI-9, have steep slopes. This indicates that adsorption is good at high concentrations, but much less at low concentrations. In general, the steeper the slope of an isotherm, the greater the efficiency in column operation.

The information to be gained from the isotherms is establishment of the fact that carbon adsorption of pyrolysis scrubber waste is possible.

The variability of the x/m values over a range of pH values at a waste concentration of 25,000 mg/l of COD is demonstrated in Table VI-2 and Figure VI-10.

Table VI-2. pH versus x/m at 25,000 mg/l of COD.

pH	x/m
4.3	0.96
5.5	0.88
7.0	0.76
8.5	1.86
10.0	1.50

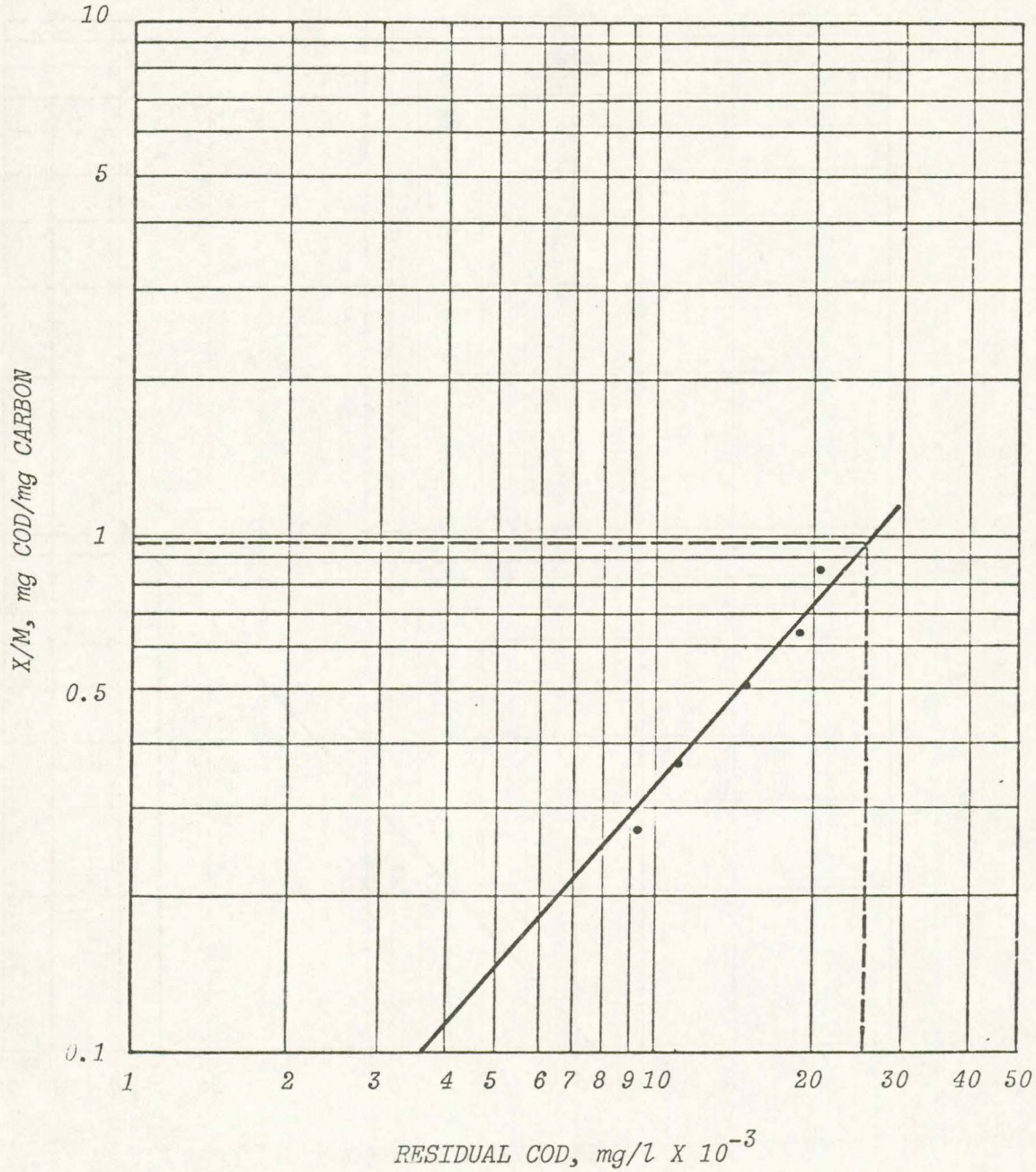


Figure VI-5. Adsorption Isotherm at pH 4.3.

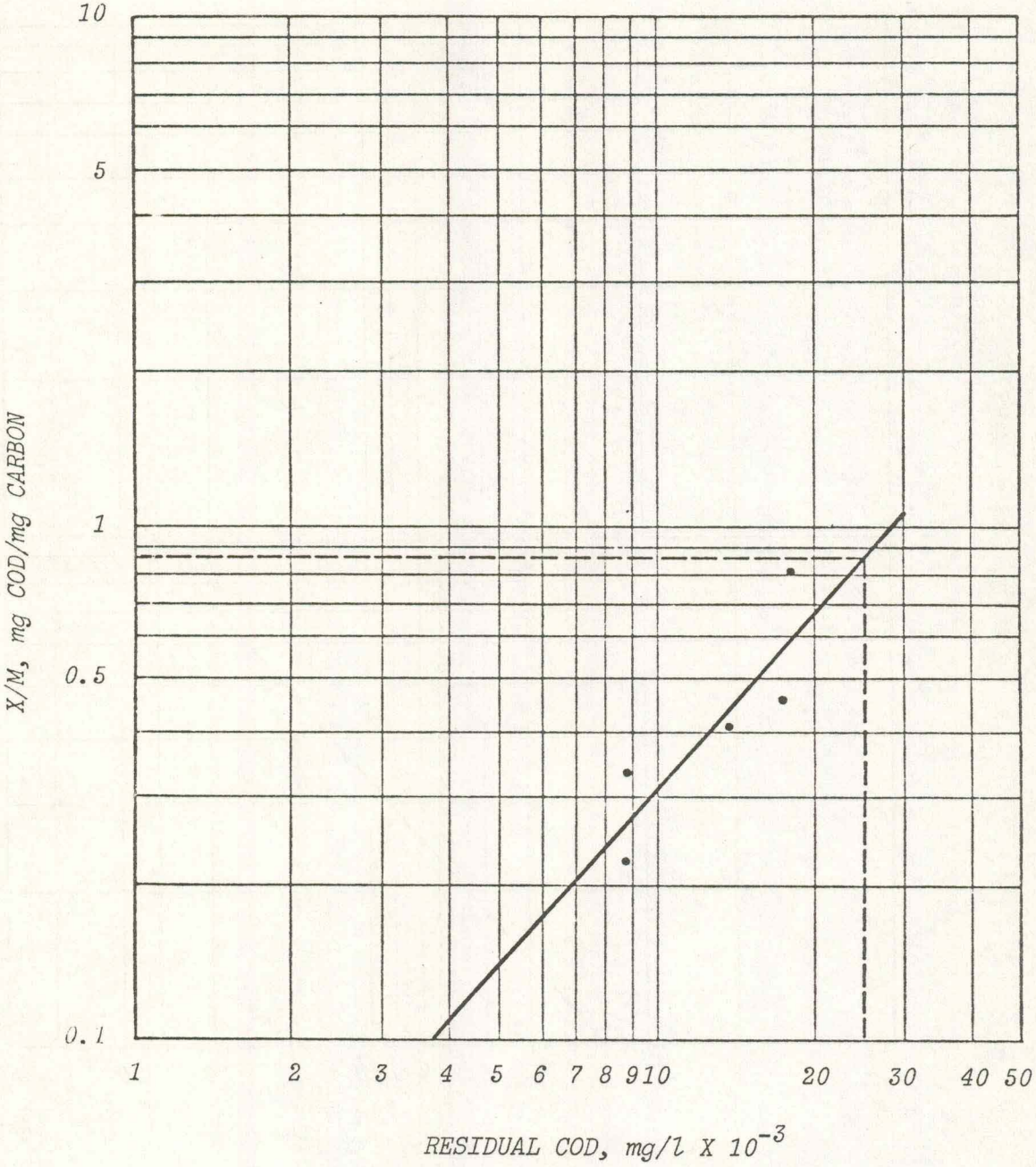


Figure VI-6. Adsorption Isotherm at pH 5.5.

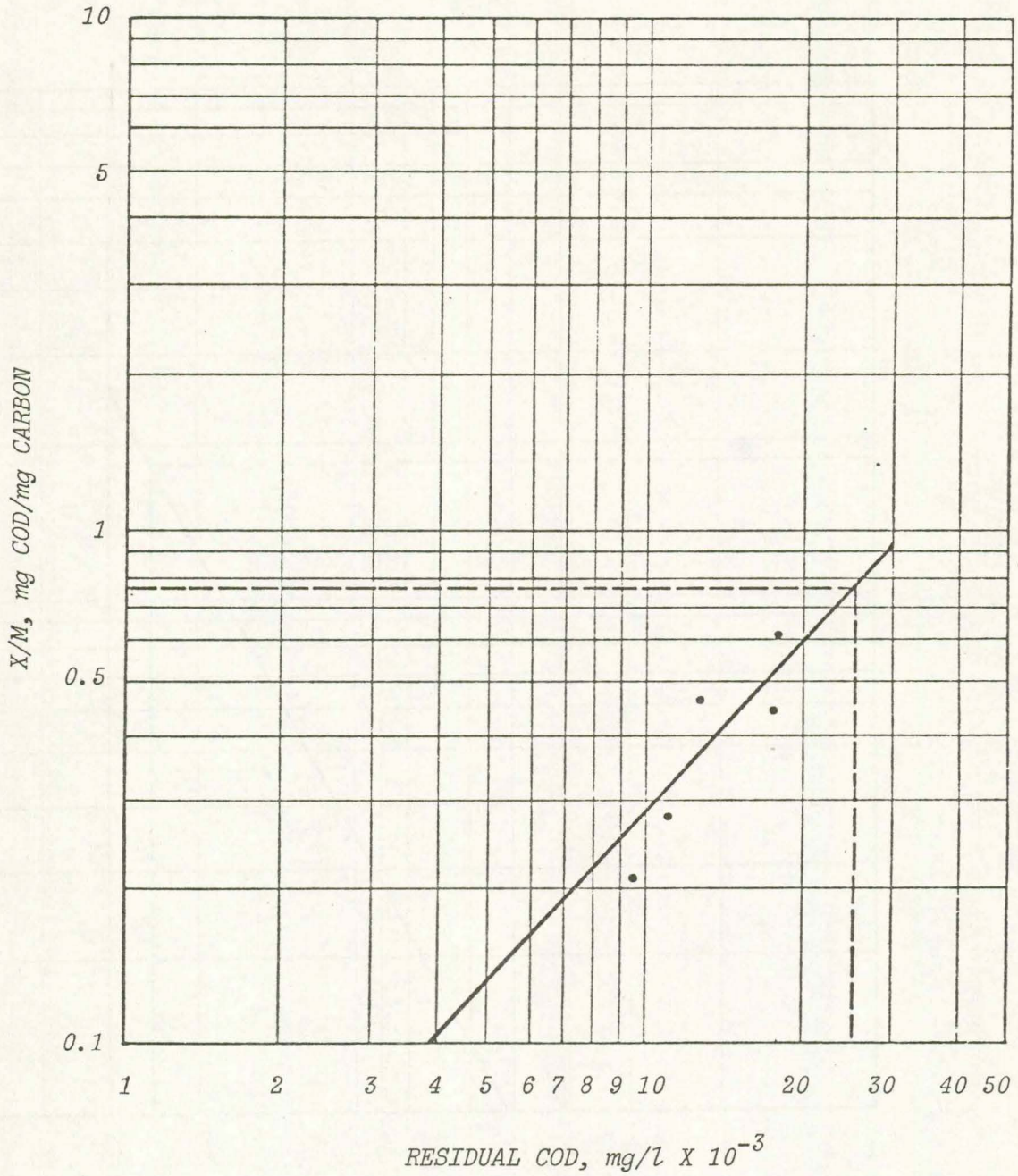


Figure VI-7. Adsorption Isotherm at pH 7.0.

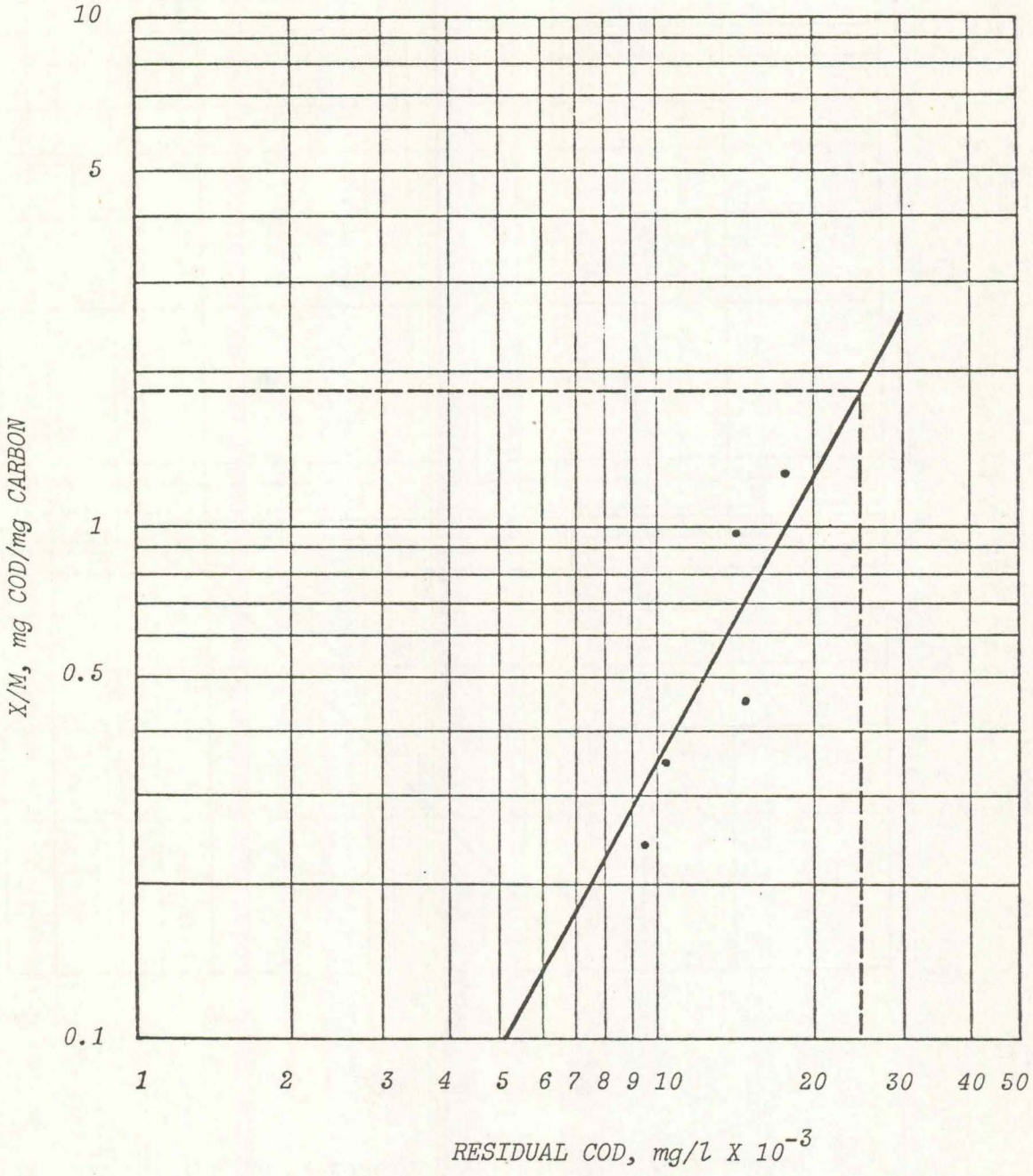


Figure VI-8. Adsorption Isotherm at pH 8.5.

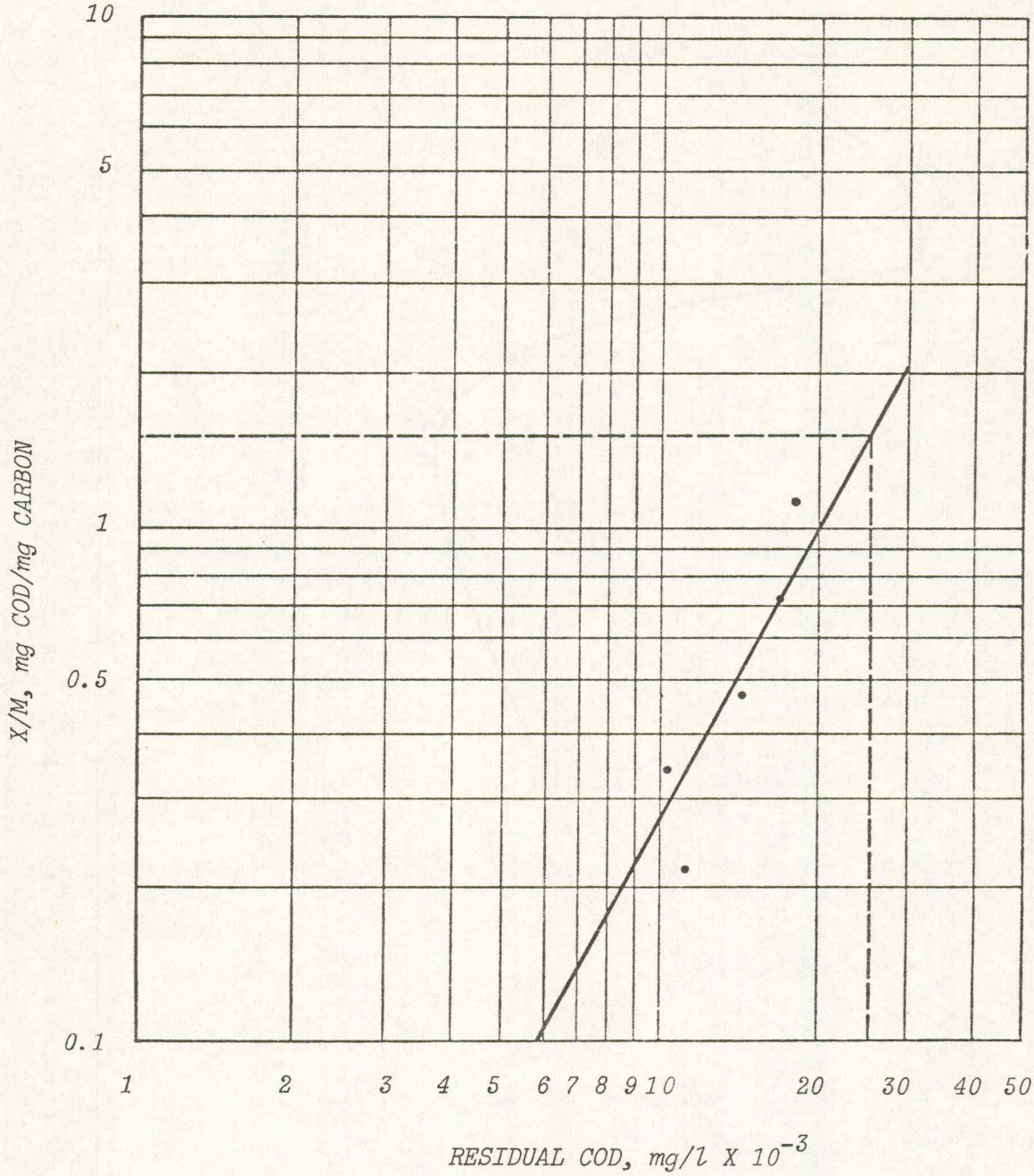


Figure VI-9. Adsorption Isotherm at pH 10.0.

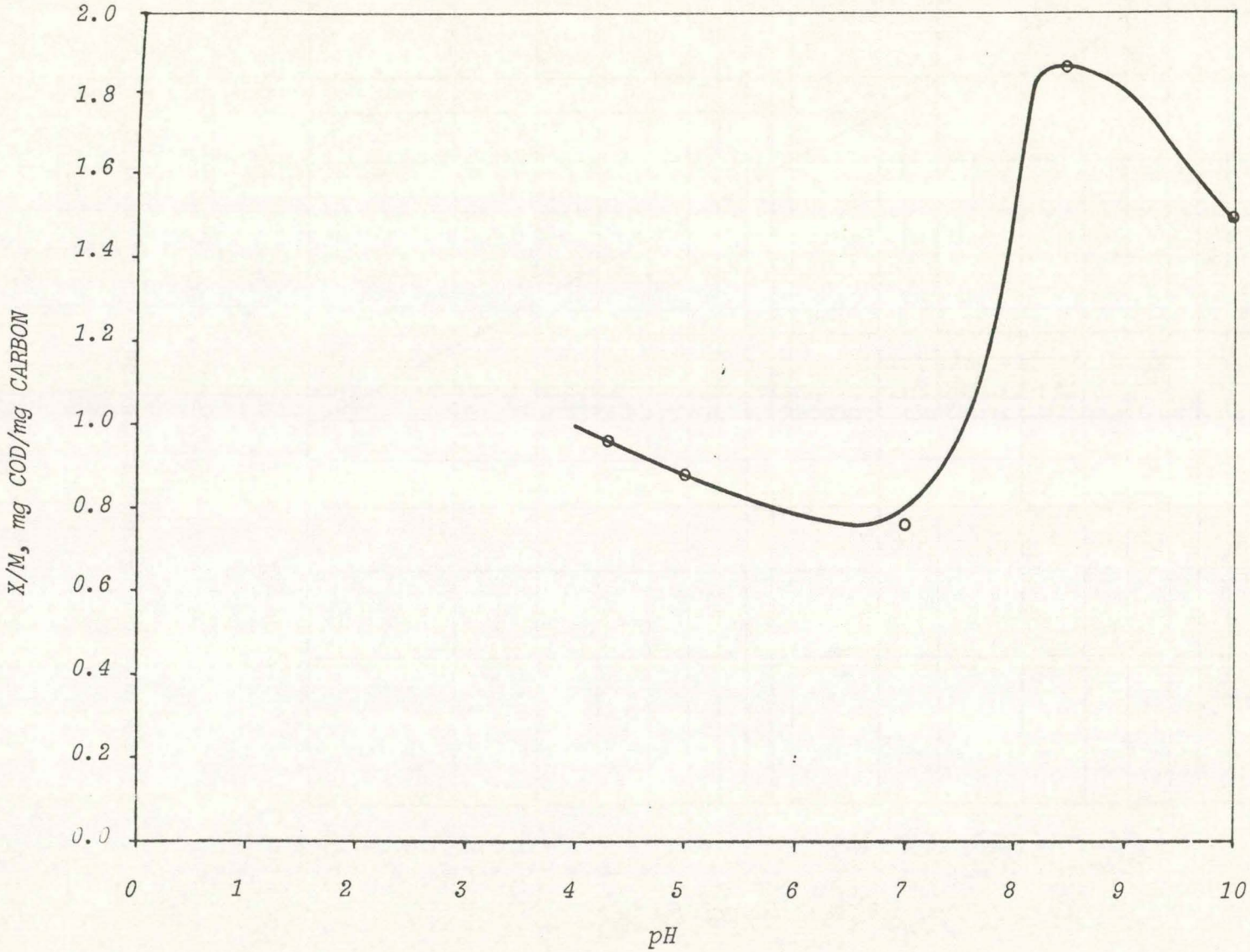


Figure VI-10. Variations in X/M Values as a Function of pH.

The adsorptive capacity is high at the original acidic pH of the waste. Then, as the pH approaches neutrality (pH = 7.0), adsorption capacity gradually declines. Once into the basic range, the adsorptive capacity increases rapidly until it peaks at a pH of around 8.5. Adsorption capacity then declines somewhat as the pH continues to increase. The improved adsorptive capacity at high pHs is similar to the results observed in batch reactions by Zuckerman and Molof (74).

The exceedingly high adsorptive capacity values achieved at the pH of 8.5 could be an incentive to adjust adsorption if it were not for the large disparity between it and the original pH. Such an adjustment of pH would be costly.

The isotherm tests conducted on the anaerobic biological effluent also showed promise in the ability of carbon to adsorb the COD causing contaminents in the effluent, as shown in Figure VI-11 and Table VI-3. The COD levels involved in this test were lower than in those conducted on pyrolysis waste alone. However, the adsorptive capacity at a typical COD value of 2,500 mg/l was still high at x/m = 0.6. Column tests were not conducted due to the small amounts of effluent obtainable from the anaerobic reactor.

Without column tests, isotherm results are not conclusive. However, it appears that anaerobic treatment of the waste followed by carbon adsorption seems to hold promise and should be investigated further.

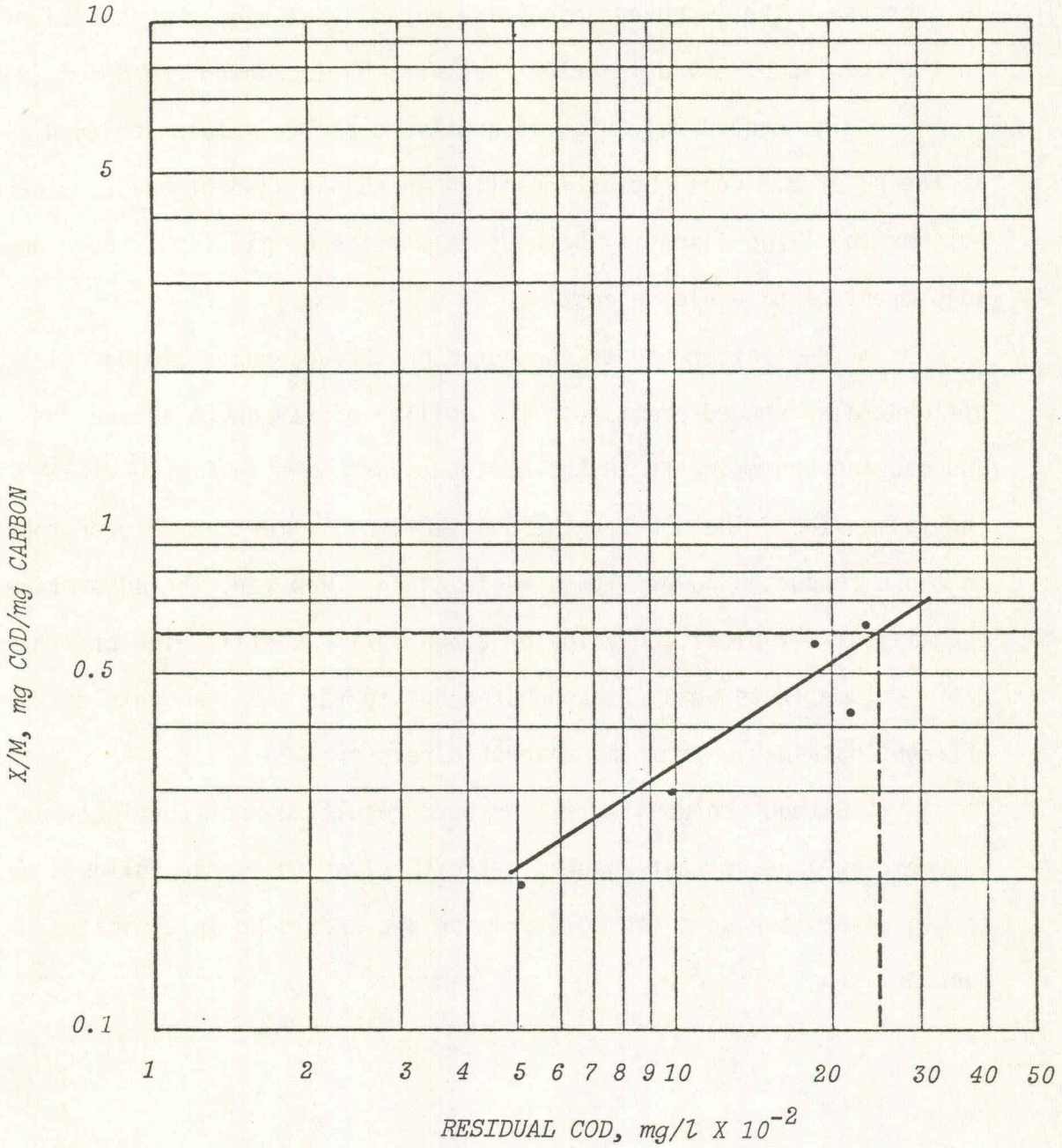


Figure VI-11. Anaerobic Digester Effluent Isotherm.

Table VI-3. Adsorption Isotherm Data for Anaerobic Digester Effluent.

Carbon Dosage(m) (mg/l)	Carbon Used (grams)	Remaining COD (mg/l)	Adsorbed COD (x) (mg/l)	x/m
0		2,480		
200	0.02	2,350	130	0.65
500	0.05	2,260	220	0.44
1,000	0.1	1,880	600	0.60
5,000	0.5	980	1,500	0.30
10,000	1.0	510	1,970	0.20

4.2 Carbon Column Runs

Carbon column runs were conducted at three different loading rates; 1, 2.5 and 5.0 gallons per minute per square foot (gpm/sq.ft.) of column area. Each flow rate was applied to three different bed depths ranging from 2.5 to 7.0 feet.

The plots of the breakthrough curves reveal typical S-shape curves but with very short breakthrough times. This is illustrated in Figures VI-12 through VI-14.

Using the data in Table VI-4, bed depth versus service time curves were plotted for all three loading rates using 90% removal as the breakthrough concentration and shown in Figure VI-15. Using the curves to determine slope and intercept, Equations 2, 3 and 4 can be solved. The results are displayed in Table VI-5.

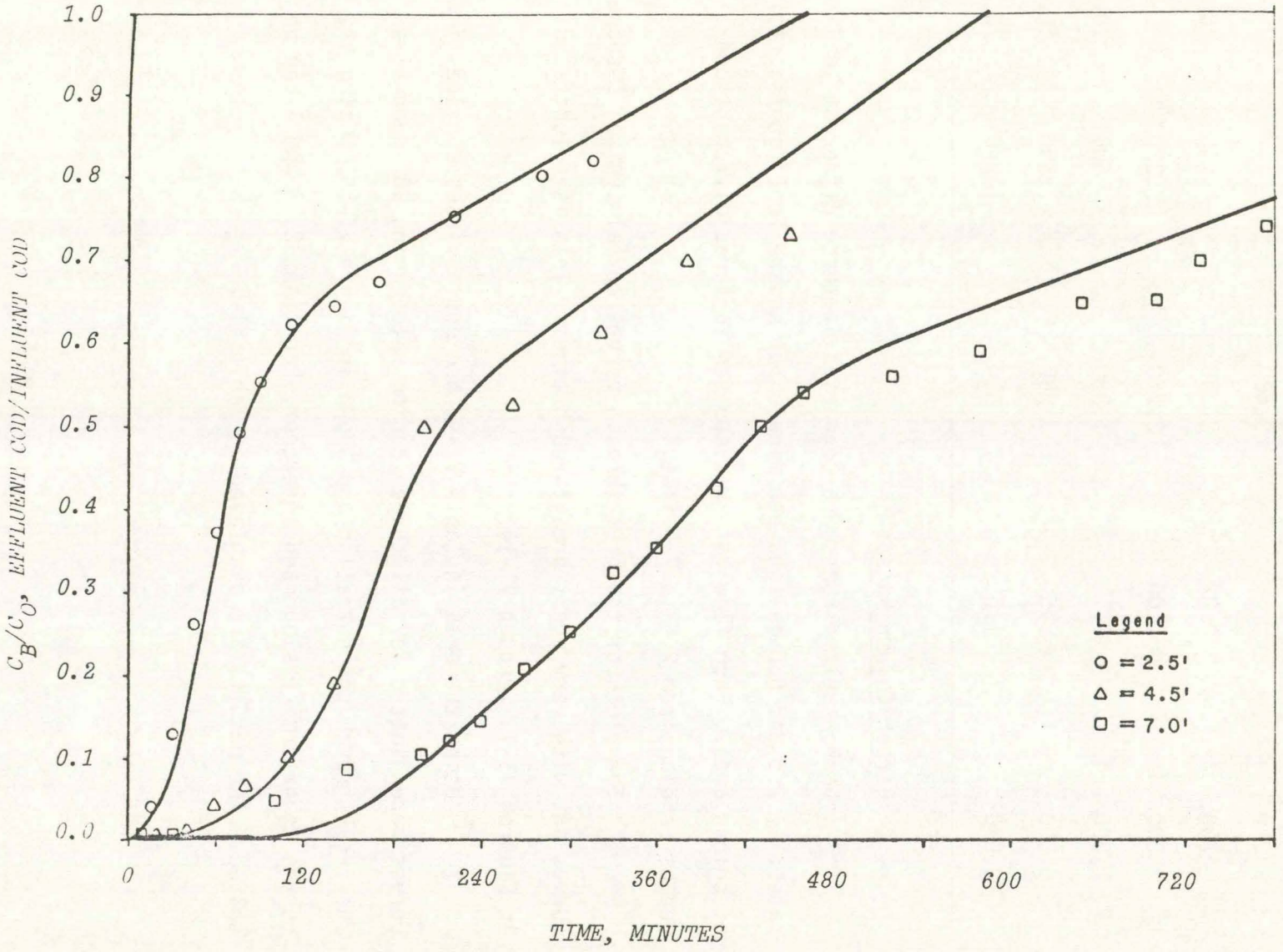


Figure VI-12. Breakthrough Curves for Various Bed Depths - 1.0 gpm/sq. ft. Flow Rate.

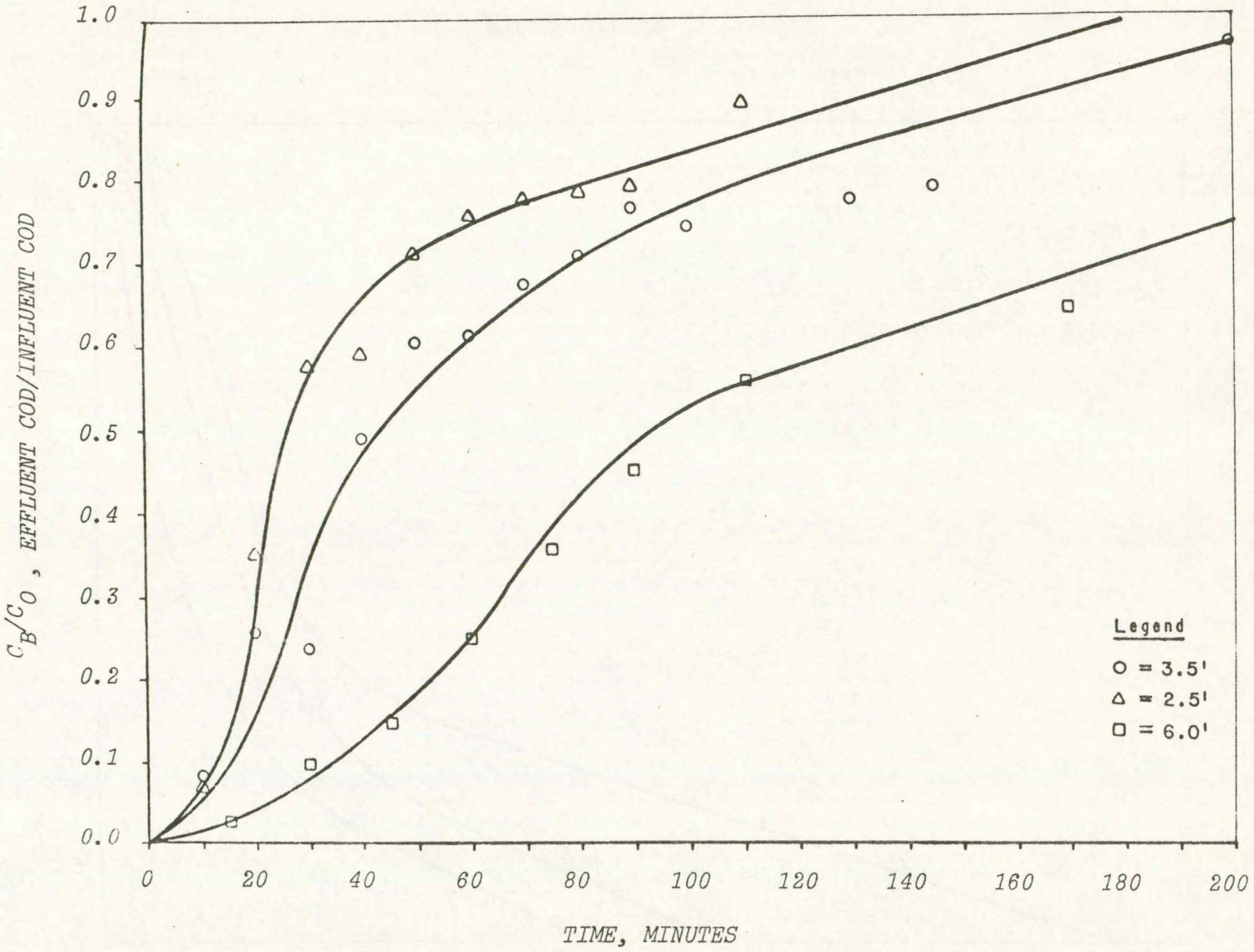


Figure VI-13. Breakthrough Curves for Various Bed Depths - 2.5 gpm/sq. ft. Flow Rate.

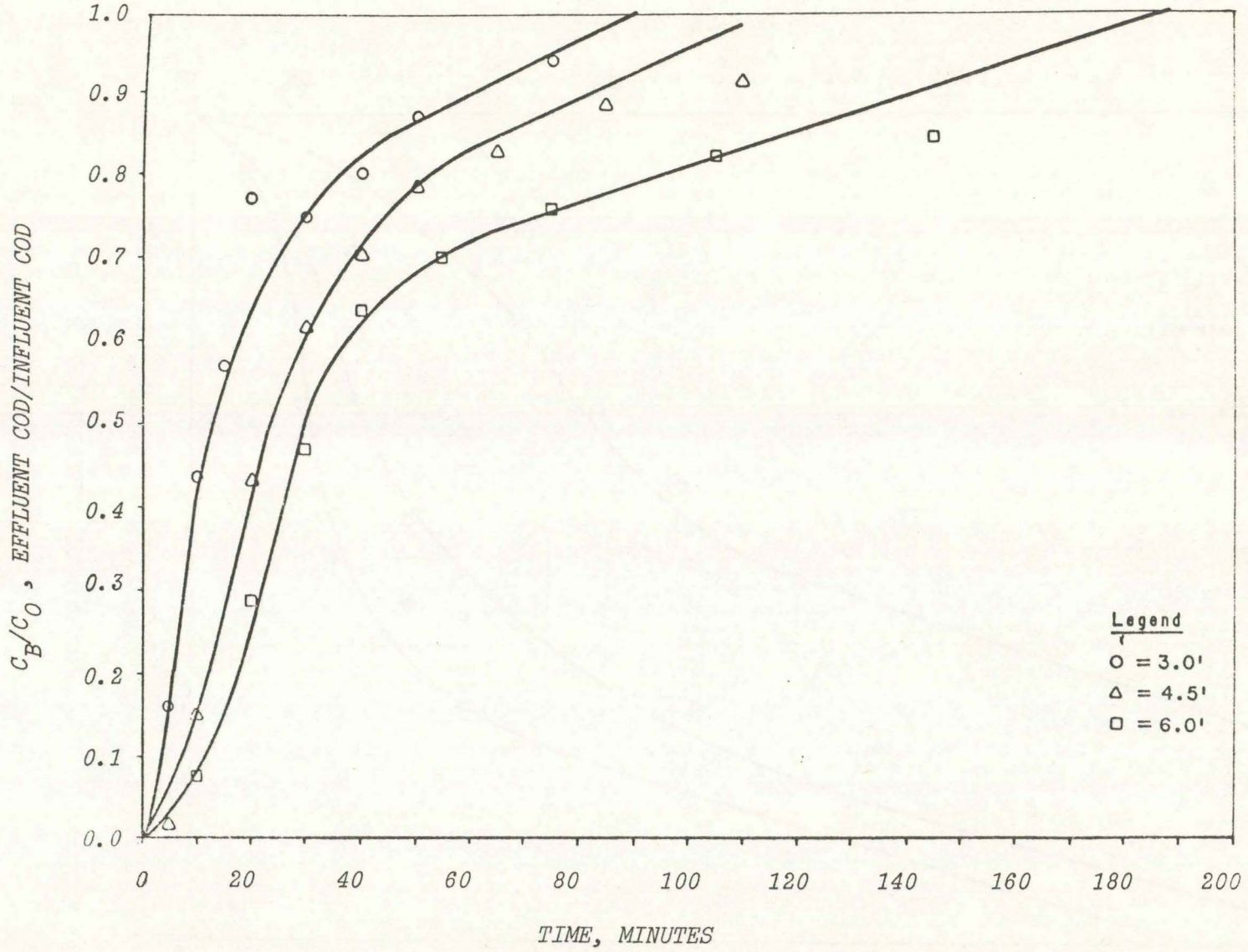


Figure VI-14. Breakthrough Curves for Various Bed Depths - 5.0 gpm/sq. ft. Flow Rate.

Table VI-4. Bed Depth - Service Time Summary at 90% Removal

Flow Rate (gpm/ft^2)	Bed Depth (feet)	Throughput Volume (Gallons)	Time (Hours)
1	2.5	0.15	0.41
1	4.5	0.66	1.83
1	7.0	1.00	2.75
2.5	2.5	0.15	0.18
2.5	3.5	0.16	0.20
2.5	6.0	0.54	0.66
5.0	3.0	0.08	0.05
5.0	4.5	0.19	0.11
5.0	6.0	0.32	0.20

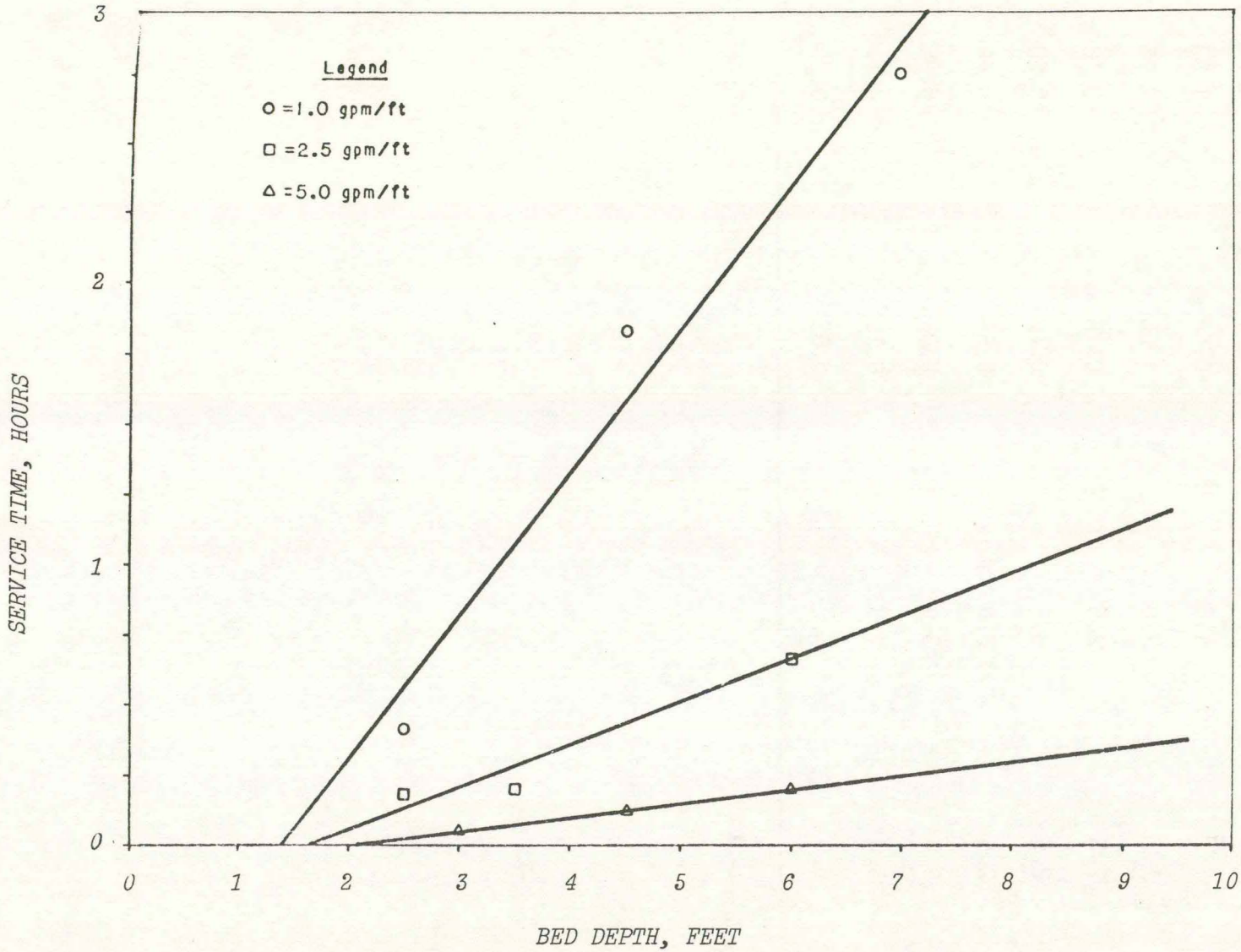


Figure VI-15. Bed Depth - Service Time Curves at 90% Removal.

Table VI-5. Analyses Summary.

Flow Rate (gpm/ft^2)	Slope	N_0 (lb/ft^3)	Intercept	K ($ft^3/lb\text{-}hr$)	D_0 (ft)
1.0	0.51	6.54	-0.725	10.99	0.24
2.5	0.14	4.64	-0.233	5.90	1.61
5.0	0.05	3.18	-0.103	13.42	2.06

In order to determine the performance of an actual column in operation, a size must be chosen that would be similar to ones in actual use. This sizing was based on Union Carbide data stating that a typical PUROX plant would serve 400,000 people and handle 1,000 tons of refuse a day. The scrubber waste is produced at the rate of 100 gallons per ton of refuse. This means that on an average day 100,000 gallons of scrubber wastes are produced. Using the design parameters stated earlier and a 5 gpm/sq.ft. flow rate, three ten-foot columns in series, each with a diameter of five feet were chosen. This gives an empty bed contact time of forty-five minutes, an aspect ratio of 6:1 and thirty feet of column depth.

Using Equation 1, the column service time to break through was found to be 1.39 hours. This would allow 8,216 gallons of waste to be treated before regeneration becomes necessary. This would mean 13 regenerations per day.

If Nuchar WV-H (30 lb/ft^3) were used, the columns would require 17,640 lbs. of carbon. The required regeneration capacity per day would then be 230,000 lb/day.

5.0 ECONOMIC ANALYSIS

Using the EPA guideline of forty pounds of carbon per square foot of multiple hearth furnace area, this system would require a 5,750 square foot furnace. An average of seven per cent loss of carbon per regeneration cycle would require 16,100 lbs. of makeup carbon per day.

Using the cost curves presented by Zanitsch and Stenzel (75), it was found that the capital cost of the columns plus piping would be $150,000. The capital cost of the storage and handling facilities plus a five-day supply of both reactivated and spent carbon would be $1,000,000. The capital cost of a regeneration system capable of handling 230,000 lbs. of carbon per day would be $4,000,000. Thus, the capital cost for the installation would total about $5,150,000. The annual cost to operate the regeneration facility alone would be $7,555,500. Labor and maintenance costs would add another $300,000 per year. Amortization of the capital investment at 10 percent interest rate over twenty years would require annual payments of $605,000 per year. The total annual cost of the operation would then total $8,460,000. With a flow rate of 100,000 gallons per day of pyrolysis waste, the cost per thousand gallons would be $230 or about 23 cents per gallon.

By reducing the breakthrough desired to 60 percent removal, a similar analysis indicates costs of about 13 cents per gallon or $130 per thousand gallons of waste treated. A sample calculation sheet to demonstrate the procedure used is presented in Appendix C.

Even by reducing the breakthrough requirement, the cost per thousand gallons of waste is very high. Average industrial wastes treated

with activated carbon range from about $0.03 to $20.00 per thousand gallons. The major reason for the high cost is the size of the regenerating equipment needed to keep the carbon activated. The high concentration of the waste causes the carbon to rapidly lose its capacity to adsorb. Although technically there are no limits on the concentration of solute in the waste stream, Zanitsch and Stenzel (75) state that the highest concentration influent that has been treated on a continuous basis contains 10,000 mg/l TOC. This fact also demonstrates the impracticality of treating a waste as high in COD as the scrubber waste with only granular activated carbon. Since column runs were not performed on the anaerobic digester effluent, the economic analysis was performed using the bed depth and loading rate determined for the pyrolysis waste as shown earlier. This was three columns in series each ten feet deep and five feet in diameter with a loading rate of five gallons per minute per square feet of column area.

Using the x/m value of 0.6 as shown in Figure VI-11, an average influent concentration of 2,500 mg/l as shown in Table VI-3, and 90% removal as a breakthrough concentration, a breakthrough time can be established for a carbon column required to treat the quantity of anaerobic digester effluent expected from a full scale operation. As before, a typical plant would serve 400,000 people and produce 100,000 gallons at scrubber waste per day. The column service time was found to be 5.6 days.

Again using the cost curves, it was found the capital cost of the columns plus piping would be $150,000. The capital cost of the storage and handling facilities plus a five-day supply of both reactivated and spent carbon would be $100,000. The capital cost of the necessary regen-

eration facility would be $600,000. The capital cost for the whole installation would be $850,000. The annual cost to operate the regeneration facility would be $154,000. Labor and maintenance costs would be $51,000 per year. Amortization of the capital investment at 10% interest rate over twenty years would require annual payments of $100,000 per year. The total annual cost would be $305,000. The cost per thousand gallons would be $8.35 or about 0.84 cents per gallon.

This is a reasonable treatment cost and demonstrates a real economic feasibility in using anaerobic biological systems in connection with carbon columns to treat the pyrolysis waste. A sample calculation sheet is presented in Appendix D.

6.0 CONCLUSIONS

The conclusions that can be gained from this study are summarized as follows:

1) Activated carbon, both powdered and granular, has a high affinity for the adsorbate molecules in the PUROX pyrolysis scrubber wastes.

2) Applications of the pyrolysis scrubber waste to a granular activated carbon column will result in a purified effluent, however, breakthrough in the columns is reached rapidly.

3) The application of granular activated carbon columns as the sole treatment scheme for pyrolysis scrubber waste is technically possible but economically prohibitive. Estimated treatment costs are in the range of $0.23 per gallon of waste.

4) Activated carbon has a high affinity for the organics in the effluent from a complete mix anaerobic digester that is being fed pyrolysis wastes. Estimated treatment costs are about 0.84 cents per gallon of effluent.

CHAPTER VII

PRACTICAL APPLICATION OF RESEARCH RESULTS

1.0 RESEARCH ACCOMPLISHMENTS

The work of the past three years on the treatment of PUROX pyrolysis wastes has shown that the wastes can be treated effectively in anaerobic biological systems. Both suspended growth or attached growth systems are effective, as discussed in Chapters V and VI.

It has been shown, particularly for the suspended growth systems, that up to 70 percent of the COD of the PUROX pyrolysis waste can be removed with the anaerobic systems. This is a very high COD removal percentage and indicates that much of the organic matter in the pyrolysis waste is biologically degradable.

The research has also shown that the PUROX wastes contain organics that are highly toxic and strongly inhibitory to unacclimated anaerobic systems. It is necessary to acclimate biological systems slowly to the waste and not to exceed the threshold level of toxicity once acclimation is achieved. In this work, the PUROX pyrolysis wastes in the feed to the suspended growth reactors could not exceed 17 percent without inhibition. This was for the PUROX wastes having a COD of 41,300 mg/l. For stronger pyrolysis wastes a higher degree of dilution may be required.

It is also clear from this work that anaerobic treatment, by itself, is not sufficient for complete treatment of the PUROX pyrolysis wastes. This work and that of others (Refs. 52 through 64) indicates that virtually complete removal of all organics from the pyrolysis wastes could be achieved by treating the anaerobic effluent further with one or a

combination of activated sludge, activated carbon, and chemical oxidation with ozone, hydrogen peroxide, chlorine or chlorine dioxide.

2.0 PRACTICAL TREATMENT SYSTEMS

The results of this research indicate that it may be feasible to treat PUROX pyrolysis wastes on a large scale along with the usual organic sludges or liquid wastewaters from a typical city.

A PUROX plant capable of handling 1,000 tons per day of mixed municipal refuse would serve a city of about 400,000 people. This assumes a typical average refuse generation rate of five pounds per capita per day. The PUROX pyrolysis system would produce about 100,000 gpd of liquid wastes (Table II-9).

A city of 400,000 people would generate about 240,000 gpd of domestic wastewater sludge, assuming a typical solids generation rate of 0.2 pound per capita per day and a sludge concentration from wastewater treatment of four percent.

If it is assumed that the PUROX waste is to make up 17 percent of the total feed to an anaerobic system, the total feed volume would have to be about 588,000 gpd (100,000/0.17 = 588,000). If the wastewater sludge were thickened to only about two percent solids (rather than four percent), the sludge volume would be 480,000 gpd and the total feed to an anaerobic digester receiving both pyrolysis wastes and sludge would be 580,000 gpd. This would provide the necessary dilution to enable treatment of the entire waste stream without inhibition as a result of the pyrolysis wastes.

If it is assumed that the digestion system is sized to provide a 15 day SRT, the total primary digestion volume required would be 8,700,000 gallons or 1,160,000 cu. ft. This is not an unusually large volume of digestion for a city of 400,000 population. If the city happened to produce more sludge than assumed above, then the impact of the PUROX wastes on the sludge treatment system of the city may be even less than that shown by the example.

Also of significance is the fact that the digestion system would remove about 70 percent of the COD of the pyrolysis wastes. If the pyrolysis wastes had a COD of 40,000 mg/l, the COD removed per day would be 28,000 mg/l or 23,324 lb/day from 100,000 gpd of PUROX wastes. This would result in the production of 131,080 cu.ft. of methane per day having a heating value of about 131 million BTUs. This is about 65 percent of the normal gas production as a result of the anaerobic digestion of domestic wastewater sludges only from a city of 400,000 population. The added methane fuel production resulting from the anaerobic treatment of the pyrolysis wastes is therefore quite significant.

Attached growth anaerobic systems may have some significant advantages in treating the high-strength, highly soluble PUROX wastes. As discussed in Chapter V, the anaerobic filters of this research were capable of treating PUROX pyrolysis wastes up to 33 percent of the total feed volume and achieved an overall COD removal of 72 percent. This means that a practical treatment system for PUROX pyrolysis wastes might be an anaerobic filter receiving two parts primary wastewater effluent and one part PUROX pyrolysis wastes.

If the pyrolysis wastes had the same COD as that used in the anaerobic filter studies of this research (COD = 18,400 mg/l), the actual feed COD to the filter after dilution would be about 6,100 mg/l (18,400/3 = 6,100 mg/l). The 5-day BOD of this diluted waste would be about 2,150 mg/l, or approximately 35 percent of the COD, based on the BOD_5 to COD ratios determined in this research (Chapter III). This wastewater strength is still well above the practical lower limit of 1,000 mg/l BOD_5 for the treatment of wastewaters with an anaerobic filter.

Based on the results of this research, a COD removal of about 70 percent could be expected through the anaerobic filter system. The effluent from the anaerobic filter could then be treated by one or a combination of activated sludge, carbon adsorption or chemical oxidation for complete removal of the toxic refractory organics.

It must be emphasized that the systems described for the treatment of PUROX pyrolysis wastes are only suggestions. There are strong indications, based on the results of this research and that of others, that the proposed systems would be effective in the removal of both toxic and non-toxic organics from the pyrolysis wastes. Further research and pilot treatability work would be necessary before success of the proposed treatment schemes could be insured.

CHAPTER VIII

CONCLUSIONS

In each of the chapters of this report in which research results were presented (Chapter IV, V and VI) conclusions were presented for the work presented. Listed below are the overall conclusions that appear warranted for the entire project:

1) The wastewaters from the PUROX pyrolysis process are high in organics (COD of 18,400 to 41,300 mg/l) and contain polycyclic hydrocarbons and other organics that are toxic to biological wastewater treatment systems, some of which are known to be carcinogenic.

2) The PUROX pyrolysis wastes are treatable with either suspended or attached growth anaerobic processes but the microorganisms must be acclimated to the pyrolysis wastes.

3) To prevent inhibition of the biological systems, the PUROX wastes must be diluted to below a threshold level of concentration before feeding to acclimated anaerobic systems. In this research, the PUROX wastes could not exceed 17% of the total feed volume to the suspended growth reactors and 33% of the total feed volume to the attached growth reactors. The COD of the PUROX wastes fed to the suspended growth and attached growth reactors was 41,300 mg/l and 18,400 mg/l, respectively.

4) The anaerobic systems are capable of removing approximately 70% of the COD of the PUROX pyrolysis wastes.

5) To remove refractory organics, including toxics, the effluent from the anaerobic processes would require further treatment prior to discharge. Based on this research and that of others, this could be accomplished by one or a combination of treatment with activated sludge, activated carbon, or chemical oxidation with ozone, hydrogen peroxide, chlorine, or chlorine dioxide.

6) Practical systems for application to the PUROX pyrolysis wastes could involve treatment with the usual wastewater sludges produced by cities in an anaerobic digestion system or dilution of the pyrolysis wastes with primary effluent, in the case of an attached growth anaerobic treatment system.

REFERENCES

1. Gottschalk, G.: Bacterial Metabolism. Springer-Verlag Inc., New York, N.Y., 1979.

2. Sokatch, J.R.: Bacterial Physiology and Metabolism. Academic Press Inc., New York, N.Y., 1969.

3. Dole, H.W.: Bacterial Metabolism. 2nd Edition, Academic Press Inc., New York, N.Y., 1975.

4. Bryant, M.P.: "The Microbiology of Anaerobic Degradation and Methanogenesis with Special Reference ot Sewage." Microbial Energy Conversion. Pergamon Press, 1977.

5. Jones, J.B., and Stadtman, T.C.: "*Methanococcus vanielii*: Growth and Metabolism of Formate." Microbial Production and Utilization of Gases. Akademi Der Wissenschaften Zu Göttingen, 1976.

6. Kasper, H.F., and Wuhrman, K.: "Kinetic Parameters and Relative Turnovers of Some Important Catabolic Reactions in Digesting Sludge." Applied and Environmental Microbiology, 1-7, July 1978.

7. Keikus, J.G.: "The Biology of Methanogenic Bacteria." Bacteriological Reviews, 41, 514-541, June 1977.

8. McInerney, M.J., Bryant, M.P., and Pfennig, N.: "Anaerobic Bacterium that Degrades Fatty Acids in Syntrophic Association with Methanogens." Archives of Microbiology, 122, 129-135, 1979.

9. McCarty, P.L.: "Kinetics of Waste Assimilation in Anaerobic Treatment." Developments in Industrial Microbiology, American Institute of Biological Science, Washington, D.C., Vol. 7, 1966.

10. Wolin, M.J.: "Interactions Between H_2-Producing and Methane Producing Species." Microbial Production and Utilization of Gases. Akademia Der Wissenschaften Zu Göttingen, 1976.

11. Mah, R.A., Smith, M.R., and Baresi, L.: "Studies on an Acetate-Fermenting Strain of *Methanosarcina*." Applied and Environmental Microbiology, 1174-1184, June 1978.

12. Doddema, H.J., and Vogels, G.D.: "Improved Identification of Methanogenic Bacteria by Fluorescence Microscopy." Applied and Environmental Microbiology, 36, 752-754, Nov. 1978.

13. Taylor, G.T., Kelly, D.P., and Pirt, S.J.: "Intermediary Metabolism In Methanogenic Bacteria." Microbial Production and Utilization of Gases. Akademia Der Wissenschaften Zu Göttingen, 1976.

14. Abram, J.W., and Nedwell, D.B.: "Inhibition of Methanogenesis by Sulfate Reducing Bacteria Competing for Transferred Hydrogen." Archives of Microbiology, 117, 89-92, 1978.

15. Braun, M., Schoberth, S., and Gottschalk, G.: Enumeration of Bacteria Forming Acetate from H_2 and CO_2 in Anaerobic Habitats." Archives of Microbiology, 120, 201-204, 1979.

16. Mah, R.A., Hungate, R.E., and Ohwaki, K.: "Acetate, A Key Intermediate in Methanogenesis." Microbial Energy Conversion. Pergamon Press, 1977.

17. Baresi, L., Mah, R.A., Ward, D.M., and Kaplan, I.R.: "Methanogenesis from Acetate: Enrichment Studies." Applied and Environmental Microbiology, 186-197, July 1978.

18. Dague, R.R.,: "Application of Digestion Theory to Digester Control." Journal Water Pollution Control Federation, 40, 2021-2032, Dec. 1968.

19. Loll, V.: "Engineering, Operation and Economics of Biodigestion." Microbial Energy Conversion. Pergamon Press, 1977.

20. Konstandt, H.G.: "Engineering, Operation and Economics of Methane Gas Production." Microbial Energy Conversion. Pergamon Press, 1977.

21. McCarty, P.L.: "Anaerobic Waste Treatment Fundamentals: Part I - Chemistry and Microbiology; Part II - Environmental Requirements and Control; Part III - Toxic Materials and Their Control; Part IV - Process Design." Public Works, Sept., Oct., Nov., Dec., 1964.

22. Young, J.C., and McCarty, P.L.: "The Anaerobic Filter for Waste Treatment." Journal Water Pollution Control Federation, 41, R160-R173, May 1969.

23. Sanders, F.A., and Bloodgood, D.E.: "The Effect of Nitrogen to Carbon Ratio on Anaerobic Decomposition." Journal Water Pollution Control Federation, 37, 1741-1752, Dec. 1965.

24. Stenesh, J.: "Information Transfer in Thermophilic Bacteria." Extreme Environments: Mechanisms of Microbial Adaptation. Academic Press Inc., New York, N.Y., 1976.

25. Heukelekian, H., and Kaplovsky, A.J.: "Effects of Change of Temperature on Thermophilic Digestion." Sewage Works Journal, 20, 806-816, 1948.

26. Berg, L., and Lentz, C.P.: "Anaerobic Digestion of Pear Waste: Laboratory Equipment Design and Preliminary Results." Canadian Institute of Food Technology Journal, 4, 159-165, 1971.

27. Rolfe, R.D., Hentges, D.J., Cambell, B.J., and Barrett, J.T.: "Factors Related to the Oxygen Tolerance of Anaerobic Bacteria." Applied and Environmental Microbiology, 306-313, Aug. 1978.

28. "Inhibition in the Anaerobic Digestion Process for Sewage Sludge." Notes on Water Pollution, Department of the Environment. No. 53, June 1971.

29. Fuller, G.W.: Sewage Disposal, McGraw-Hill Book Co., Inc., New York, N.Y. (1912).

30. Kinnicutt, L.P., Winslow, A., and Pratt, W.R., Sewage Disposal, 2nd Ed., John Wiley and Sons, Inc. (1919).

31. Kivell, W.A., "Trend and Developments in Separate Sludge Digestion." Sewage Works Journal, 3, 54, (1931).

32. Dague, R.R., McKinney, R.E., and Pfeffer, J.T.: "Solids Retention in Anaerobic Waste Treatment Systems." Journal Water Pollution Control Federation, 42, 2, Part 2, R29, (Feb. 1970).

33. Torpey, W.N., and Melbinger, N.R., "Reduction of Digested Volume by Controlled Recirculation." Journal Water Pollution Control Federation, 39, 9, 1464 (Sept. 1967).

34. Dague, R.R., McKinney, R.E., and Pfeffer, J.T.: "Anaerobic Activated Sludge." Journal Water Pollution Control Federation, 38, 2, 220 (Feb. 1966).

35. Rawn, A.M. and Candell, E.J.: "Some Effects of Anaerobic Digestion on Sewage Sludge." Transactions, American Society of Civil Engineers, 115, 1261, No. 2421 (1950).

36. Fullen, W.J.: "Anaerobic Digestion of Packing Plant Wastes." Sewage and Industrial Wastes, 25, 576 (1953).

37. Schroepfer, G.J., Fullen, W.J., Johnson, A.S., Ziemke, N.R., and Anderson, J.J.: "The Anaerobic Contact Process as Applied to Packinghouse Wastes." Sewage and Industrial Wastes, 27, 460 (1950).

38. Speece, R.E.: "Methane from Petrochemical Wastewaters." Research Directions, A Report on Research Activities at Drexel University, Vol. 1, No. 1, 1978.

39. Richter, G.A., and Mackie, J.A.: "Low Cost Treatment for High Strength Waste." Report by CH2M/Hill Engineers, Corvallis, Oregon (Oct. 1971).

40. LaMotta, E.J.: "Kinetics of Growth and Substrate Uptake in a Biological Film System." Applied and Environmental Microbiology, 286-293, Feb. 1976.

41. Atkinson, B., and Fowler, H.W.: "The Significance of Microbial Film in Fermenters." Advances in Biochemical Engineering. Vol. 3, 1974.

42. Tchobanoglous, G., Theisen, H.M., and Eliassen, R.: Solid Wastes: Engineering Principles and Management Issues. McGraw-Hill Book Company, New York, N.Y., 1977.

43. Weinstein, N.J., and Toro, R.F.: Thermal Processing of Municipal Solid Waste for Resource and Energy Recovery. Ann Arbor Science Publishers Inc., Ann Arbor, Mich., 1976.

44. Young, J.C.: "Assessment of Biological Processes for Treating Pyrolysis Wastewaters." Summary Report made to U.S. Department of Energy, Washington, D.C., April 1979.

45. Union Carbide Corporation, "Solid Waste Disposal Resource Recovery." Publication F-3698.

46. Drobny, N.L., Hull, H.E., and Testiu, R.F.: Recovery and Utilization of Municipal Solid Waste. U.S. EPA Publication SW-47r, Washington, D.C., 1971.

47. Dague, R.R.: "Anaerobic Biological Treatment of Liquid Wastes from Pyrolysis Processes." Preliminary Proposal submitted to U.S. Department of Energy, July 1976.

48. Gorman, P., Marcus, M., Ananth, K., and Golembiewski, M.: "Environmental Assessment of Waste-to-Energy Process: Union Carbide PUROX^{R} System." Mid-west Research Institute, Kansas City, MO, Nov. 1978.

49. Courtesy of Linde Division of Union Carbide Corporation.

50. Herbes, S.E., and Schwall, L.R.: "Microbial Transformation of Polycyclic Aromatic Hydrocarbons in Pristine and Petroleum-Contaminated Sediments." Applied and Environmental Microbiology, 306-316, Feb. 1978.

51. Guerin, M.R.: "Energy Sources of Aromatic Hydrocarbons." Polycyclic Hydrocarbons and Cancer, Volume 1, Environment, Chemistry, and Metabolism. Academic Press Inc., New York, N.Y., 1978.

52. Suess, M.J.: "The Environmental Load and Cycle of Polycyclic Aromatic Hydrocarbons." The Science of the Total Environment, 6, 239-250, 1976.

53. Baun, E.J.: "Occurrence and Surveillance of Polycyclic Aromatic Hydrocarbons." Polycyclic Hydrocarbons and Cancer, Volume 1, Environment, Chemistry, and Metabolism. Academic Press Inc., New York, N.Y., 1978.

54. Harrison, R.M., Perry, R., and Wellings, R.A.: "Polynuclear Aromatic Hydrocarbons in Raw, Potable and Waste Waters." Water Research, 9, 331-346, May 1975.

55. Degradation of Synthetic Organic Molecules in the Biosphere. Proceedings of a Conference in San Francisco, California, June 12-13, 1971, National Academy of Sciences Inc., Washington, D.C., 1972.

56. Gibson, D.T.: "Microbial Degradation of Aromatic Compounds." Science, 161, 1093-1097, Sept. 1968.

57. Hackett, W.F., Connors, W.J., Kirk, J.K., and Zeikus, J.G.: "Microbial Decomposition of Synthetic ^{14}C-Labeled Lignins in Nature: Lignin Biodegradation in a Variety of Natural Materials." Applied and Environmental Microbiology, 33, 43-51, 1977.

58. Dutton, P.L., and Evans, W.C.: "The Metabolism of Aromatic Compounds by *Rhodopseudomonas palvstris*." Biochemistry Journal, 113, 525-536, 1969.

59. Taylor, B.F., Campbell, W.L., and Chinoy, I.: "Anaerobic Degradation of the Benzene Nucleus by a Facultatively Anaerobic Microorganism." Journal of Bacteriology, 102, 403-437, May 1970.

60. Williams, R.J., and Evans, W.C.: "Anaerobic Metabolism of Aromatic Substrates by Certain Microorganisms." Biochemical Society Transactions, 1, 186-187, 1973.

61. Nottingham, P.M., and Hungate, R.E.: "Methanogenic Fermentation of Benzoate." Journal of Bacteriology, 98, 1170-1172, June 1969.

62. Ferry, J.G., and Wolfe, R.S.: "Anaerobic Degradation of Benzoate to Methane by a Microbial Consortium." Archives of Microbiology, 107, 33-40, 1976.

63. Keith, C.L., Bridges, R.L., Fina, L.R., Iverson, K.L., and Cloran, J.A.: "The Anaerobic Decomposition of Benzoic Acid During Methane Fermentation. IV. Dearomatization of the Ring and Volatile Fatty Acids Formed on Ring Rupture." Archives of Microbiology, 118, 173-176, 1978.

64. Healy, J.B. jr., and Young, L.Y.: "Catechol and Phenol Degradation by a Methanogenic Population of Bacteria." Applied and Environmental Microbiology, 35, 216-218, Jan. 1978.

65. APHA, AWWA, WPCF, Standard Methods for the Examination of Water and and Wastewater. 14th Edition, American Public Health Association, New York, 1976.

66. Courtesy of Harry Boren, Iowa City, Iowa Wastewater Treatment Plant.

67. Courtesy of the Ross Company, manufacturers of Similac liquid concentrate.

68. Cheremisinoff, P.N. and Moressi, A.C.: Carbon Adsorption Applications, Carbon Adsorption Handbook, Ann Arbor Science Publishers, Inc., Ann Arbor, Mich. (P.N. Cheremisinoff and F. Ellerbusch, Eds.) (1978).

69. Weber, W.W., Jr.: Physio Chemical Processes for Water Quality Control, John Wiley and Sons, Inc., New York, N.Y., (1972).

70. U.S. Environmental Protection Agency, Process Design Manual for Carbon Adsorption, Technology Transfer Manual, EPA 625/1-71-002a, (1973).

71. Adams, C.E., Jr. and Eckenfelder, W.W., Jr.: Process Design Techniques for Industrial Waste Treatment, Enviro Press, Nashville, Tenn. (1974).

72. Cookson, J.T., Jr.: Adsorption Mechanisms: The Chemistry of Organic Adsorption on Activated Carbon, Carbon Adsorption Handbook, Ann Arbor Science Publishers, Inc., Ann Arbor, Mich. (P.N. Cheremisinoff and F. Ellerbusch, Eds.) (1978).

73. Culp, R.L. and Culp, G.L.: Advanced Wastewater Treatment, Van Nostrand Reinhold Company, New York, N.Y. (1971).

74. Zucherman, M.M. and Molof, A.H.: High Quality Reuse Water by Chemical-Physical Wastewater Treatment, Journal Water Pollution Control Federation, 42:437-463, (March, 1980).

75. Zanitsch, R.H. and Stenzel, M.H., Economics of Granular Activated Carbon Water and Wastewater Treatment Systems, Carbon Adsorption Handbook, Ann Arbor Science Publishers, Inc., Ann Arbor, Mich. (P.N. Cheremisinoff and F. Ellerbusch, Eds.) (1978).

APPENDIX A

LETTER FROM UNION CARBIDE ON PUROX WASTES SHIPMENT

UNION CARBIDE CORPORATION
LINDE DIVISION
P. O. BOX 44, TONAWANDA, NEW YORK 14150
TELEPHONE: 716 - 877 - 1600

August 17, 1977

Dr. Richard R. Dague
College of Engineering
University of Iowa
Iowa City, Iowa 52242

Dear Dr. Dague:

Thank you for sending me a copy of your proposal directed to ERDA together with your note concerning some details on the quantities of samples required from us for your work.

I need to advise you that the PUROX System presently operating at South Charleston will be shut down during the second half of September. I therefore suggest that we collect enough material for your entire project and send it to you in a single shipment not later than mid September. The material can be stored for fairly extensive time periods without concern that its properties will change in any significant way. So, please advise how much material you need for your project and the exact address to which we should send the drums of liquid.

Best regards,

UNION CARBIDE CORPORATION
Linde Division

L. C. Matsch
Senior Engineering Fellow

LCM/ehf

APPENDIX B

TENTATIVE ANALYTICAL PROTOCOL FOR COMPOSITIONAL ANALYSIS OF PYROLYSIS WASTES

TENTATIVE ANALYTICAL PROTOCOL FOR COMPOSITIONAL ANALYSIS OF PYROLYSIS WASTES*

Subject: Analytical protocol for the qualitative identification of compounds found in pyrolysis waste.

A summary of the analysis is given below and in Table IV-2.

1) Level 1 fractionation - preliminary analysis of the whole sample by column chromatography to ascertain the approximate composition of the sample.

2) Sequential separation of the individual fractions by high performance liquid chromatography resulting in a high resolution fractionation.

3) Partial characterization of the material amenable to further fractionation by gas chromatography with subsequent identification of the major components by mass spectrometry.

The objective of Level 1 analytical strategy is to provide a semi-quantitative estimation of the predominant classes of organic compounds present. To achieve this result, the extracted sample will be subjected to liquid chromatography using stepwise solvent gradient elution. The fractionation will result in the separation of the sample into eight fractions containing different classes (Table IV-2). Each fraction will subsequently be subject to gravimetric analysis in order to estimate the weight of material present. In order to confirm the presence or absence of various functional groups an infrared analysis of each fraction will be performed. From previous experience it is apparent that the proposed scheme will fractionate on the basis of polarity rather than simply providing clean separation according to functional groups. Generally, there is some carryover between adjacent fractions;

From reference .

however, infrared analysis will enable the major classes of organic compounds in each of the eight fractions to be identified.

The second major step of the analytical scheme consists of a sequential separation of each fraction by high performance liquid chromatography (HPLC). Table IV-2 lists the classes of organic compounds eluting in each HPLC fraction. By varying the time of the gradient from water to methanol a fractionation pattern or profile may be obtained for each of the various classes or fractions. Presumably, a qualitative comparison of the chromatographic profiles will give an indication of the types of chemical changes taking place. In addition, these high resolution fractions will not only give comparisons between sample fractions such as raw PUROX waste and PUROX feed waste but also allow collection of major components for mass spectral identification.

The final step in the analytical protocol will be the characterization of the major components or components of interest by mass spectrometry. These fractions or compounds amenable to fractionation by gas chromatography will be analyzed by gas chromatography-mass spectrometry. Organic species not amenable to G.C. will be analyzed by HPLC and tentatively assigned structures by retention times.

The above analytical protocol is designed to be a cost-effective survey technique. By comparing the data on weight compositions of the individual fractions as well as the differences or similarities in chromatograms (fingerprinting), information on component losses or formations may be obtained. With this information some questions concerning changes of components should be answered and, in addition, give new direction to future research efforts.

Objective: To provide a qualitative and semi-quantitative estimation of the predominant classes of organic compounds present in a pyrolysis waste sample.

Source: Department of Environmental Engineering (Richard R. Dague).

Reference: "Technical Manual for Analysis of Organic Materials in Process Streams". EPA-600/2-76-072, March, 1976.

Procedure:

1. 100 ml of aqueous pyrolysis waste extracted with 3 x 50 ml of distilled-in-glass $MeCl_2$. Approximately 100 mg NaCl was added to aid in the dispersion of emulsions.
2. The extract was treated with hexane/acetone extracted Na_2SO_4 to remove any residual H_2O and was reduced to 10 ml on a K.D. apparatus.
3. The sample was then subjected to column liquid chromatography as outlined in the EPA protocol with a few exceptions.
   a) A 2.0 cm I.D. column was used.
   b) Use 4x bed volume of EPA method.
   c) Used 4x volume solvent for elution of various fractions.
4. Eight fractions were obtained by eluting the column with solvents of increasing polarity. These fractions were individually reduced on a K.D. apparatus.

FIGURE 1

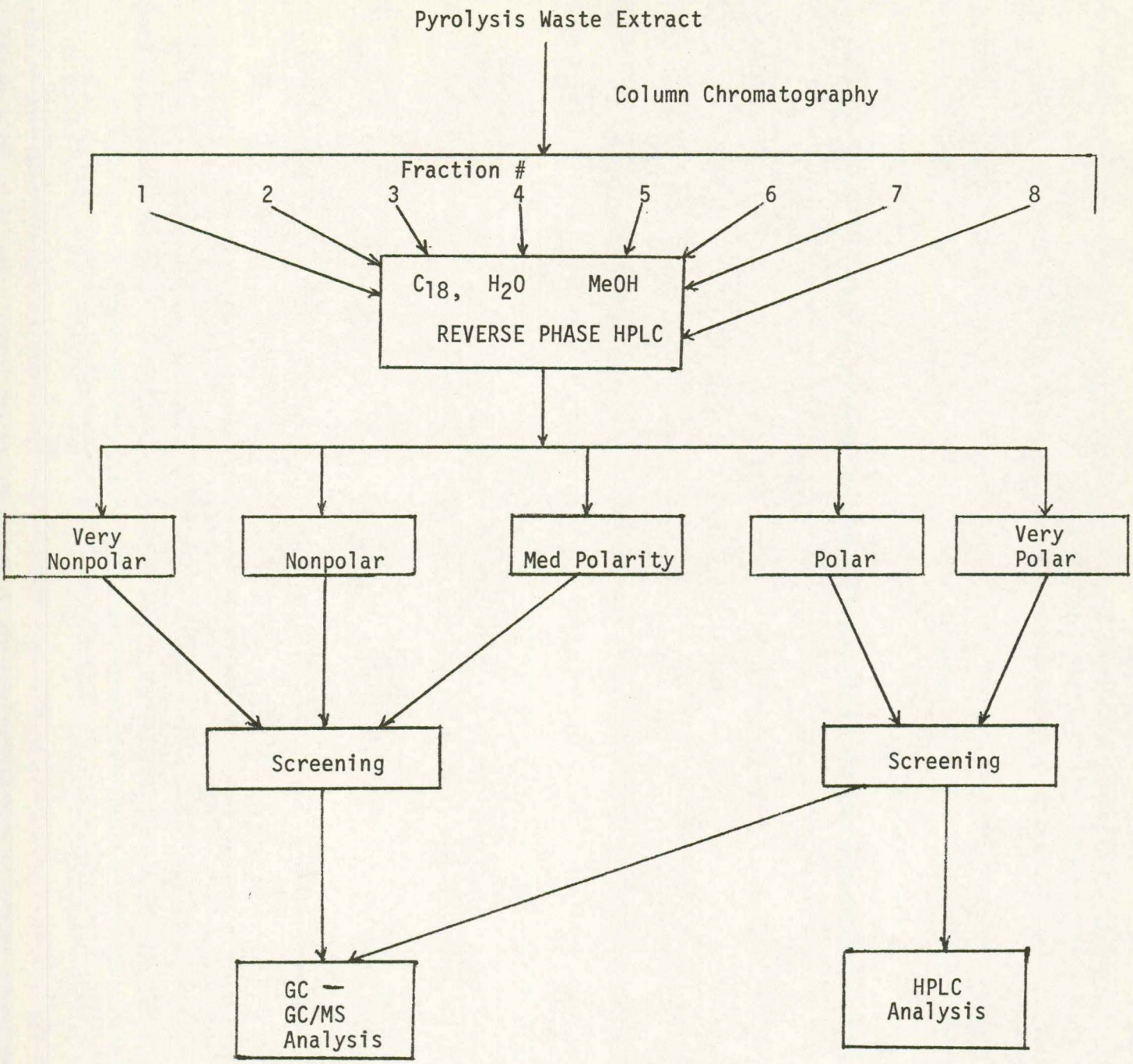

Pyrolysis Waste Extract
Column Chromatography
Fraction #
1
2
3
4
5
6
7
8
C_{18}, H_2O MeOH
REVERSE PHASE HPLC
Very Nonpolar
Nonpolar
Med Polarity
Polar
Very Polar
Screening
Screening
GC — GC/MS Analysis
HPLC Analysis

TABLE 1

Classes of Organic Compounds
Eluting in Each Liquid Chromatography Fraction

Fraction #	Compound Type
1	Aliphatic Hydrocarbons
2	Aromatic Hydrocarbons Polynuclear Aromatic Hydrocarbons Halides
3	Esters Ethers Nitro compounds Epoxides
4	Phenols Ketones Aldehydes Phthalates
5	Phenols Alcohols Amines
6	Amides Sulfonates Aliphatic/Aromatic acids
7	Sulfonates/Sulfonic acids
8	Sulfonic acids

APPENDIX C

COMPUTATIONS FOR CARBON COLUMN SERVICE TIME AND ECONOMIC ANALYSIS

COMPUTATIONS

Carbon Column

From Figure 14 at 90% removals:

C_0 = 25,500 mg/l = 1.59 lb./cu.ft.

C_B = 2,550 mg/l = 0.159 lb./cu.ft.

From Figure 17:

at 1 gpm/sq. ft. = 8.02 ft./hr.

Slope = 0.52

Y-intercept = -0.73

N_0 = 6.54 (Equation 3)

K = 10.99 (Equation 4

D_0 = 0.24 (Equation 2)

at 2.5 gpm/sq. ft. = 20.05 ft./hr.

Slope = 0.15

Y-intercept = -0.24

N_0 = 4.64 (Equation 3)

K = 5.90 (Equation 4)

D_0 = 1.51 (Equation 2)

at 5.0 gpm/sq. ft. = 40.10 ft./hr.

Slope = 0.05

Y-intercept = -0.10

N_0 = 3.18 (Equation 3)

K = 13.42 (Equation 4)

D_0 = 2.06 (Equation 2)

at 100,000 gallons per day

5 gpm/sq. ft. loading

30 ft. of column depth

5 ft. diameter

Breakthrough time = 1.39 hrs. (Equation 1)

Volume treated = 8,216 gallons

Regenerations per day = $\frac{100,000 \text{ gal.}}{8,216 \text{ gal.}} = 13$

Column Volume = 17,640 lbs.

Regeneration Capacity or Inventory = 230,000 lbs./day

Economics

Capital Cost:

Adsorption System & Piping (Figure 6-10, Page 223, C & E 1978*)	= $ 150,000
Carbon Storage & Handling (5 day spent & 4 day regenerated inventory) (Figure 6-11, Page 223, C & E 1978)	= $1,000,000
Regeneration Facilities	= $4,000,000
Annual Cost	$5,150,000
Reactivation System Operating Cost (Figure 6-12, Page 223, C & E 1978)	= $7,555,000
Maintenance & Labor @ 6% Capital Investment	= $ 300,000
Amortization @ 10% for 20 years	= $ 605,000
	$8,460,000

Cost at 100,000 gallons per day = 23¢/gal. or $230/1,000 gal.

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* Carbon Adsorption Handbook by Cheremisinoff and Ellerbusch

APPENDIX D

COMPUTATIONS FOR ECONOMIC FEASIBILITY OF DIGESTER TREATMENT

COMPUTATIONS

Carbon Column

Using 30' Bed depth 5' diameter:

Volume = 590 cu. ft. = 17,665 lbs.

at 100,000 gallons per day = 0.1 million gallons

at 90% removal:

(2,500 mg/l - 250 mg/l) = 2,250 mg/l COD removed

(2,250 mg/l) x (8.34) x (.1) = 1,876 lbs./day

with $x/m = .6 \frac{\text{lb. COD}}{\text{lb. carbon}}$ (Figure 9)

Carbon used per day = 3,127 lbs./day

Regeneration time = $\frac{17,664 \text{ lbs.}}{3,127 \text{ lbs./day}}$ = 5.65 days

Economics

Adsorption System & Piping	$150,000
Carbon Storage & Handling (5 days spent & 5 days regenerated inventory)	$100,000
Reactivation System	$600,000
	$850,000
Reactivation System Operating Cost	= $154,000
Maintenance & Labor @ 6% Capital Investment	= $ 51,000
Amortized @ 10% 20 yr.	= $100,000
	$305,000

at 100,000 gallons per day = 0.84¢/gallon or $8.35/1,000 gallons