AN EVALUATION OF FACTORS AFFECTING THE DESIGN AND OPERATION OF ANAEROBIC FILTERS

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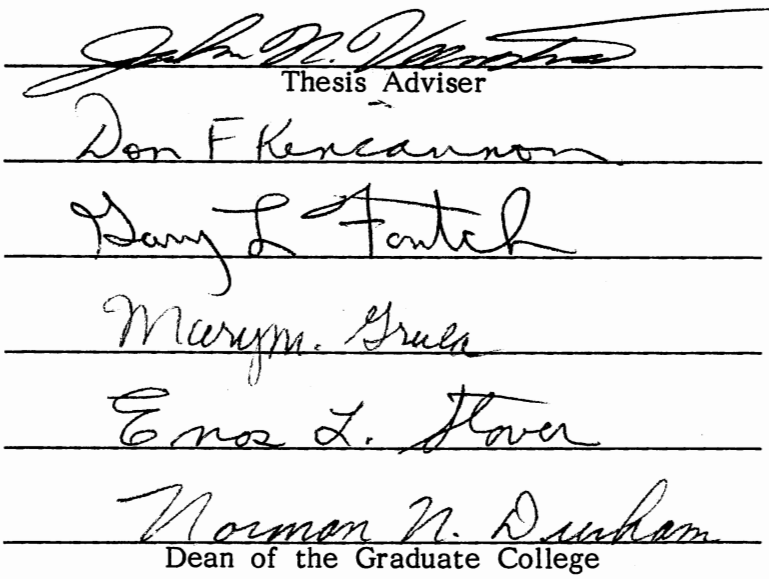

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CHAPTER I

INTRODUCTION

In recent years, anaerobic systems have experienced a rebirth in the wastewater treatment industry. No longer relegated to just the digestion of biological sludges, anaerobic processes are increasingly being recommended for the treatment of both soluble and particulate high-strength waste streams.

To a great extent, this increased acceptance is due to an improved understanding of those environmental conditions best suited for anaerobic growth. The identification of many required nutrients and inhibitory toxicants has resulted in enhanced operational control of these systems. Likewise, the recognition of rate-limiting steps in the anaerobic process has allowed microbiologists and environmental engineers to focus their efforts on overall process performance.

The anaerobic degradation of complex organics into methane is a multiphasic process involving several groups of interdependent bacteria. Descriptions of the complexity of the process vary from two-stage (McCarty, 1964) to a pathway involving nine recognizable steps (Harper and Pohland, 1986). For a basic but relatively accurate understanding of anaerobic metabolism, it is necessary to acknowledge at least four important steps.

The process begins with the extracellular hydrolysis of organic polymers such as polysaccharides, proteins, and fats into their

respective monomers. While not necessarily anaerobic in nature, this step is required prior to intracellular substrate transport. Once the sugars, amino acids, and organic acids are formed, they are converted to hydrogen, bicarbonate, and short-chain volatile acids by a group of bacteria referred to as acidogens. For many years, it was thought that this acidogenic step was directly followed by the final, methane-producing step. However, there is now strong evidence suggesting that methanogenic bacteria are capable of catabolizing only one- and two-carbon compounds (Bryant, 1979). In fact, of the two-carbon compounds, acetic acid is the only one which can serve as a sole carbon source. Because of the limited source of substrates available to the methanogens, an intermediate step is required following acidogenesis. This third step is carried out by a subgroup of acidogenic bacteria, the acetogens, which further oxidize volatile acids such as propionic and butyric acid to form acetic acid. This acetic acid, in addition to hydrogen and bicarbonate, is then converted into methane in the fourth and final step, methanogenesis.

As the pathways of anaerobic metabolism were elucidated by microbiologists and biochemists, environmental engineers set out to apply this information in the design of anaerobic treatment systems. One of the first advances in design came with the introduction of the anaerobic filter concept by Young and McCarty (1969). It was known that methanogens exhibit a very slow rate of growth and, therefore, require long retention times to effectively stabilize organic wastes. Prior to the introduction of anaerobic filters, this long retention time was accomplished by employing large reactor volumes and high solids recycle. As was often the case, these measures were not sufficient to handle organic and hydraulic shock loads. However, by using the anaerobic filter design, an increase in process

stability was realized while reactor volume and solids recycle were reduced. Nevertheless, even with these advances, the methanogenic step often remained rate-limiting in the anaerobic treatment process.

Stover et al. (1984) examined the use of anaerobic fixed-films for the treatment of fuel alcohol production wastewaters. They found that the system was capable of treating mass substrate loadings as high as 35 lbs COD/day/1000 ft^2 without pH control problems or volatile acid accumulations. However, at higher substrate loads the volatile acid production rate was faster than the methane conversion rate. This indicated that, despite the use of a fixed-film reactor, the rate of methanogenesis was still the controlling factor.

Attention has recently been drawn to possible inhibitory effects resulting from the methane and carbon dioxide gases themselves. End product inhibition in methane fermentations from acetate has been exhibited for carbon dioxide and, to a lesser extent, for methane (Hansson and Molin, 1981). It has also been proposed that the gas bubbles generated during fermentation inhibit transfer of substrate into intracellular spaces by enveloping the bacterium and imposing a barrier to diffusion (Finney and Evans, 1975).

Whether the nature of inhibition is biochemical in the form of an end product or physical by way of a substrate barrier, facilitating release of the product gas should result in an enhanced methanogenic step. Such logic has been followed by several investigators in attempts to improve anaerobic treatment efficiencies (Finney and Evans, 1975; Podolak et al., 1984; Cordoba et al., 1984). These efforts have included the use of applied vacuums, reduced hydrostatic pressure, and agitation. Though improved treatment efficiency was the aim of each of these process modifications,

the realized effects varied from insignificant to very beneficial, with no evident agreement among the results. A different approach was taken by Messing (1982) in that a positive pressure, rather than a vacuum, was applied to the system. Contrary to the gas inhibition theories, Messing reported improved treatment performance from his anaerobic reactors.

In light of these reports, it is apparent that much remains to be learned regarding the impact of product gas on the microbial transformation of complex organics into methane. In particular, a greater understanding is needed of the effects which process changes have on each of the individual steps of anaerobic degradation. To gain such knowledge, this research program was undertaken.

The objective of the study was two-fold. First, an evaluation was to be made of the several reactor designs and operational conditions suggested to address the gas inhibition theory. Second, the effect which these process modifications have on the various steps of anaerobic degradation was to be identified.

CHAPTER II

LITERATURE REVIEW

Many environmental engineers have developed novel reactor designs or made process modifications to anaerobic systems in attempts to improve treatment efficiencies. Consequently, the literature is filled with such proposed systems. For the purposes of this review, they will be categorized into three separate groups: agitation, pressure, and horizontal flow studies.

Agitation Studies

The need for adequate mixing in anaerobic systems exists for many reasons. Maintenance of a uniform temperature, prevention of unfavorable microenvironments, and the disintegration of biodegradable particulate matter are but a few of the reasons cited (Grady and Lim, 1980). However, the duration and magnitude of agitation required varies from application to application, and there is some evidence that suggests induced agitation may not always be necessary.

In a detailed study of methods to enhance the production of methane from anaerobic digesters, Finney et al. (1978) examined the effects of mixing speed and duration on the rates of volatile acid catabolism. With regard to mixing speed, they found that increasing the speed from 50 to 100 rpm resulted in essentially no change in catabolic rates. However, rates underwent an almost two-fold gain when speeds were increased to 150

rpm. Further, they found that in using pulsed agitation an optimum duration existed, above and below which performance deteriorated.

In a follow-up study by Hashimoto (1982), intermittent and continuous mixing were compared in relation to methane production from beef cattle waste. Preliminary experiments indicated that intermittent mixing (one, two, and three hours per day) resulted in slightly greater production of methane than did 24 hour per day mixing. However, when more controlled experiments were conducted, the opposite held true. The continuously mixed fermenters produced 8 to 11% more methane than did those mixed intermittently.

In studying thermophilic fermentation of municipal sludge, Kandler et al. (1981) found that the effect of different agitation rates on gas production was insignificant. However, they did note that either fast mixing or intermittent mixing resulted in higher volatile acids concentrations than did slow continuous mixing. Possible reasons for the change in volatile acids without a corresponding change in gas production were not given.

Van den Berg and Kennedy (1983) reviewed the various characteristics of several advanced anaerobic reactors, including the nature of reactor mixing. Systems examined in the review included the contact reactor, the fluidized bed reactor, and both the upflow and downflow anaerobic filters. With the exception of the downflow filter, each system required that considerable attention be paid to mixing by either mechanical means or by high recycle rates in order for optimum performance to be realized. It was suggested that the downflow filter provides its own mixing by means of internal gas bubbling and requires little or no external source of mixing.

Using a full-scale dairy manure digester, Coppinger et al. (1979) experienced no decrease in gas production when mixing was discontinued. As with the downflow filter, they believed that internal gas bubbling was all that was needed to provide sufficient mixing.

A recent study by Samson et al. (1985) indicated that only slight improvements in the mixing regime of downflow filters could be realized by high rates of gas production. Instead, it was found necessary to increase the recycle ratio to 4:1 before a change in residence time distribution from plug flow to completely mixed could be achieved.

To overcome the difficulties in obtaining a completely mixed, fixed-film system, Tait and Friedman (1980) introduced the anaerobic rotating biological contactor (AnRBC). Treatment results were positive and many benefits of such a system cited. In addition, they were able to demonstrate that anaerobic microorganisms adhere to and grow on rotating surfaces.

Using an AnRBC of their own design, Bachmann and McCarty were reported to have examined the effects of disc rotation on the reactor's overall treatment efficiency (Josephson, 1982). They concluded that the system worked equally as well with or without disc rotation. In both of the AnRBC studies cited, a soluble synthetic substrate was used, thereby precluding much of the need for mixing. Feeding the systems with a particulate substrate may yield different results as to the effect of AnRBC mixing.

Pressure Studies

One of the earliest reports on the effects of positive and negative pressure on a continuously-fed sludge digester was that of Bloodgood and

Anderson (1963). In their study, primary sludge was fed to laboratory digesters operated at 5, 10, 15, and 20 psia. Volatile solids destruction in the 10, 15, and 20 psia units averaged around 61%, with little significant difference among them. The 5 psia unit, on the other hand, destroyed only 50% of the volatile solids fed to it, a full 10% less than for the other three units. In addition, the 5 psia unit exhibited the highest concentrations of volatile acids under all loading conditions. It was suggested that this apparent inhibition may have been caused by changes in digester pH brought about by the use of subatmospheric pressures. In the 10 to 20 psia units, the digester pH was in a normal range of 7.2 to 7.5. However, when the absolute pressure was dropped to 5 psia, the system pH rose to between 7.8 and 7.9, outside the recommended range for a stabilized digester. It is interesting to note that this rise in pH occurred despite the increase in volatile solids concentration.

Following up on their theory that gas bubbles surround the bacterium and interfere with substrate diffusion, Finney et al. (1978) examined the effects of subatmospheric pressures on anaerobic fermenters fed sewage sludge. Operating at 300, 500, and 700 mm of Hg absolute pressure, they monitored changes in pH and volatile acid concentrations with time. The effects of the operating conditions on these parameters were minimal and inconsistent, and it was concluded that there was no practical justification for operation at subatmospheric pressure.

A similar experiment was conducted by Hashimoto (1982) using beef cattle manure as a substrate. Operating at both 4 and 6 day hydraulic retention times (HRT) and a subatmospheric pressure of 0.96 atm, Hashimoto compared methane production rates to those obtained from conventional, atmospheric fermentation systems. No significant change in

methane production was seen for the 6 day HRT system, and only a 5% rate increase was observed for the 4 day HRT unit operated under subatmospheric conditions. The unpromising results were believed to be due, in part, to the operating vacuum being only 10% of that used by Finney et al. (1978).

Podolak et al. (1984) investigated the effects of subatmospheric pressure on an AnRBC treating a synthetic sucrose waste. The reactor was operated at pressures ranging from 0.54 to 1.0 atm and under several organic loading conditions. They found that both increased microbial growth yields and increased removals of soluble chemical oxygen demand (SCOD) were related to decreases in the atmospheric pressure. They also found that better volatile acid and pH control were obtained at reduced pressures. Based on these findings, Podolak et al. concluded that reduced pressure operation would be advantageous to anaerobic reactors during start-up and whenever upset conditions begin to set in.

Taking an approach opposite to that of the reduced pressure proponents, Messing (1982) advocated the use of positive pressure for improved system performance. Using filtered sewage as a substrate, his product gas contained greater than 90% methane, as compared to typical digester values of 65 to 70%. Though several innovations were used in his treatment scheme, Messing was confident that the use of low pressure check valves (rated from 1 to 3 psi) was responsible in part for the high methane productivity.

In another study on the effects of pressure on methane production (Mangel et al., 1980), it was found that, at up to 4 effective bars (58 psig), increased pressure resulted in an increased percentage of methane but a reduction in the total gas flow rate. Taken together, these competing

effects resulted in a relatively constant production of methane. Above 4 bars pressure, an inhibitory effect was experienced and methane production decreased. Gas evolution was still observed, however, under 16 effective bars (232 psig). In unrelated research (Wise et al., 1978), methanation has even been carried out by microbial cultures at 450 psig. For operation at such an elevated pressure, however, it was initially necessary to increase the pressure gradually to provide sufficient opportunity for microbial adaptation. Once adapted to the high pressures, subsequent pressure changes were well tolerated.

Horizontal Flow Studies

In the previously cited study by Messing (1982), one of the several innovations credited for the high methane content of the product gas was in relation to reactor orientation. Messing's anaerobic stage was horizontally mounted with a 50% fluid depth and a 50% gas volume. By being configured in such a way, the gas-to-liquid interface was maximized which, as Messing proposed, was responsible for greater transfer of methane into the gaseous phase.

Others have also advocated the use of horizontally configured anaerobic reactors. Tait and Friedman (1980) stated that one advantage their horizontal AnRBC had over a vertical anaerobic filter was a lower energy input requirement for throughput and side-stream recirculation pumping. Cordoba et al. (1984) selected a horizontal design for their anaerobic reactor so that hydrostatic pressures would be minimized. Though the benefits of horizontal flow and maximized gas-to-liquid interface may be significant, vertical and horizontal systems need to be examined in parallel studies before definitive conclusions can be drawn.

CHAPTER III

MATERIALS AND METHODS

To achieve the stated objectives of this study, the research program was carried out in two separate phases. The first phase was a study of the effects of agitation on anaerobic filters. The second phase addressed the effects of pressure and reactor design on those same systems.

Phase I - Agitation

Three anaerobic filters were constructed and operated in a side-by-side fashion. The external shell of each reactor was made from 20 cm (8 in) ID polyvinyl chloride (PVC) pipe. Into each reactor were placed an equal number of 2.5 cm (1 in) diameter pall rings, which by specification provided a porosity of 90% and a media surface area of 207 m^2/m^3 (63 ft^2/ft^3). The initial liquid volume in each anaerobic filter was 13.2 liters.

The experimental variable for this phase of the study was obtained by way of reactor design and operation. The control reactor was modelled after conventional bench-scale anaerobic filters in that it was vertically oriented and operated in an upflow mode. The other two reactors were of identical construction, employing an anaerobic cage design. Both reactors were horizontally oriented and possessed a cage mounted on a shaft which ran the length of the reactors. The pall rings were placed inside the cage which itself was placed inside the horizontal reactor. Feed for these two anaerobic filters was cross-flow and the liquid level maintained at two-

thirds depth, similar to the operation of an RBC. The agitation variability for Phase I was obtained by attaching a variable-speed motor to the shaft of one of the two horizontal cage filters and rotating the cage at 5 rpm. For anaerobic operation, all three reactors were constructed to be gas-tight and housed in a thermostatically-controlled room with temperatures maintained at 35°C (±1°C). A schematic of the Phase I anaerobic filters is presented in Figure 1.

The organic feed source used during both Phases I and II was pig manure obtained from the concrete floors of finishing hogs at Oklahoma State University's swine barn. Typical composition of the pig's feed was milo, 62%; yellow corn, 21%; soybean meal, 15%; vitamins and minerals, less than 2%; and antibiotics (either chlortetracycline or tylosin) 0.1%. The manure was periodically collected and stored at 4°C. When feed was to be made, the manure was diluted to the desired concentration and large solids removed by passing the solution through a screen with 1.5 mm (1/16 in) openings. This diluted and screened feed was then placed in a converted refrigerator from which each of the Phase I anaerobic filters were directly fed. The units were fed by way of timer-controlled peristaltic pumps, one minute of pumping per thirty minute timer cycle (69 mL/cycle).

For start-up of the reactors, anaerobic digester sludge was collected from the Stillwater, Oklahoma, municipal wastewater treatment plant and approximately six liters placed in each of the units. The anaerobic filters were then purged with nitrogen gas and sealed to ensure anaerobic conditions. The following day, feeding was begun at an organic loading rate of 1 kg COD/m^3·d (62.4 lb/1000 ft^3·d) and an influent COD of 3300 mg/L. Loading and influent concentrations were gradually increased over the next

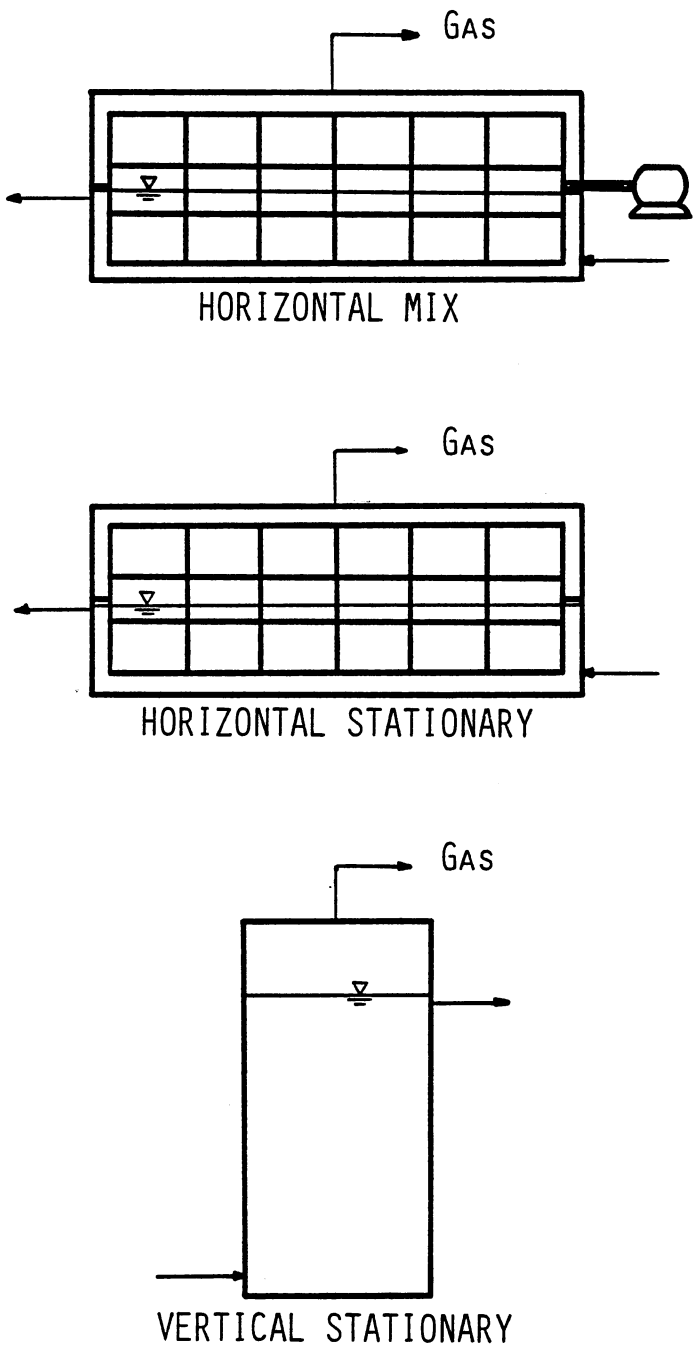

FIGURE 1. SCHEMATIC OF THE PHASE I REACTORS

two months until the respective target values of 5 kg COD/m^3·d (312 lb/1000 ft^3·d) and 20,000 mg/L were attained.

Phase II - Pressure and Reactor Design

For the second phase of this study, three anaerobic fixed-film reactors were again constructed and operated in a side-by-side fashion. In addition to studying the effects of positive and negative pressures on anaerobic systems, Phase II was designed so that the role of gas-to-liquid interface could be examined. To accomplish this, two of the existing reactors were modified and one new unit constructed.

Only minor modifications were made to the vertical control reactor of Phase I. In addition to fitting the reactor with pressure connections, the liquid volume was reduced to 9.5 liters. The gas-to-liquid interface for this unit was 315 cm^2 (49 in^2).

One of the two horizontal cage reactors of Phase I was also modified for the pressure studies. The cage and shaft were removed and, instead, the reactor was randomly packed with the 2.5 cm (1 in) pall rings. The 20 cm (8 in) ID horizontal reactor was filled with digester sludge to a depth of 10 cm (4 in), resulting in a liquid volume of 9.5 liters and a gas-to-liquid interface of 1380 cm^2 (214 in^2).

The newly constructed horizontal reactor was made from 15 cm (6 in) ID PVC pipe and randomly packed with pall rings. Digester sludge was added to a depth of 12.5 cm (5 in), resulting in a liquid volume of 9.5 liters and a gas-to-liquid interface of 790 cm^2 (122 in^2). By making the modifications just described, the three reactors had equal hydraulic volumes but significantly different gas-to-liquid interfaces. A schematic of the Phase II reactors is presented in Figure 2.

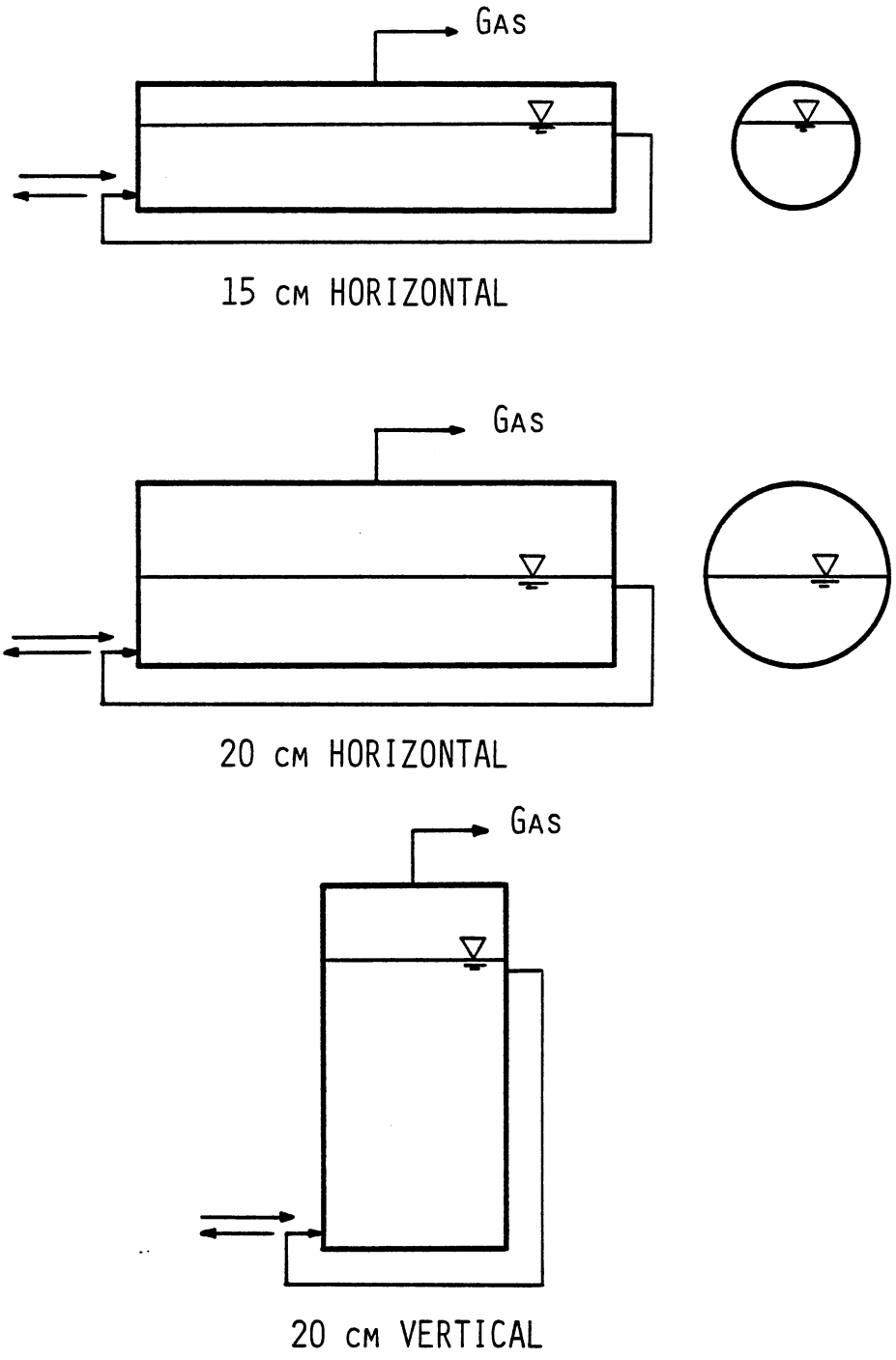

FIGURE 2. SCHEMATIC OF THE PHASE II REACTORS

Application of positive and negative pressures was accomplished by use of peristaltic pumps and adjustable check valves set at a relief pressure of 3 psig. For positive pressure conditions, the valve was placed directly in the gas line between the reactor and the gas collection bag. The reactors were self-pressurized by way of microbial gas production. For negative pressure conditions, peristaltic pumps were used to evacuate the reactors. The direction of the check valves was reversed so that they would open when a negative pressure of 15 mm Hg (-3 psig) was attained.

Due to difficulties encountered in maintaining a vacuum while feeding the reactors once every thirty minutes, the systems were changed over to once daily feedings in Phase II. In addition, the liquid contents of each reactor were continuously recycled to ensure equal distribution of the substrate. As with the Phase I units, all reactors were fed screened swine manure and operated at $35^{o}C$ ($\pm 1^{o}C$).

After seeding each reactor with 9.5 liters of digester sludge, the units were sealed and feeding begun. Loading rates were increased from 1 to 5 kg COD/m^3·d (62.4 to 312 lb/1000 ft^3·d) over a three week period and then held at 5 kg COD/m^3·d for the next two months to allow the systems to become stabilized. At each of the three design loading conditions of 5, 10, and 16.7 kg COD/m^3·d (312, 624, and 1040 lb /1000 ft^3·d, respectively), the reactors were alternately operated under positive, negative, and atmospheric pressure conditions, thereby yielding nine experimental combinations for each reactor. The combinations and the order in which they were completed are shown in Table I.

TABLE I

PHASE II OPERATING CONDITIONS

Chronological Order	Absolute Pressure (atm)	Influent COD (g/L)	Hydraulic Retention (days)	Organic Loading (kg COD/m^3·d)
1	1.0	50.1	10	5.0
2	0.8	49.9	10	5.0
3	1.2	49.7	10	5.0
4	1.2	51.9	5	10.4
5	0.8	47.7	5	9.5
6	1.0	51.7	5	10.3
7	1.0	48.5	3	16.2
8	1.2	51.3	3	17.1
9	0.8	51.4	3	17.1

Data Collection and Analytical Procedures

Steady state conditions for the anaerobic reactors were based on the effluent volatile fatty acid (VFA) concentrations. During organic loading transition periods, the VFA levels were routinely monitored and, when they appeared to be stable, the systems were considered to be operating at steady state. Due to fluctuations in the influent COD and VFA, a slight fluctuation was always observed in the effluent VFA's, therefore making it more appropriate to refer to this condition as quasi-steady state.

In addition to volatile acids, alkalinity and pH were routinely monitored during transition periods. Determinations of the VFA and alkalinity levels during this period were made by titration using the method of DiLallo and Albertson (1961). During the quasi-steady state period for each condition, data was collected every other day for a minimum of two weeks. The data collected for system evaluation included total and volatile

solids, total and soluble COD, gas production and composition, and individual volatile acids.

Total and volatile solids (TS and VS, respectively) were measured using porcelain evaporating dishes as described in Standard Methods (1976). Total and soluble COD (TCOD and SCOD, respectively) were determined following the micro-technique of Jirka and Carter (1975). Due to the high particulate solids content, samples were centrifuged at 32,000 x G for 15 minutes and the centrate passed through a glass microfiber filter (Whatman 934-AH) before SCOD analyses were performed.

Tedlar gas sampling bags were used for the collection of product gas from the individual reactors. Measurements of gas volume were made by evacuating the bags with a peristaltic pump and passing the gas through a wet-test meter. Gas volumes were corrected to standard temperature ($0^{o}C$) and pressure (1 atm) (STP).

When methane and carbon dioxide determinations were to be made, a 250 mL gas sampling bulb was placed in-line between the peristaltic pump and wet-test meter. After a minimum of 20 volumes had passed through the sampling bulb, it was removed for gas analysis. Gas composition was determined by the method of van Huyssteen (1967) using a 3.2 mm by 3 m (1/8 in by 10 ft) Porapak S stainless steel column on a Perkin Elmer Sigma 3 gas chromatograph. The column was held at $65^{o}C$ and the thermal conductivity detector at $110^{o}C$. Helium was used as the carrier gas.

Analyses of individual volatile fatty acids were performed on a Perkin Elmer Sigma 3B gas chromatograph equipped with a flame ionization detector. A 3.2 mm by 1.8 m (1/8 in by 6 ft) glass column packed with 0.2% Carbowax 1500 on Carbopak C 80/100 was used for the VFA separations. Nitrogen was used as the carrier gas and the detector held at

225°C. To minimize ghosting and tailing problems of the VFA peaks, formic acid was added to the carrier gas using a vapor entrainer, as recommended by Cochrane (1975). When only acetic, propionic, isobutyric, and butyric acids were to be determined, the column was operated isothermally at 135°C. When 2-methyl butyric, isovaleric, and valeric acids were also to be determined, it was necessary to increase the column temperature to 157°C after the butyric acid had eluted. Due to the generally low concentration of these last three VFA's (less than 10 mg/L), they were only quantified in the feed and, on occasion, in the effluent at high organic loadings.

CHAPTER IV

RESULTS AND DISCUSSION

Selection and Feeding of Substrate

When not performing a wastewater treatability study, the selection of an appropriate substrate for experimental purposes is often a difficult matter. Usually, the tendency is to select a synthetic substrate which provides all the required nutrients and is easily reproduced. By using such a controlled feed source, any changes in effluent quality can be attributed to operational, and not substrate, variability.

There are several drawbacks, however, in using a synthetic substrate. According to Grady (1985), a complex feed is necessary to promote maximum diversity in the system's microbial population. He also noted that the continuous inoculation of microorganisms, which a natural waste provides, is lost when a sterile, synthetic feed is used. For these reasons, a natural waste was used in this study.

After examining several possibilities, swine manure was selected as the natural feed for these experiments. As can be seen from Table II, the screened manure used in this study contained a well-balanced combination of the various compounds involved in anaerobic degradation. With such an assortment of metabolic substrates, it was possible for any one of the four steps of degradation to become rate-limiting. The swine manure also ensured a diverse microbial population and continuous inoculation of the

system. Finally, the free and practically unlimited supply of manure made it a logical choice.

The inability to locate a swine herd fed an antibiotic-free ration caused some concern at the outset of this study. Brumm and Nye (1981) experienced digester failure when swine manure containing antibiotics was fed to their systems. Others have made a point of using manure obtained from growers not using antibiotics in their finishing ration (Kennedy and van den Berg, 1982a). However, in a study of the effects of antibiotics on anaerobic digestion, Poels et al. (1984) found that chlortetracycline and tylosin (the two antibiotics pertaining to the present study) were not inhibitory to the anaerobic process at levels typically used. In fact, they found that, even at levels ten times higher than the veterinary prescribed dosage, chlortetracycline and tylosin did not cause anaerobic inhibition.

To further minimize any possibility of antibotic inhibtion, it was decided to use manure only from finishing, or fattening, hog pens. These hogs are generally fed the lowest dosage of antibiotics since their immune systems are relatively well-established. An added advantage in feeding this manure to the reactors was realized in its high nutritional value. The metabolism of finishing hogs is less efficient than that of other pigs. Therefore, much of the nutritional value in the feed ration is passed on to the manure.

TABLE II

AVERAGE INFLUENT COMPOSITION DURING PHASE II

Compound	Mean Concentration (mg/L)*	Standard Deviation
Acetic Acid	2,511	519
Propionic Acid	1,693	398
Isobutyric Acid	177	69
Butyric Acid	2,110	682
2-Methyl Butyric Acid	197	71
Isovaleric Acid	198	70
Valeric Acid	404	126
Volatile Fatty Acids	7,292	1,163
Soluble Complex Organics	5,650	1,942
Particulate Organics	37,179	2,895
Total Influent	50,122	2,632

* All values are expressed as COD equivalents. COD equivalents for the volatile acid compounds were calculated using the following generalized formula for total oxidation:

$$C_aH_bO_c + (a + b/4 - c/2)\cdot O_2$$

Example for acetic acid ($C_2H_4O_2$) oxidation:

$$C_2H_4O_2 + (2 + 4/4 - 2/2)\cdot O_2$$

$$C_2H_4O_2 + 2O_2$$

Molecular Weight: 60 64

Total oxidation of one mole of acetic acid requires 64 g of oxygen, or 1.066 g of oxygen per gram of acetic acid (64/60). Therefore, if the concentration of acetic acid was 1000 mg/L, the COD equivalent would be 1066 mg/L.

With the possible exception of one instance, no obvious antibiotic-related problems were experienced in this study. That one instance occurred during the initial acclimation period when the digesters were fed manure gathered from young pigs and lactating sows. This change in feed source resulted in near cessation of gas production and a two-fold increase in volatile acids (from 900 mg/L to 2000 mg/L). When it became apparent that digester failure was imminent, the feed source was reverted to finishing hog manure. After doing so, almost three weeks (two hydraulic retention times) were required for the volatile acid concentrations to return to their previous levels.

It still remains possible that the presence of trace quantities of antibiotics in the feed resulted in a constant level of inhibition in the reactors during the study. If such was the case, however, this inhibition would have been present to the same degree in all reactors. Relative changes in system performance, therefore, would be due to the controlled variables (pressure, agitation, etc.) and not the antibiotics.

As was mentioned previously, the mode of digester feeding was switched from semi-continuous (once every 30 minutes) during Phase I to once daily during Phase II. The primary reason for the change was the difficulty in feeding the digesters while either a vacuum or pressure was being applied. To accommodate, once per day the digesters were returned to atmospheric pressure and the screened manure solution added within a 30 minute period. By slug loading the reactors, problems encountered in pumping the highly particulate waste were minimized. Also, the once daily feeding has commonly been used for anaerobic research on swine waste (Hobson and Shaw, 1973; van Velsen, 1977; and Brumm and Nye,1981) and more accurately simulates the patterns used with farm-scale digesters.

The comparative effects of continuous and slug loading were investigated by Kennedy and van den Berg using piggery waste as the feed source (1982b). They found that the COD removal and gas production rates of the two systems compared quite favorably regardless of the organic loading rate or method of feeding. In fact, at the lower loadings of 5 and 10 kg COD/m^3·d, the slug loaded unit exhibited slightly better treatment efficiencies than did the continuously fed system. This being the case, it was decided to use slug loading during Phase II of this study.

Phase I - Agitation

Adequate mixing and recirculation are often difficult to obtain with anaerobic filters. Due to the internal media being stationary, short circuiting and plugging frequently occur. For all practical purposes, these shortcomings limit the anaerobic filter to treatment of wastes low in suspended solids.

To make thorough mixing with an anaerobic filter possible, the cage concept was developed for this study. The cages were filled two-thirds full with plastic pall rings so that, upon rotation, a tumbling effect occurred. The agitation created by the tumbling pall rings was provided so that an evaluation of the effects of mixing on gas inhibition could be made for anaerobic filters.

Unfortunately, the Phase I studies never reached the point where such an evaluation could be made. As can be seen from Tables III and IV, the effluent solids and TCOD concentrations during both experimental trials were higher for the mixed filter than for either of the stationary units. Also, the biogas production from the mixed filter was the lowest of the three systems.

TABLE III

RESULTS OF PHASE I, TRIAL I - AGITATION

Hydraulic Retention Time:	4 days
Organic Loading:	5.08 kg COD/m^3·d
Volatile Solids Loading:	2.55 kg VS/m^3·d
Duration of Mixing:	20 minutes/30 minute cycle
Cage Rotation:	5 RPM

Parameter	Horizontal Stationary	Horizontal Mix	Vertical Stationary
TCOD (g/L)			
Influent	20.32	20.32	20.32
Effluent	7.88	9.43	8.03
% Removal	61.2	53.6	60.5
SCOD (g/L)			
Influent	6.81	6.81	6.81
Effluent	1.40	1.37	1.39
% Removal	79.4	79.9	79.6
Total Solids (g/L)			
Influent	13.74	13.74	13.74
Effluent	7.14	8.48	7.18
% Removal	48.0	38.3	47.7
Volatile Solids (g/L)			
Influent	10.18	10.18	10.18
Effluent	4.42	5.30	4.40
% Removal	56.6	47.9	56.8
Biogas Yield (m^3/m^3 reactor·d)	1.97	1.79	1.98
pH	7.6	7.4	7.6

TABLE IV

RESULTS OF PHASE I, TRIAL II - AGITATION

Hydraulic Retention Time:	17.5 days
Organic Loading:	1.10 kg COD/m^3·d
Volatile Solids Loading:	0.55 kg VS/m^3·d
Duration of Mixing:	1 minute/30 minute cycle
Cage Rotation:	2 RPM

Parameter	Horizontal Stationary	Horizontal Mix	Vertical Stationary
TCOD (g/L)			
Influent	19.34	19.34	19.34
Effluent	1.74	4.56	3.47
% Removal	91.0	76.4	82.1
SCOD (g/L)			
Influent	6.32	6.32	6.32
Effluent	0.87	0.85	0.88
% Removal	86.2	86.6	86.1
Total Solids (g/L)			
Influent	12.95	12.95	12.95
Effluent	3.15	5.37	4.39
% Removal	75.7	58.5	66.1
Volatile Solids (g/L)			
Influent	9.69	9.69	9.69
Effluent	1.38	2.96	2.49
% Removal	85.8	69.5	74.3
Biogas Yield (m^3/m^3 reactor·d)	0.49	0.45	0.48
pH	8.1	7.9	8.0

It is noted, however, that the effluent SCOD concentrations were essentially equivalent for the three anaerobic filters. Equivalent SCOD removals were attained by the mixed filter despite its relative inability to retain biological solids. This would indicate that mixing is not detrimental to soluble substrate removal but, in fact, may enhance it. However, the solids imbalance among the anaerobic filters precluded an accurate evaluation of the effects of filter mixing on gas inhibition. This led to attempts to correct the high solids loss from the mixed filter.

During the first experimental trial, cage rotation in the mixed filter was set at 5 rpm for 20 minutes of every 30-minute cycle. Since effluent exited the reactor primarily during and a few minutes after each feeding period, a ten-minute quiescent period was provided so that the agitated solids would have a longer period for settling. However, this measure was not sufficient as the mixed filter consistently lost 20% more effluent volatile solids during Trial I than either of the other units.

It was believed that lower hydraulic and solids loadings were necessary to correct the solids imbalance among the anaerobic filters. As a result, the hydraulic retention time was increased from 4 to 17.5 days, thereby decreasing the organic load from approximately 5 to 1 kg COD/m^3·d (317 to 68.6 lb/1000 ft^3·d). In addition, the rotational speed of the mixed filter's cage was reduced from 5 to 2 rpm and the quiescent period extended from 10 to 29 minutes. In other words, minimal mixing was applied for only one minute of every 30-minute cycle.

Indeed, removal efficiencies were improved, though the mixed filter continued to exhibit the worst solids and TCOD removal efficiencies. TCOD removal for the mixed filter increased from 54% to 76%, with volatile solids removal increasing from 48% to 69%. At the same time,

however, the TCOD and solids removals of the other two anaerobic filters also improved considerably. The vertical filter was capable of removing 82% of the TCOD and 74% of the volatile solids. The stationary horizontal unit removed 91% of the TCOD and 86% of the volatile solids. As during Trial I, the SCOD removals during Trial II were essentially equivalent among the three anaerobic filters.

At this point, mixing was considered to have a negative impact on solids retention by the anaerobic filter. However, before reaching such a conclusion, one final measure was taken. The variable-speed motor was detached from the shaft of the horizontal mixed filter and attached instead to the shaft of the horizontal stationary filter. In making the switch, it was possible to examine the effects of introducing agitation to a well established and highly efficient system. The results of making the switch in mixing regimes are presented in Figure 3.

The results were not surprising. Within a few days of removing the motor, the effluent volatile solids concentration of the previously mixed filter improved from an average of 3200 mg/L to 1400 mg/L, whereas the newly mixed filter's effluent deteriorated almost instantly once the mixing motor was engaged. The volatile solids concentration of the newly mixed filter rose from an average of 1400 mg/L to a high of 54,000 mg/L. This value dropped steadily for the next several weeks but never attained the previous low concentration. The observed gas production rate from the newly mixed filter initially surpassed that of the nonmixed unit (218 mL/hr and 186 mL/hr, respectively) but, within a week, the relative values were reversed (220 mL/hr and 241 mL/hr, respectively). The changes in production were probably related to gas entrapment. When agitation was applied to the previously stationary system, gas bubbles which had been

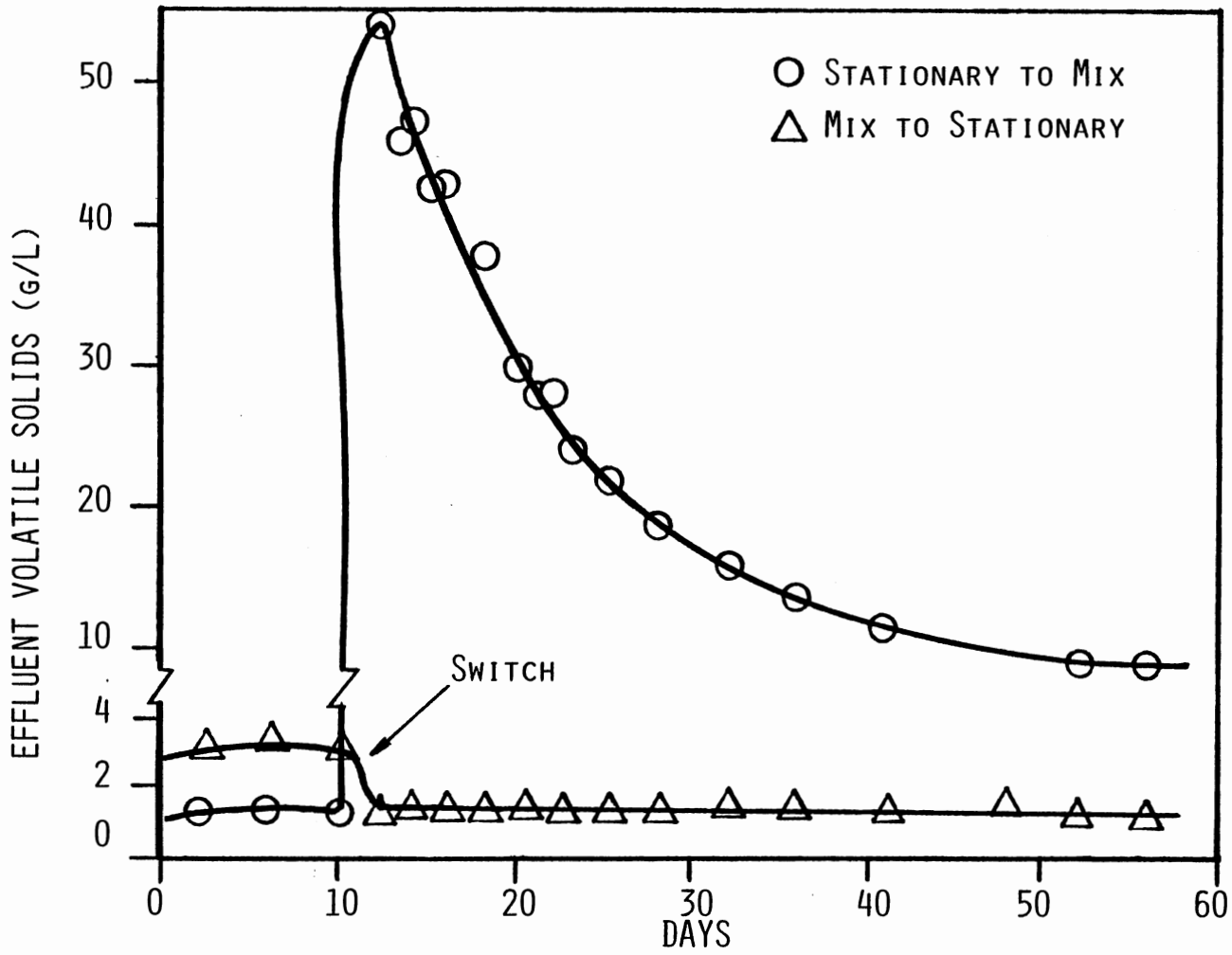

FIGURE 3. EFFECT OF SWITCHING MIXING REGIMES ON THE TWO HORIZONTAL REACTORS

entrapped in the sludge and pall rings were suddenly released, resulting in an apparent increase in gas production. Conversely, when mixing was stopped for the previously mixed system, a portion of the product gas initially became lodged in the liquid phase. After a brief equilibration period, the observed gas production rates more closely represented the true gas production rates.

After operating for almost seven weeks in the switched mixing mode, the newly mixed filter's effluent volatile solids concentration became relatively stable at around 8000 mg/L. Though it is quite likely that, given enough time, this value would have decreased a bit further, it was believed that the effects of mixing on an anaerobic filter system had been well established.

After the Phase I mixing studies had been completed, all three units were drained, opened up, and their contents examined. The results are presented in Table V. As can be seen, a substantial portion of the original 13.2 L void volume was lost in both of the stationary filters. The loss in void volume, however, was countered with a corresponding increase in the concentration of volatile solids.

An examination of the contents of the newly mixed horizontal filter revealed almost no anaerobic sludge attached to the media. A small amount of biological film was found attached to the reactor walls near the influent port but little elsewhere. Much of the media looked practically new, as if no growth had ever occurred on it. An unidentified granular scale was noticed on some of the media as well as on other interior surfaces. The gritty substance was very firmly attached and its removal required scraping of the surfaces. The liquid which had been drained from the reactor was a light brownish-black in color.

TABLE V

REACTOR CONTENTS AFTER PHASE I STUDY

Reactor	Volume Drained (L)	Void Volume Loss (%)	Total Solids (g/L)	Volatile Solids (g/L)	Percent Volatile
Horizontal Mix	13.0	1.5	19.1	11.6	61
Horizontal Stationary	10.3	22	31.8	16.7	53
Vertical Stationary	8.0	39	60.7	39.0	64

The horizontal stationary filter (previously mixed) had large quantities of anaerobic sludge entrapped within the pall rings. The sludge was very loosely attached to the media, as only a light rinsing was required to remove it. Practically none of the granular scale was seen on the media, though some was found attached to the reactor walls. The rinsed media had a uniform gray coloration, similar to that of smoked plastic. This condition, which was not found in either of the other two systems, could not be altered by scraping and further rinsings. The drained liquid from this unit had a black color, much darker than the liquid from the mixed filter.

The media in the vertical filter was very similar to that in the horizontal mixed filter, with perhaps even more scale-type deposits. However, almost no scale was noticed on the reactor walls. The lack of wall scale was probably due to mild but constant abrasion by the pall rings. This condition was not found in the horizontal filters since the pall rings

were enclosed by cages. The vertical unit, on the other hand, was the only system in which the media was in direct contact with the walls. As evidenced by the loss in void volume, the vertical filter also contained the largest quantity of entrapped anaerobic sludge. This sludge was very loosely associated with the media and could be removed with a light rinsing. In addition, the drained liquid from the vertical filter had the same black color as that from the horizontal stationary filter.

In examining all of the information obtained during the Phase I study, it was concluded that agitation did not result in a net benefit to the anaerobic filter. Rather than improving process performance by enhancing gas release, agitation resulted in decreased removals of volatile solids and TCOD.

Upon first examination, these results do not seem to coincide with those obtained in other studies of mixing in anaerobic fixed-film systems. In treating a sucrose-based waste, Tait and Friedman (1980) were capable of achieving total organic carbon (TOC) removal rates as high as 96% with their AnRBC. Pescod et al. (1984) removed 92.5% of the influent COD from a brewery waste using a two-stage anaerobic packed cage reactor (similar to that used in this study). Both of these studies provided mixing by rotation of a horizontal shaft, plastic media assembly. However, neither study employed a non-mixed control reactor to which the results could be compared. Therefore, reactor mixing could not be conclusively credited for the notable treatment efficiencies obtained in those studies.

The treatment results obtained during the mixing study, as well as the examination of the reactors' contents at the end of Phase I, indicated that the attachment of the anaerobic microorganisms to the plastic media was not like that observed in aerobic systems. Successful applications of

aerobic rotating fixed-film systems are commonplace and, in fact, are what suggested their use in anaerobic treatment. However, the interaction between anaerobe and support system are not well understood. The selection of media and design for the support system, as well as the mode of attachment, are areas that researchers have recently investigated.

Wilkie et al. (1983) examined the effects of various support systems on the anaerobic treatment of pig slurry supernatant. The four support materials studied were plastic rings, mussel shells, coral, and fired clay fragments. They found that the clay fragments, though having the lowest porosity (69%), yielded the highest treatment efficiency and most rapid start-up rate. At the end of their study, an attached film was noted on all surfaces. However, as in the present study, placing the plastic media under running water caused the biofilm to slough off with relative ease.

Murray and van den Berg (1981) studied the development of methanogenic fixed films on polyvinyl chloride (PVC) plastic, etched glass, and baked clay. The film development on clay was three times faster than on either the PVC or glass. When the porosity and roughness of the clay was reduced by refiring and polishing, the rate of film development was reduced by about 20%. They concluded that the roughness and porosity of the clay, in addition to the presence of micronutrients, made it a superior media for the support of methanogenic growth.

Similar conclusions were reached by Huysman et al. (1983) in their study of nine different porous and non-porous materials. For the non-porous media, biofilm development was dependent on the availability of microbial size crevices on the surface of the material. Biofilm growth on porous material was based on pore size and quantity as well as the availability of microbial size niches. In their report, the authors suggested that the

methanogens adhere to the media by mechanical rather than electrostatic means.

Fynn and Whitmore (1984) studied the binding forces between methanogens and particle surfaces and found them to be quite weak. Flow velocities as low as 1.5 cm/sec were capable of removing colonized bacteria from the support matrix. However, colonies growing on the downstream side of the media were shielded from the hydrodynamic shearing force of the flow and were retained within the system.

All of these studies lend support to the findings of the Phase I mixing experiments. Microbial attachment to the plastic pall rings was extremely weak as evidenced by the amount of solids lost due to even minimal mixing. The lack of microbial-size crevices on the plastic surfaces combined with the hydrodynamic shearing force caused by the agitation resulted in a reduction in solids retention for the horizontal mixed system. At first it was considered that the biofilm sloughing was a result of abrasion from the tumbling media. However, this possibility was dismissed when an examination of the media revealed that biofilm development on the interior surfaces of the pall rings, which were protected from tumbling abrasion, was just as scarce as on the exterior surfaces.

In the two stationary filters, the biomass appeared to be entrapped within the pall rings. Anaerobic solids completely filled the interior of many of the plastic rings and rested atop the horizontal surfaces of the others. Person (1980) found basically the same occurrence in his doctoral study of anaerobic filters treating swine wastes. Organisms responsible for COD removal were those settled on horizontal surfaces and trapped within the various confining configurations.

After studying various anaerobic filter media configurations, Young and Dahab (1982) concluded that the ability of the media to entrap biological solids is more important than is the unit surface area of the media. This is in direct contrast to the design of aerobic fixed-film systems where maximizing unit surface area is one of the most important considerations. Young and Dahab suggested that, for anaerobic systems, the ability of the media to prevent washout of the microorganisms is more important than is providing those microorganisms a surface on which to attach.

Differing conclusions, however, have been drawn by Stover et al. (1984) with regard to media surface area in anaerobic systems. In their treatment of fuel alcohol production wastewaters, they found that the kinetics of substrate removal could be reliably predicted on the basis of loadings per unit surface area. They developed predictive equations for the anaerobic filter similar to those used for aerobic biological towers and RBC's and found them to be quite accurate. In light of this, it is quite possible that anaerobic attachment to support systems is dependent on the type of media being used and the type of waste being treated, as well as a host of other factors. Before a definitive statement can be made, further research is needed.

As regards the external configuration of the anaerobic filters during Phase I of this study, the results indicate that a horizontal system has a slight advantage over a vertical one in terms of TCOD and solids removal. At the higher loading of 5.1 kg COD/m^3·d (317 lb/1000 ft^3·d), the removal rates of both TCOD and volatile solids were essentially equal for the two systems. However, at the lower loading of 1.1 kg COD/m^3·d (69 lb/1000 ft^3·d), the horizontal stationary filter removed 91% of the influent TCOD and 86% of the volatile solids as compared to removals of 82% and 74%,

respectively, for the vertical filter. Despite these differences in TCOD and volatile solids removal under the low loading conditions, gas production of the two stationary reactors remained essentially equal.

It is proposed that the variations in TCOD and volatile solids removal were a result of reactor configuration. For both filters, the highest rate of gas production occurred at the influent end. Since influent entered the vertical filter near the bottom, the entire contents were moderately mixed due to the rising gas. As the gas rose through the vertical column, biological sloughing was enhanced and solids were floated to the top. At the point of effluent exit, quiescent conditions did not exist and more solids were lost than was anticipated. In the horizontal filter, the influent and effluent ports were spatially separated such that most of the product gas exited the liquid phase without impacting effluent solids.

At the higher loading of 5 kg COD/m^3·d (317 lb/1000 ft^3·d), there was over a four-fold increase in both hydraulic loading and gas production for all three anaerobic filters. These conditions are proposed to have resulted in the two stationary filters experiencing more equivalent mixing and, therefore, more equivalent treatment efficiencies. In addition, COD removal at the influent end of the reactors was less efficient at the higher loadings and, consequently, more substrate was biodegraded near the effluent end. When this occurred, gas production increased near the effluent end of the horizontal stationary unit, thereby preventing the otherwise quiescent conditions.

The fact that the two stationary filters produced nearly identical quantities of gas at the low loading was puzzling at first. If rates of COD removal vary, so should the rates of gas production. The reason for this discrepancy was discovered when the reactors were opened for inspection.

Apparently due to filtration during the higher loading, the vertical filter contained over twice the concentration of volatile solids as compared to the horizontal stationary filter. Therefore, during low loading a portion of the vertical unit's gas production resulted from the degradation of accumulated solids.

As was mentioned previously, these results indicated that the horizontal configuration presented a slight advantage over the vertical. However, since the primary aim of the Phase I program was an investigation of agitational effects, only speculative causes could be offered with regard to configuration. Therefore, design for the Phase II filters was such that the effects of configuration could be further investigated. In addition, applied vacuum and pressure were examined during the second phase in relation to their effect on treatment efficiencies.

Phase II - Pressure and Reactor Design

A matrix approach was followed throughout Phase II to maximize the number of observations that could be made under the given experimental conditions. Three organic loadings were applied to each of three anaerobc filters under each of three pressure conditions. The target organic loadings were 5, 10, and 16.7 kg COD/m^3·d (312, 624, and 1040 lb COD/1000 ft^3·d, respectively). These loadings were achieved by maintaining the feed concentration at approximately 50 g COD/L and varying the hydraulic retention times (HRT's). HRT's used in this study were 3, 5 and 10 days, based on the original void volume of the anaerobic filters. The target pressures were 0.8, 1.0, and 1.2 atmospheres, hereafter referred to as the vacuum, atmospheric, and pressure condition, respectively. The anaerobic filters varied with respect to orientation (two horizontal, one vertical) and

gas-to-liquid interface (from 315 cm^2 to 1380 cm^2). The average influent and effluent COD values obtained for each condition during the Phase II study are presented in Appendixes A through C. In the following sections, the effects of each experimental variable will be examined independently.

Pressure Study

Based on previous studies, the pressure experimental trial was expected to produce several significant results. The findings of Podolok et al. (1984) indicated that reduced pressures would result in increased microbial growth yeilds and increased removals of soluble COD. The pressurized reactor studies of Mangel et al. (1980) and Messing (1982) suggested that a direct correlation existed between applied pressure and the methane composition of the off-gas. The results of the pressure study presented here supported some but not all of these previous findings.

Plots of SCOD removal are presented in Figures 4, 5, and 6 for the 15 cm horizontal (15H), 20 cm horizontal (20H), and 20 cm vertical (20V) anaerobic filters, respectively. An examination of the data suggested that SCOD removals followed first order kinetics. Therefore, regression lines through the origin were determined and the regression coefficients calculated accordingly. Table VI presents a statistical analysis of the regression coefficients (b) developed for the plots in Figures 4-6.

To determine if a statistically significant difference existed between any two regression coefficients, the t-test for difference between regressions was used as described in Steel and Torrie's Principles and Procedures of Statistics (1960). The regression coefficient is a measure of the slope of the regression line. When a quantity removed is plotted against a quantity applied, the regression coefficient represents the slope of

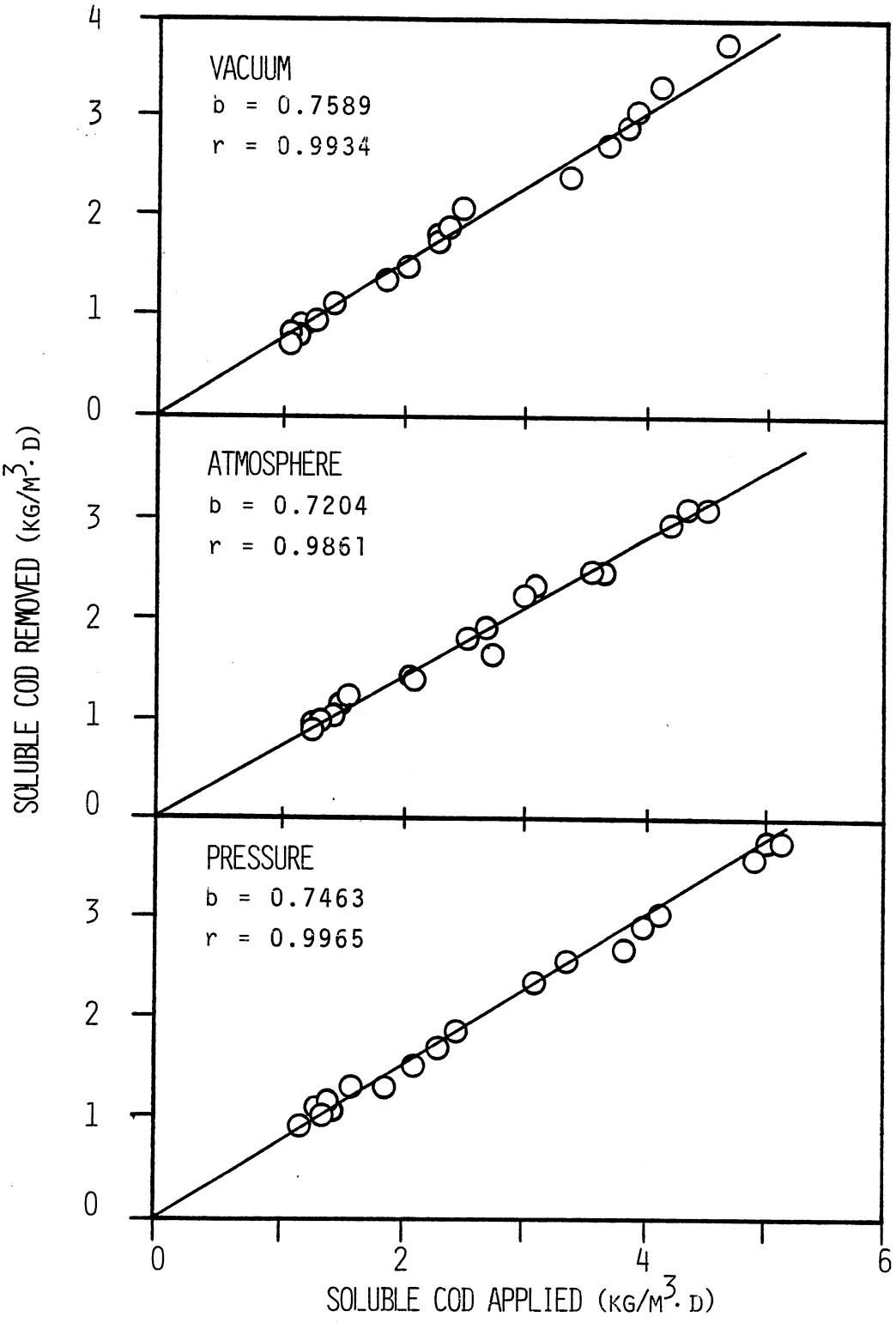

FIGURE 4. EFFECT OF PRESSURE ON SOLUBLE COD REMOVALS FOR REACTOR 15 H

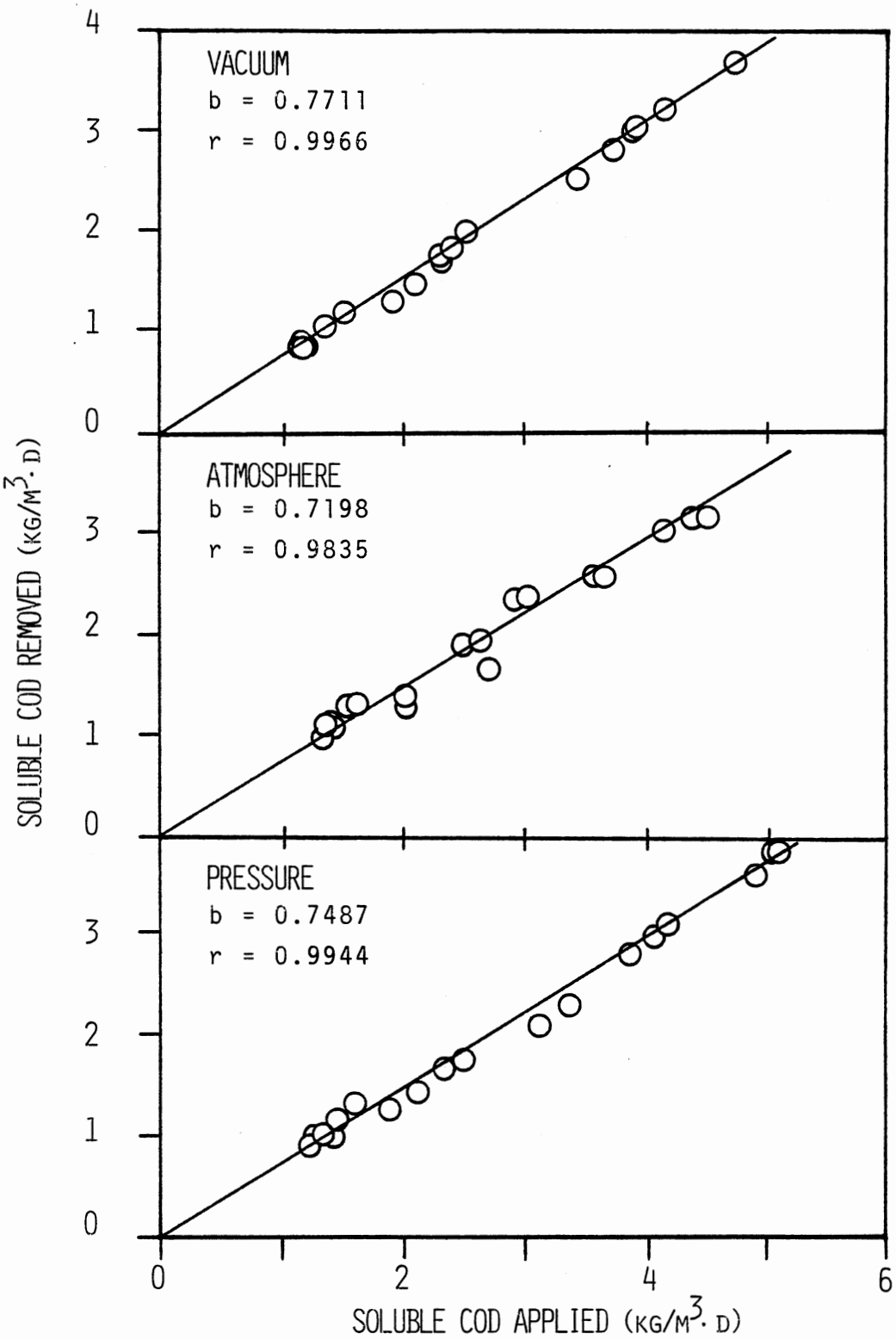

FIGURE 5. EFFECT OF PRESSURE ON SOLUBLE COD REMOVALS FOR REACTOR 20H

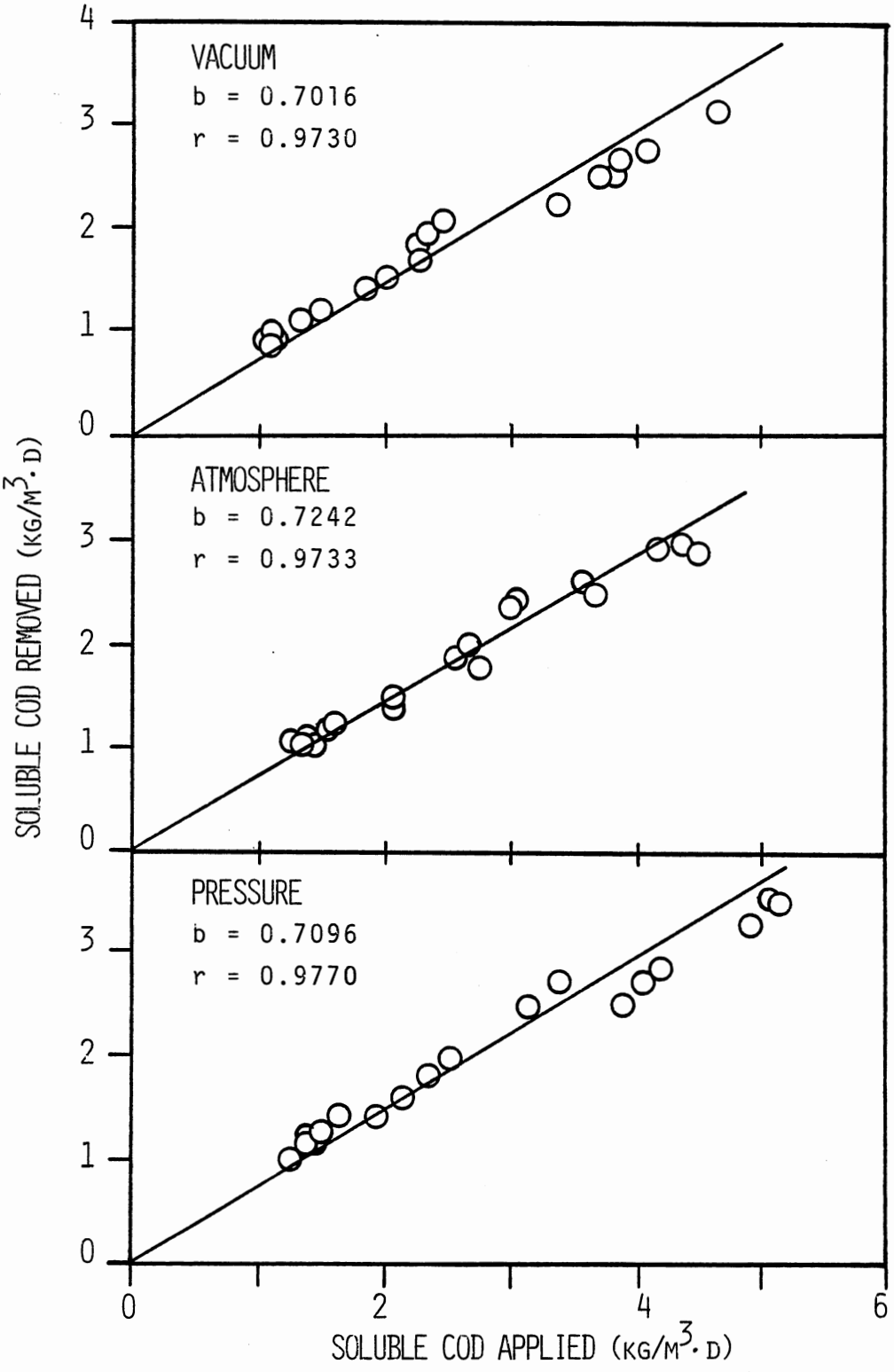

FIGURE 6. EFFECT OF PRESSURE ON SOLUBLE COD REMOVALS FOR REACTOR 20V

removal efficiency. In such a case, a steeper slope (higher regression coefficient) would represent a higher removal efficiency. Therefore, the t-test for difference between regressions is actually a test for the difference between removal efficiencies. For the tests in this chapter, two removal efficiencies were determined to be significantly different if the tabulated "t" was greater than Student's "t" at a 5% probability level with 34 degrees of freedom (5% probability for a larger value of "t"; d.f. = n_1-1+n_2-1, where $n_1 = n_2 = 18$).

TABLE VI

STATISTICAL ANALYSIS OF THE EFFECT OF PRESSURE ON SOLUBLE COD REMOVAL RATES

Regression Coefficients (b)

	15H	20H	20V
Vacuum	0.7589	0.7711	0.7016
Atmosphere	0.7204	0.7198	0.7242
Pressure	0.7463	0.7487	0.7096

Tabulated "t's" for Difference Between Regressions

	15H	20H	20V
Vacuum vs Atmosphere	2.7583*	3.8082*	1.1280
Atmosphere vs Pressure	2.1373*	2.0499*	0.7369
Vacuum vs Pressure	1.1577	2.0118	0.3898

For 34 degrees of freedom, $t_{.05} = 2.0336$

*Statistically significant difference

As can be seen in Table VI, the SCOD removal efficiency for both horizontal filters was significantly greater during the applied vacuum and applied pressure conditions than it was under atmospheric pressure. No significant difference was observed between SCOD removal efficiencies for the vertical anaerobic filter when it was operated under the three different pressure conditions. Also, there was no significant difference in SCOD removal efficiencies for any of the three anaerobic filters when the vacuum and pressure conditions were compared.

In a limited sense, these results confirm the findings of Podolak et al. (1984), who examined the effects of applied vacuums on a horizontal, anaerobic RBC. Applied pressures and vertical filters were not examined in Podolak et al.'s study. However, where the operating conditions of the two studies were most similar (horizontal systems operated under vacuum and atmospheric pressures), the findings concerning SCOD removal were in agreement. In this study, both the 15 cm and 20 cm horizontal anaerobic filters had higher SCOD removal efficiencies (larger regression coefficients) when a vacuum was applied than under the atmospheric conditions.

The theory of Finney and Evans (1975) concerning gas bubbles as a barrier to substrate diffusion was submitted by Podolak et al. (1984) as a possible reason for the enhanced SCOD removal rates under decreased pressures. The research presented here does not wholly support that theory since positive pressures also resulted in improved SCOD removals for both horizontal systems. If applied vacuums reduced the substrate barriers caused by gas bubbles, then logic would hold that applied pressures would impose more barriers and cause decreased removal of SCOD. It may be, however, that the gas inhibition theory is correct and that a different mechanism is responsible for improved SCOD removals during the

pressurized conditions. A greater driving force for substrate diffusion is one possible effect that could be caused by applied pressures. Further research is needed to clarify the mechanisms involved.

Another observation made by Podolak, et al. (1984) was an increase in growth yields when operating at subatmospheric pressures. They defined observed yield as the mass of volatile suspended solids (VSS) produced per mass of SCOD removed. The observation that reduced pressures resulted in both increased growth yields and increased SCOD removal rates suggested to the authors that the microorganisms were more efficient at directing organic carbon toward cell growth under these conditions.

In the present research, it was not possible to calculate observed yields since the swine manure substrate had high VSS concentrations (in contrast to the soluble, sucrose-based waste used by Podolak et al.). The total mass of VSS actually decreased as it moved through the reactors, thereby precluding any meaningful determination of growth yield. However, it was noted that, as reactor pressures were reduced, the removal of volatile solids (VS) decreased. This occurrence is depicted in Figure 7 for the 20 cm horizontal reactor.

The fact that effluent VS increased as pressures decreased could be interpreted as either increased growth yields or decreased digestion efficiency. If either were the case, further investigation into the nature of the biochemical processes involved would be warranted. However, a third reason is proposed that explains the increase of effluent VS in physical terms. The effluent ports on both horizontal anaerobic filters used in this study and on the horizontal AnRBC used by Podolak et al. (1984) were located near the base of the reactors. As pressures were reduced, the suspended solids were degassed and settled out. Fewer solids remained in

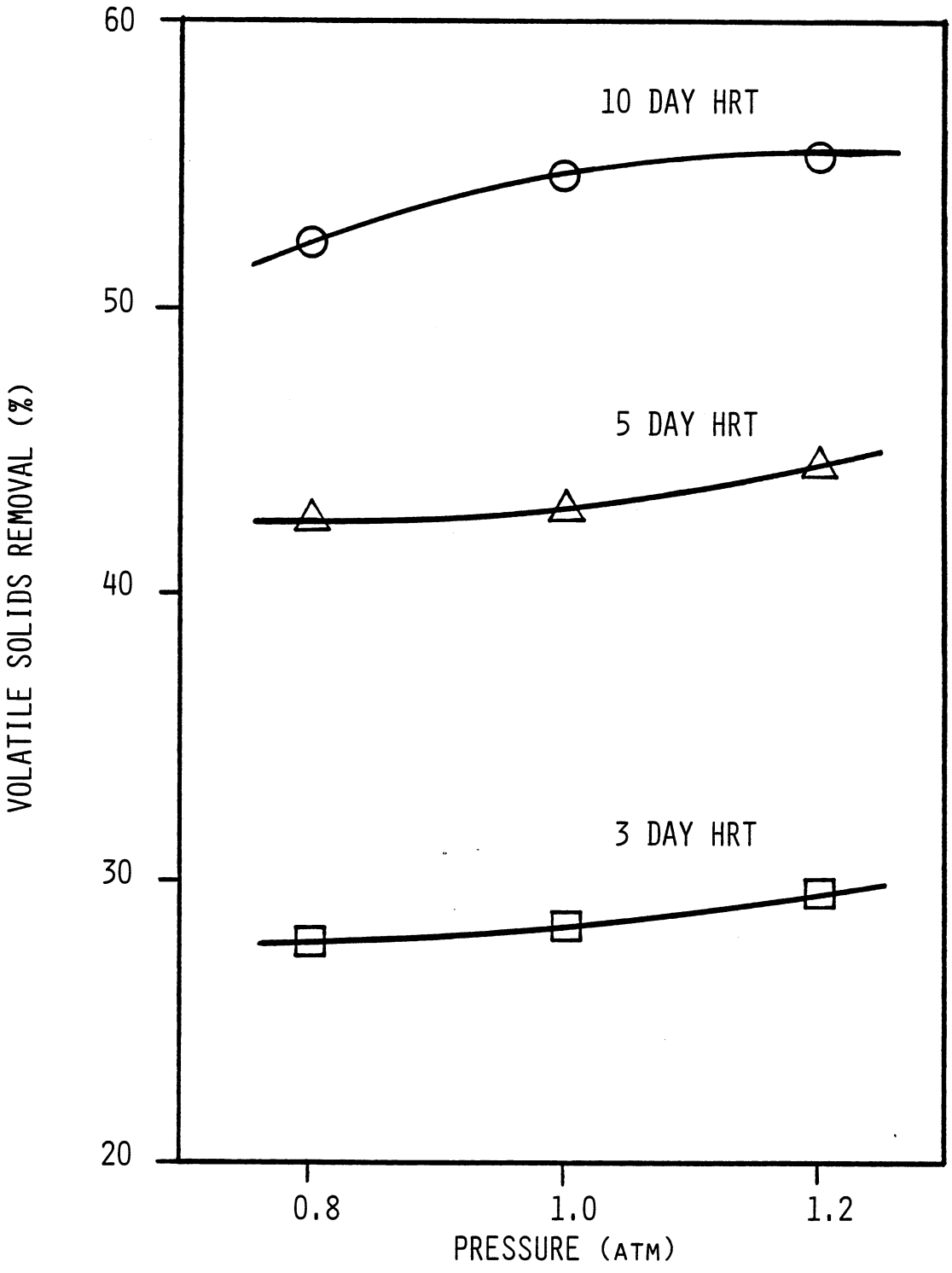

FIGURE 7. VOLATILE SOLIDS REMOVAL FOR REACTOR 20H AS A FUNCTION OF PRESSURE

suspension and more exited the reactor by way of the effluent ports. The converse was true when pressures were increased. Solids became more buoyant and remained in suspension longer. Whether this physical explanation can be applied to research other than that presented here is not known. However, for these studies it is proposed that the inverse relationship between pressure and the concentration of effluent volatile solids was primarily a result of physical processes.

In addition to the effects of pressure on volatile solids and SCOD, it was expected that a correlation would be observed between reactor pressure and the percent methane in the product gas. Table VII presents a summary of the average methane composition in the product gas for each of the Phase II experimental conditions.

TABLE VII

THE EFFECT OF PRESSURE ON THE METHANE CONTENT OF THE PRODUCT GAS

	Average Percent Methane in Product Gas		
Reactor 15H	0.8 atm	1.0 atm	1.2 atm
10 day HRT	67.7	67.7	68.8
5 day HRT	67.9	69.2	65.5
3 day HRT	67.1	67.1	67.1
Reactor 20H			
10 day HRT	67.6	68.8	68.5
5 day HRT	67.6	68.7	65.4
3 day HRT	67.2	67.3	67.9
Reactor 20V			
10 day HRT	67.6	68.5	68.1
5 day HRT	68.1	69.0	66.0
3 day HRT	65.4	67.3	66.7

As can be seen from the values in the table, there was very little variation in the methane content of the product gas, regardless of the experimental variable applied. Considering all the values in Table VII, the mean percent methane was 67.6 and the range was 65.4 to 69.2. Under the conditions examined, no correlation was observed between reactor pressure and percent methane in the product gas.

Most often, though not always, the percent methane was higher for atmospheric conditions than for either vacuum or pressure conditions. This observation might indicate that varying the system pressure to above or below atmospheric had a negative effect on the methanogens. It is not likely that this was the case, however, since SCOD removal in the horizontal filters was enhanced under the vacuum and pressure conditions. If varying the system pressure was inhibitory to the methanogens, then a corresponding decrease in SCOD removal should have been observed.

Wise et al. (1978) found no drop in methane production when they regularly depressurized a 450 psig reactor for nutrient addition, and then repressurized it. If their microbial cultures were capable of tolerating 450 psig pressure changes, then it should be expected that the systems used in this study could tolerate 3 psig pressure changes.

The percent methane values observed in this study were within the typical range (65 to 70%; Metcalf and Eddy, Inc., 1979) for anaerobic digesters treating complex wastewaters. However, Messing (1982) claimed greater than 90% methane for an anaerobic filter that treated domestic sewage and was operated in a range of 1 to 3 psig. He contended that, by operating under pressure, carbon dioxide was more soluble and, therefore, more readily converted to methane. While this logic is sound, these notable results were not observed for the systems used in the present study. It is

proposed that, if indeed the gas compositions observed by Messing were greater than 90% methane, a reactor feature other than pressure was primarily responsible.

In summarizing the effects of pressure, it is concluded that operating at 0.2 atm above or below atmospheric pressure resulted in improved SCOD removal efficiencies for both of the horizontal anaerobic filters. However, the vertical filter did not realize any improvements in SCOD removal as a result of applied vacuum or pressure conditions. Also, no apparent advantage with respect to gas composition was observed for applying either positive or negative pressure to any of the three systems. It still is possible that a more extreme pressure would have resulted in a significantly higher methane content in the product gas. However, in terms of practical applications, any potential benefits must be weighed against the increased capital cost associated with achieving the necessary conditions.

Configuration Study

As was previously mentioned, the results of the Phase I study indicated that at low organic loadings the horizontal anaerobic filter was capable of achieving slightly better volatile solids and TCOD removal rates than the vertically oriented system. Since the Phase I studies were not originally designed to examine this aspect, the Phase II studies were planned so that the effect of reactor configuration could be further investigated.

Two 20 cm (8 inch) diameter anaerobic filters were operated at three hydraulic retention times and received identical organic loadings. The surface area of the fixed media (21.8 m^2, or 235 ft^2) and the original liquid volume (9.5 L) of the two anaerobic filters were also identical.

Reactor configuration was the only experimental variable for the two systems, with one anaerobic filter being horizontal and the other vertical.

Bar graphs of the mean TCOD and volatile solids removals are presented in Figures 8 and 9, respectively, for the Phase II horizontal and vertical anaerobic filters. As can be seen in the figures, the vertical filter's removal rates were higher than the horizontal's at the lower TCOD and volatile solids loadings. Conversely, the horizontal filter's removal rates were better than the vertical's at the higher TCOD and volatile solids loadings.

This is opposite of what was expected based on the results of the Phase I studies. It was proposed that the horizontal system would have better solids removal rates at low loadings because of the spatial separation of the effluent port and the region of greatest gas production. At high loadings, it was proposed that gas production at the effluent end of the horizontal anaerobic filter would be high enough to increase turbulence and, thereby, cause solids removal rates of the two systems to become more equivalent.

In light of the Phase II results, it is apparent that the previously proposed explanation was not entirely accurate. Instead, an alternate reason is proposed which more properly explains the occurrences in both Phase I and Phase II studies. The reason is based partially on the chronological sequence of loading to the anaerobic filters, and not solely on the magnitude of that loading.

In the Phase I studies, loadings were begun at 5 kg COD/m^3·d (312 lb/1000 ft^3·d). Phase II loadings were begun at the same level as in Phase I. However, after operation at quasi-steady state levels for two months, Phase II loadings were successively increased to 10 and 16.7 kg COD/m^3·d

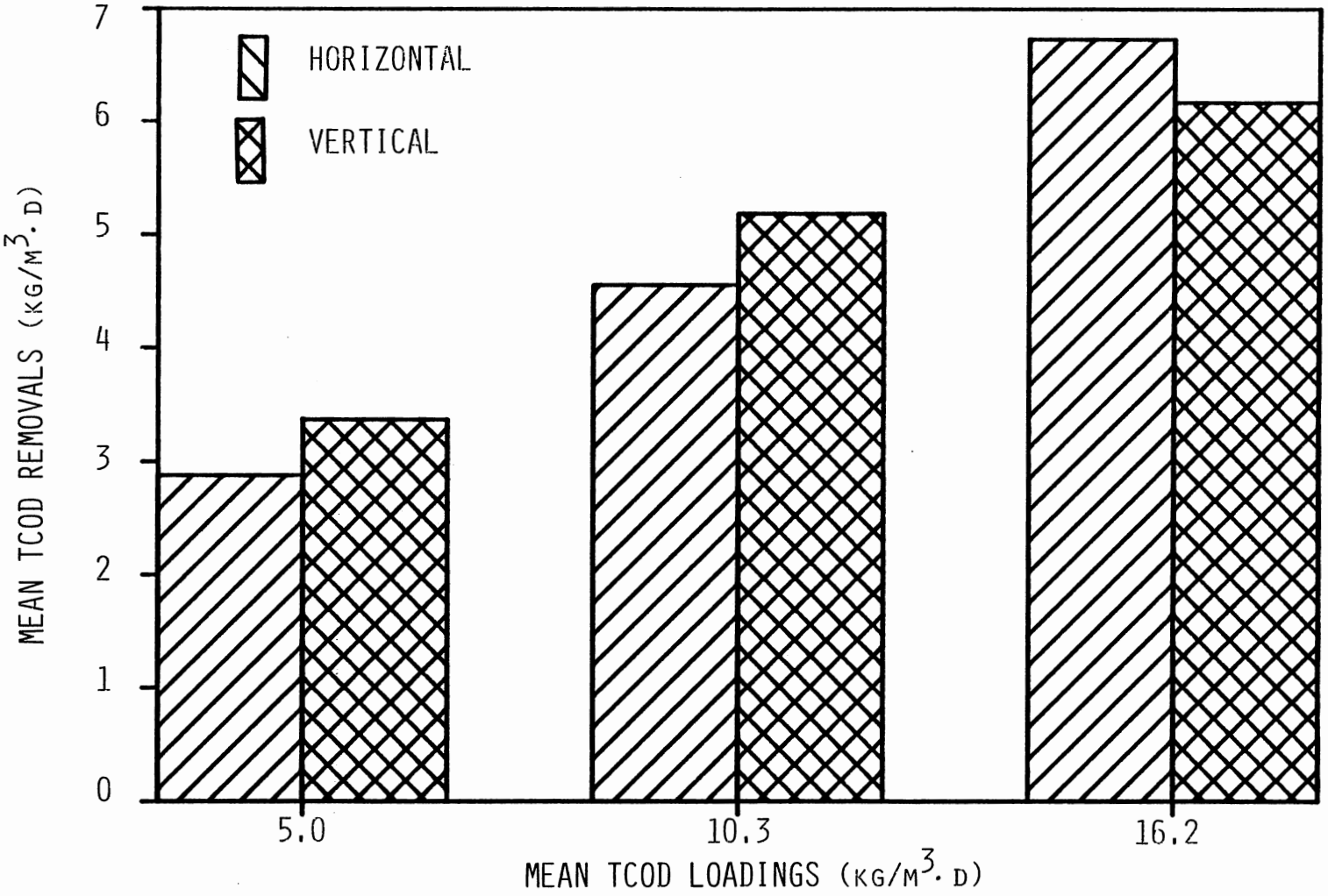

FIGURE 8. EFFECT OF REACTOR CONFIGURATION ON TCOD REMOVALS

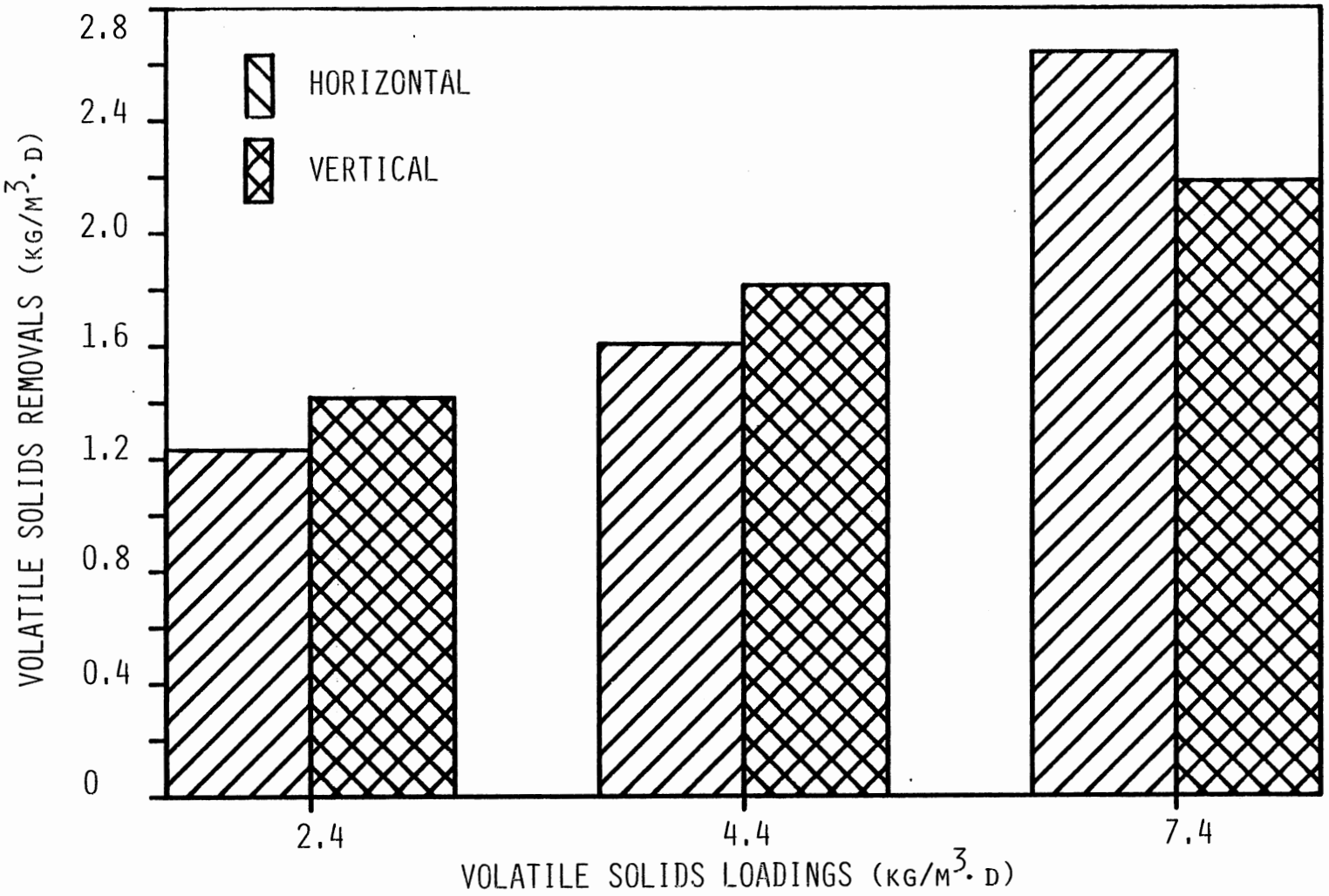

FIGURE 9. EFFECT OF REACTOR CONFIGURATION ON VOLATILE SOLIDS REMOVALS

(624 and 1040 lb/1000 $ft^3 \cdot d$). In both Phase I and Phase II, the vertical anaerobic filter exhibited comparitively better removal of volatile solids and TCOD in the early months of the study, whereas the horizontal system had the better removal of these compounds during the latter stages of the study.

As was discussed in Chapter 3, the anaerobic filters were determined to be operating at quasi-steady state when the effluent volatile fatty acid levels stabilized. This generally occurred within a few weeks after loadings were increased. The condition originally was referred to as quasi-steady state, rather than true steady state, because of the moderate variability in the feed. Based on the observations made during Phase I and Phase II, as well as on the reports of other investigators, it is now apparent that solids accumulation in the anaerobic filters was another factor in keeping true steady state from occurring.

In the study by Brumm and Nye (1981), sedimentation of volatile solids was noted throughout the experimental trial. They found a 13 to 28% difference between volatile solids removal and actual destruction in their treatment of dilute swine waste with an anaerobic filter. This difference was due to filtration of solids within the filter, which resulted in the gradual accumulation of solids throughout the study. Though volatile solids removals as high as 86.6% were observed, actual destruction of volatile solids never topped 58.5%.

In the present research, sedimentation of feed solids occurred at all organic loadings. As the study progressed chronologically, the solids inventory of each anaerobic filter gradually increased. The Phase I systems experienced this accumulation as loadings decreased whereas the Phase II systems experienced increased accumulations with increased loadings.

Gas production in the vertical anaerobic filter was greatest at or near the base of the unit and caused floating of the solids that had accumulated there. As the solids inventory increased, the chance for these floated solids to reach the effluent port also increased. Therefore, the association between solids inventory and solids removal rates in the upflow vertical filter was stronger than in the cross-flow horizontal filter. As discussed earlier, the region of greatest gas production in the horizontal filter was spatially separated from the effluent port in such a way that floated solids did not readily exit the system. For this reason, the horizontal filter exhibited better solids removal rates than did the vertical filter during the latter loadings of both Phase I and Phase II.

It is noted that the vertical filter's greater volatile solids removal rates during the initial loadings were not simply a function of sedimentation. From the methane production data presented in Table VIII it can be seen that actual destruction of volatile solids was greater in the vertical system than in the horizontal at low loadings. For equal amounts of volatile solids added, the vertical anaerobic filter removed more volatile solids and produced more methane than the horizontal filter at the 10 and 5 day HRT's. At the 3 day HRT, volatile solids removal efficiencies were reversed for the two systems. The horizontal unit removed more volatile solids and produced more methane than the vertical, given equal loadings. If enhanced volatile solids removal rates had been simply a function of sedimentation and not of solids destruction, the corresponding increases in methane production rates would not have been observed.

TABLE VIII

METHANE PRODUCTION AND VOLATILE SOLIDS REMOVAL EFFICIENCIES DURING THE CONFIGURATION STUDY

	Hydraulic Retention Times		
	10 day	5 day	3 day
Mean VS Loading ($kg/m^3 \cdot d$)	2.45	4.40	7.42
Mean VS Removal (%)			
Horizontal	50.4	36.6	35.6
Vertical	58.0	41.3	29.5
Mean Methane Production (L CH_4/g VS added)			
Horizontal	0.421	0.366	0.285
Vertical	0.442	0.393	0.277

Sedimentation of a particulate waste is generally regarded as detrimental to anaerobic digestion. In their comparison of advanced anaerobic reactors, van den Berg and Kennedy (1983) state that sedimentation and solids accumulation interfere with the operation of the reactor. This is definitely true when the settled, particulate wastes are not biodegradable. However, with biodegradable particulates it may actually be desirable to provide for some degree of sedimentation. Large organic particles that settle out generally require a longer retention time to biodegrade. Smaller organic particles that remain in suspension generally require a shorter retention time to accomplish the same degree of biodegradation. By providing for controlled sedimentation, it may be possible to increase gas production and get better digestion efficiencies.

Though the research presented here pertains to anaerobic filters, the same concept of controlled sedimentation could be applied to suspended growth systems. A major concern of anaerobic digester design is the provision for complete mixing to prevent short-circuiting. While this is a valid concern, it is possible that allowing for a small region of controlled sedimentation would result in better overall treatment efficiencies. Further work in this area is suggested.

Gas-to-Liquid Interface Study

The effect of gas-to-liquid interface on anaerobic treatment efficiencies has received little attention. It was one of several factors to which Messing (1982) attributed his gas compositions of greater than 90% methane. Since two of Messing's other proposed factors (configuration and pressure) were examined during the course of this research, it was decided that the gas-to-liquid theory would be investigated as well. In review, Messing credited the maximized gas-to-liquid interface in his horizontal filter with enhancement of methane transfer from the liquid to the gaseous phase. This attribution, however, was not based on parallel studies.

In the present study, two horizontal anaerobic filters of equal length were constructed from PVC pipe, their only difference being in pipe diameter. One anaerobic filter had an inside diameter of 20 cm (8 inches) and the other a diameter of 15 cm (6 inches). Filling the units with equal volumes of liquid resulted in differing gas-to-liquid interfaces. The 20 cm ID filter (20H) had an interface of 1380 cm^2 (214 in^2) whereas the 15 cm ID filter (15H) had an interface of 790 cm^2 (122 in^2). As in the previously described studies of Phase II, each anaerobic filter was operated at three

hydraulic retention times (3, 5, and 10 days) with a target influent COD of 50 g/L.

Referring to the gas composition data for anaerobic filters 15H and 20H in Table VII (presented previously), it can be seen that gas-to-liquid interface had no apparent effect on the methane composition of the product gas. Under atmospheric conditions (1.0 atm pressure), the largest difference in methane composition under any loading was 0.5%. Therefore, it seems that the difference in the gas-to-liquid interface of the two horizontal filters had no effect on gas composition.

If the magnitude of the gas-to-liquid interface actually had a significant impact on methane transfer rates, then Finney and Evans' (1975) gas inhibition theory would suggest that it would also have an effect on methanogenic substrate removal rates. To examine this, plots of acetic acid removal were developed. The plots are presented in Figure 10 for the Phase II 15H and 20H anaerobic filters and a statistical analysis for difference between regressions is presented in Table IX. As Table IX shows, the acetic acid removal efficiencies for anaerobic filter 20H (larger gas-to-liquid interface) and 15H were not statistically significantly different.

The lack of an observed significant difference may be due to an insufficient difference in size of the two interfaces employed. If that were the case, future studies should employ interfaces that vary by a much higher magnitude than that used in this study. However, at this point it is proposed that, under practical limitations, the size of the gas-to-liquid interface has no effect on anaerobic treatment efficiencies.

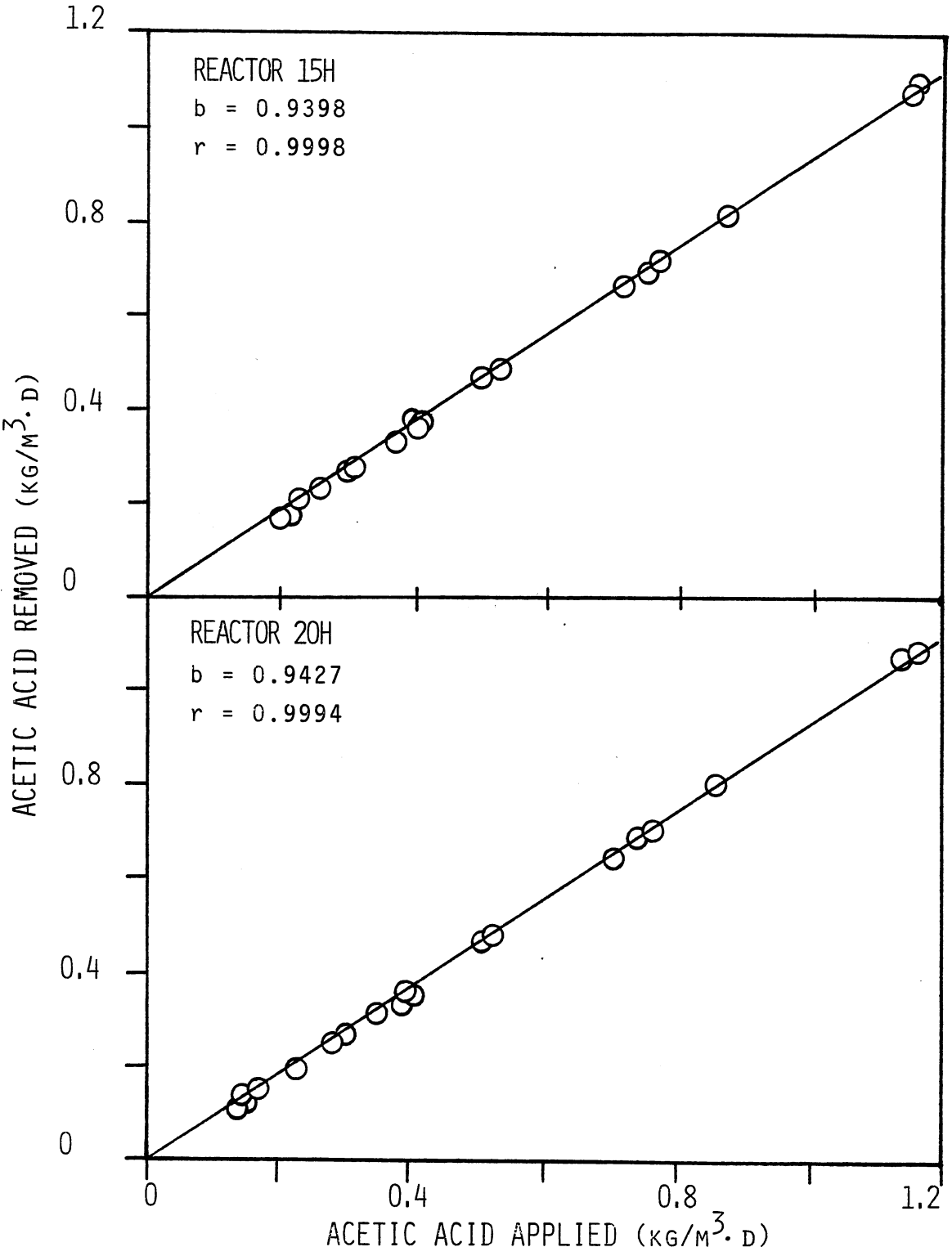

FIGURE 10. EFFECT OF GAS-TO-LIQUID INTERFACE ON ACETIC ACID REMOVALS

TABLE IX

STATISTICAL ANALYSIS OF THE EFFECT OF GAS-TO-LIQUID INTERFACE ON ACETIC ACID REMOVAL RATES

	15H	20H
Regression Coefficients (b)	0.9398	0.9427
Correlation Coefficients (r)	0.9998	0.9994

Tabulated "t" for difference between regressions of 15H and 20H = 0.7163

Since $t_{.05}$ = 2.0336 for 34 degrees of freedom, this is not a statistically significant difference.

Rate-Limitation Study

In anaerobic treatment, one of the primary objectives of process modification is to overcome the rate-limiting step. In all metabolic sequences, there is one step whose slow rate of reaction retards the rate of all subsequent reactions. In anaerobic degradation, this rate-limiting step is generally thought to be the conversion of acetic acid and carbon dioxide to methane. However, as Speece (1983) points out in his review of anaerobic biotechnology, the actual identity of the rate-limiting step depends upon the nature of the substrate, the process configuration, and the loading rate. At low loading rates, acid formation may be rate-limiting whereas, at high loading rates for the same waste, methane formation may be rate-limiting. Hydrolysis often limits the rate of degradation for cellulosic wastes, whereas acid formation is rate-limiting for grease and lipid wastes.

In studies concerning the treatment of piggery wastes, hydrolysis of organic solids is generally cited as the rate-limiting step. Kennedy and van

den Berg (1982a) found hydrolysis of pig manure to be rate-limiting up to fermenter loading rates of 40 kg COD/m^3·d. However, in swine waste studies by van Velsen (1977), hydrolysis was limiting only up to an organic load of 8 kg COD/m^3·d. Beyond 8 kg COD/m^3·d, methanogenesis became rate-limiting.

In order to estimate the efficiency of each major biochemical step involved in anaerobic degradation, van Velsen (1977) developed the following equations:

$$\text{Hydrolysis (\%)} = 100(G + S)/M$$

$$\text{Acidogenesis (\%)} = 100(G + V)/M$$

$$\text{Methanogenesis (\%)} = 100\ G/M$$

where

G = COD removed via methane gas (g O_2/liter manure)

S = soluble COD in digester effluent (g O_2/liter)

M = total manure COD (g O_2/liter manure)

V = volatile acid COD in the digester effluent (g O_2/liter).

For the purpose of his analysis, van Velsen assumed that (1) suspended organics are converted to soluble organics in hydrolysis; (2) VFA, hydrogen, and carbon dioxide are exclusively formed by the acidogenic bacteria; and (3) all methane produced originated from the end-products of acidogenesis.

These same equations were applied to the atmospheric data for all three anaerobic filters operated during Phase II. The results are plotted in Figures 11, 12, and 13. As can be seen in the figures, the rates of all three biochemical steps decreased to essentially the same extent. This indicates that the first step in anaerobic degradation (i.e., hydrolysis), was

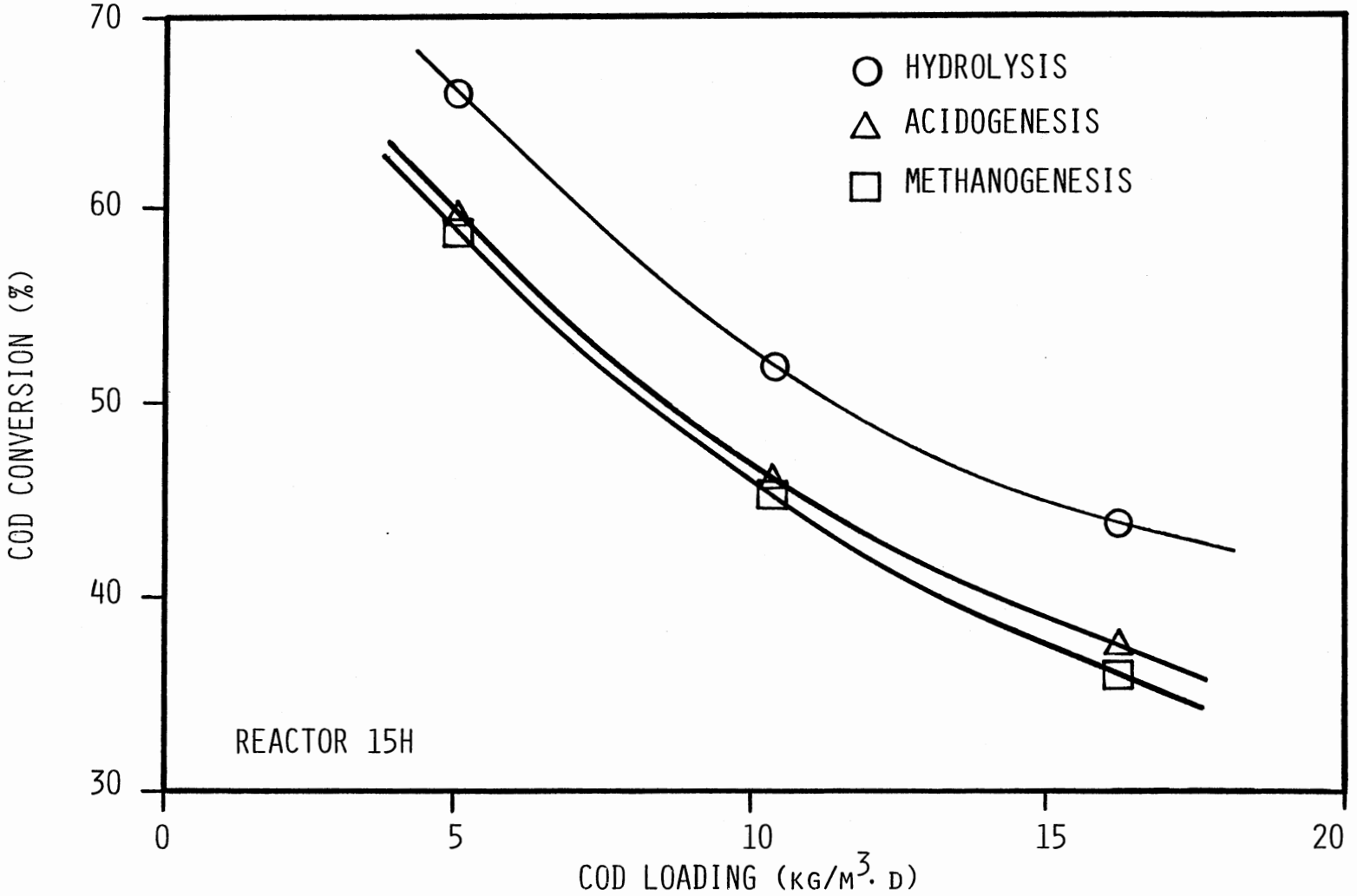

FIGURE 11. EFFECT OF ORGANIC LOADING ON HYDROLYSIS, ACIDOGENESIS, AND METHANOGENESIS FOR REACTOR 15H

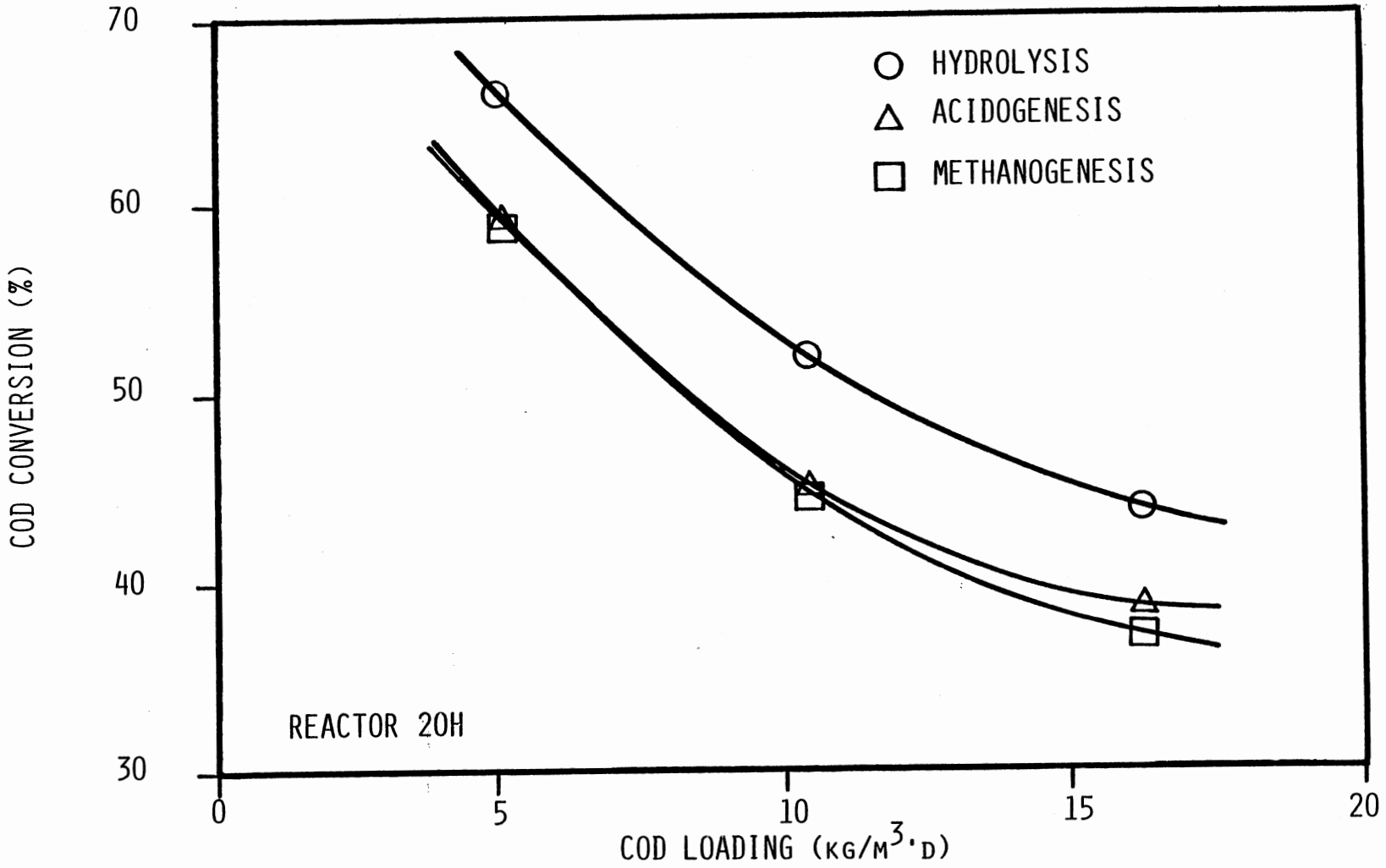

FIGURE 12. EFFECT OF ORGANIC LOADING ON HYDROLYSIS, ACIDOGENESIS, AND METHANOGENESIS FOR REACTOR 20H

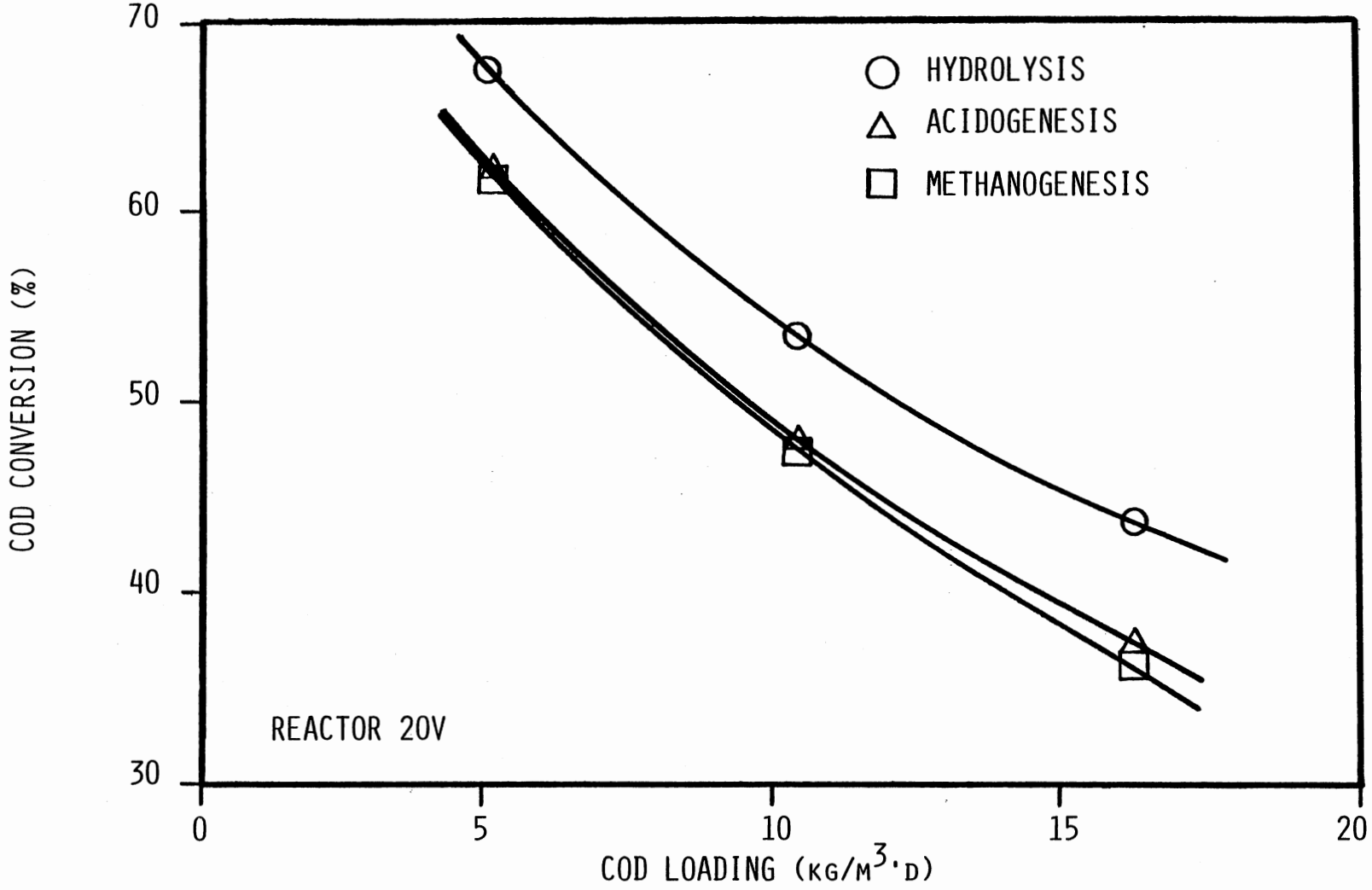

FIGURE 13. EFFECT OF ORGANIC LOADING ON HYDROLYSIS, ACIDOGENESIS, AND METHANOGENESIS FOR REACTOR 20V

the rate-limiting step. If the rate of either acidogenesis or methanogenesis had decreased to a greater extent than the rate of hydrolysis, it would have indicated that one of the latter steps of anaerobic degradation (acidogenesis or methanogenesis) had become rate-limiting.

While these equations assist in identifying the rate-limiting step under a range of organic loadings, an inaccurate portrayal of the anaerobic process is produced as a result of several of the assumed conditions . The hydrolysis equation assumes that all methane and soluble COD produced are an indirect result of hydrolysis. This would only be true if the substrate solely consisted of particulate organics. In the present study, the substrate used during Phase II had an approximate composition of 75% particulate and 25% soluble organics. These soluble organics could serve as methane precursors without having passed through the hydrolysis step. Another inaccuracy resulted from basing the rates of acidogenesis and methanogenesis on the total manure COD. Those particulate organics that have not been hydrolyzed should not be considered as substrate for the acidogenic and methanogenic bacteria. Van Velsen's equations result in very low rates of acidogenic and methanogenic degradation when in reality those microorganisms may have been very efficient at metabolizing the substrate available to them. Finally, the omission of a rate equation for acetogenesis implies that the methanogens are capable of metabolizing all volatile acids when, in reality, only the 1- and 2-carbon volatile acids are known to be methanogenic substrates.

To more accurately represent the metabolic processes occurring during anaerobic biodegradation, modified equations were developed for each of the four steps previously described (hydrolysis, acidogenesis, acetogenesis, and methanogenesis). The modified equations are as follows:

Hydrolysis (%) = (1-Pe/Pi)100

Acidogenesis (%) = [1-NVe/(Pi-Pe+NVe)]100

Acetogenesis (%) = [1-Ve/(Pi-Pe+NVi-NVe+Vi)]100

Methanogenesis (%) = [1-Ae/(Ti-Te+Ae)]100

where

T = total COD (g/L)

P = particulate (non-soluble) COD (g/L)

NV = non-VFA soluble COD (g/L)

V = C3 to C5 VFA COD (g/L)

A = acetic acid COD (g/L)

i = influent

e = effluent.

Assumptions made for this analysis were (1) acidogenesis resulted in no acetic acid formation and (2) particulate organics are converted to soluble organics in hydrolysis. The first assumption allows for a relatively accurate estimate of acetogenesis though the assumption itself is not entirely correct. The second assumption is similar to one made by van Velsen. The modified equations were applied to the atmospheric data for all three anaerobic filters operated during Phase II. The results are plotted in Figures 14-17.

The modified hydrolysis equation was based only on the removal of particulate COD, which was defined for this study as the fraction of total COD that was sedimented by centrifugation at 32,000 X G for 15 minutes (similar to van Velsen's definition of particulates). Applying the modified equation to the 10 day HRT data for the 15H anaerobic filter (refer to Appendix A), a hydrolysis efficiency of 53.9% was achieved, based on a

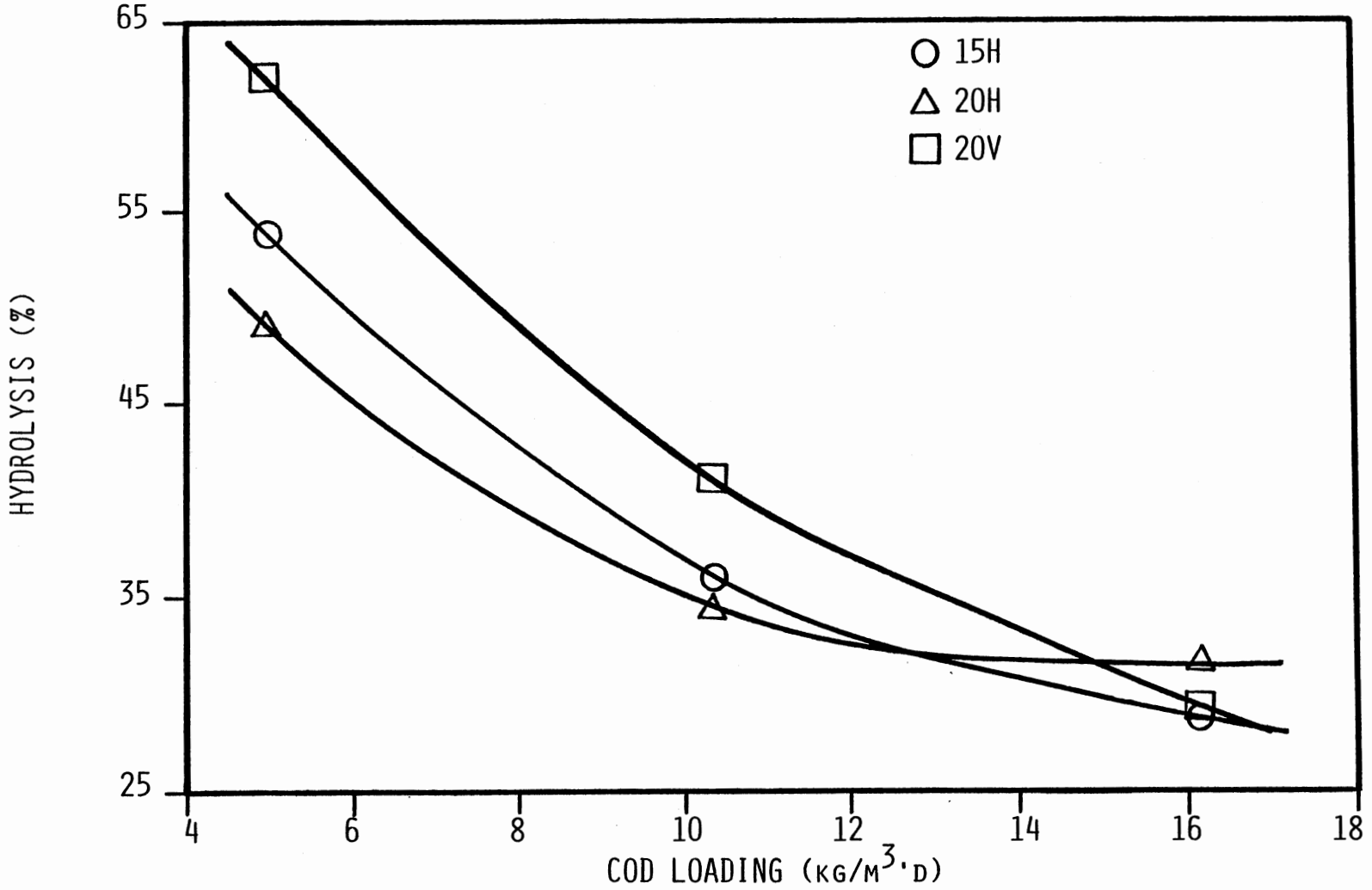

FIGURE 14. EFFECT OF ORGANIC LOADING ON HYDROLYSIS, USING MODIFIED EQUATIONS

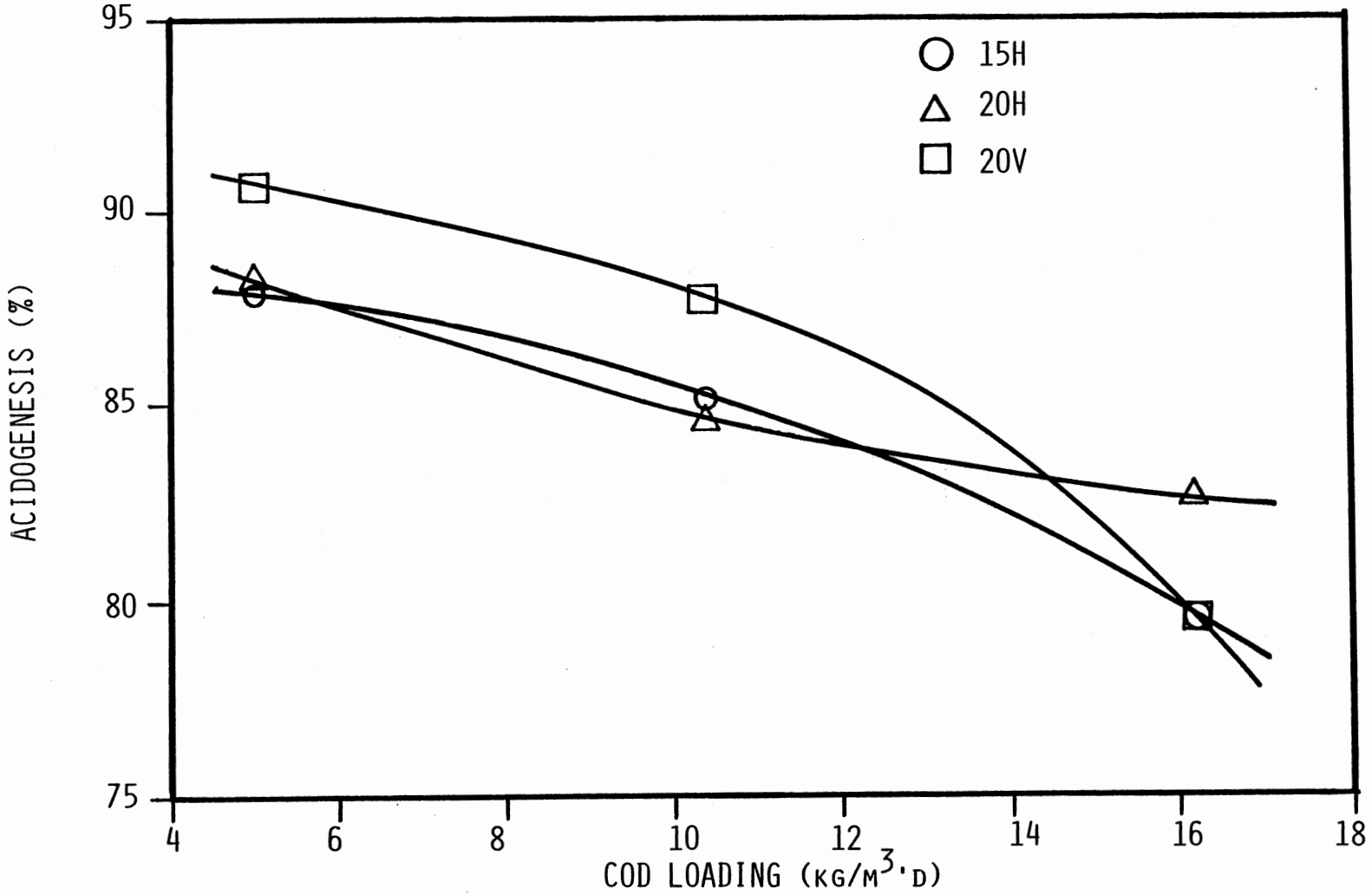

FIGURE 15. EFFECT OF ORGANIC LOADING ON ACIDOGENESIS, USING MODIFIED EQUATIONS

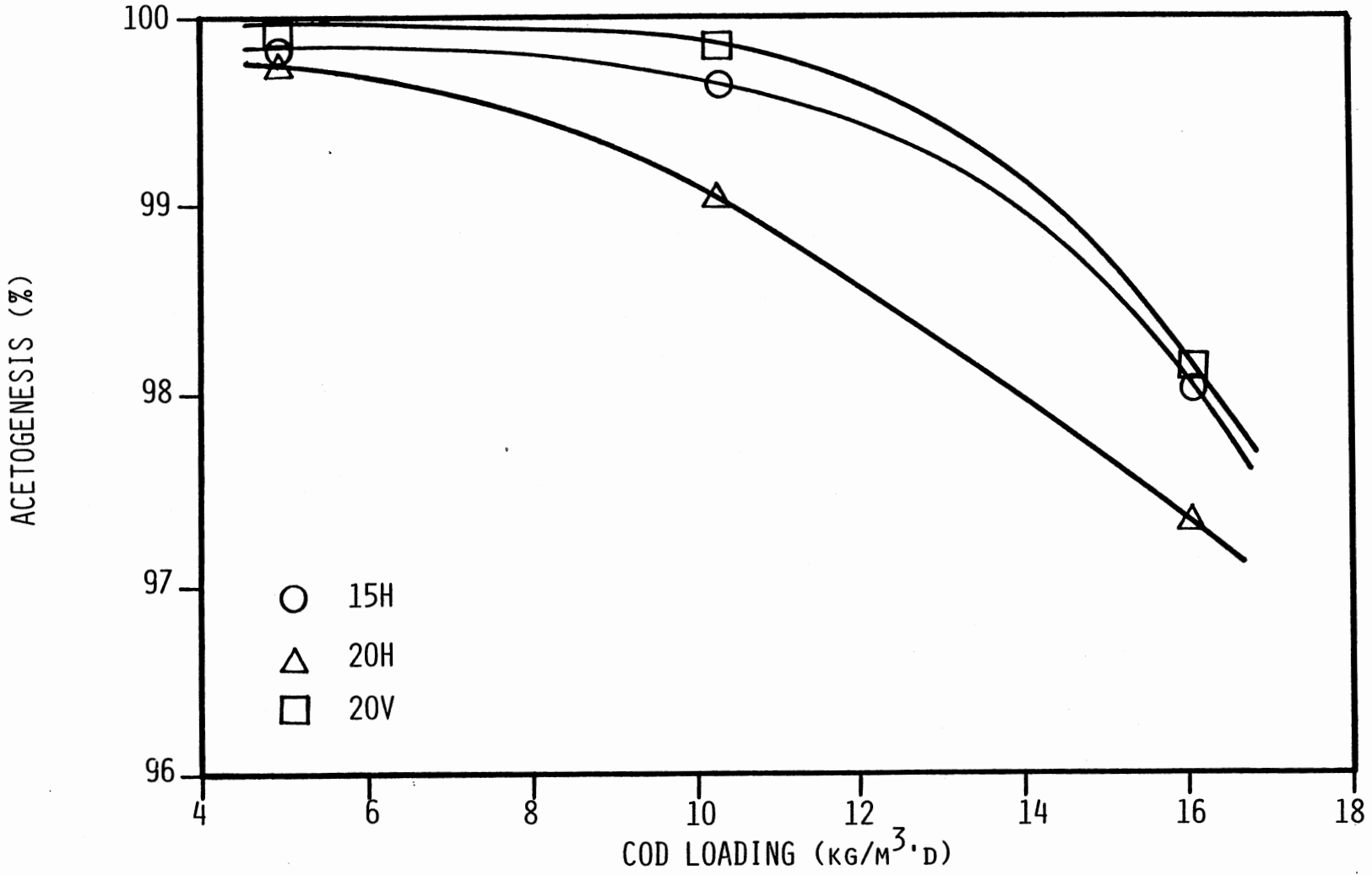

FIGURE 16. EFFECT OF ORGANIC LOADING ON ACETOGENESIS, USING MODIFIED EQUATIONS

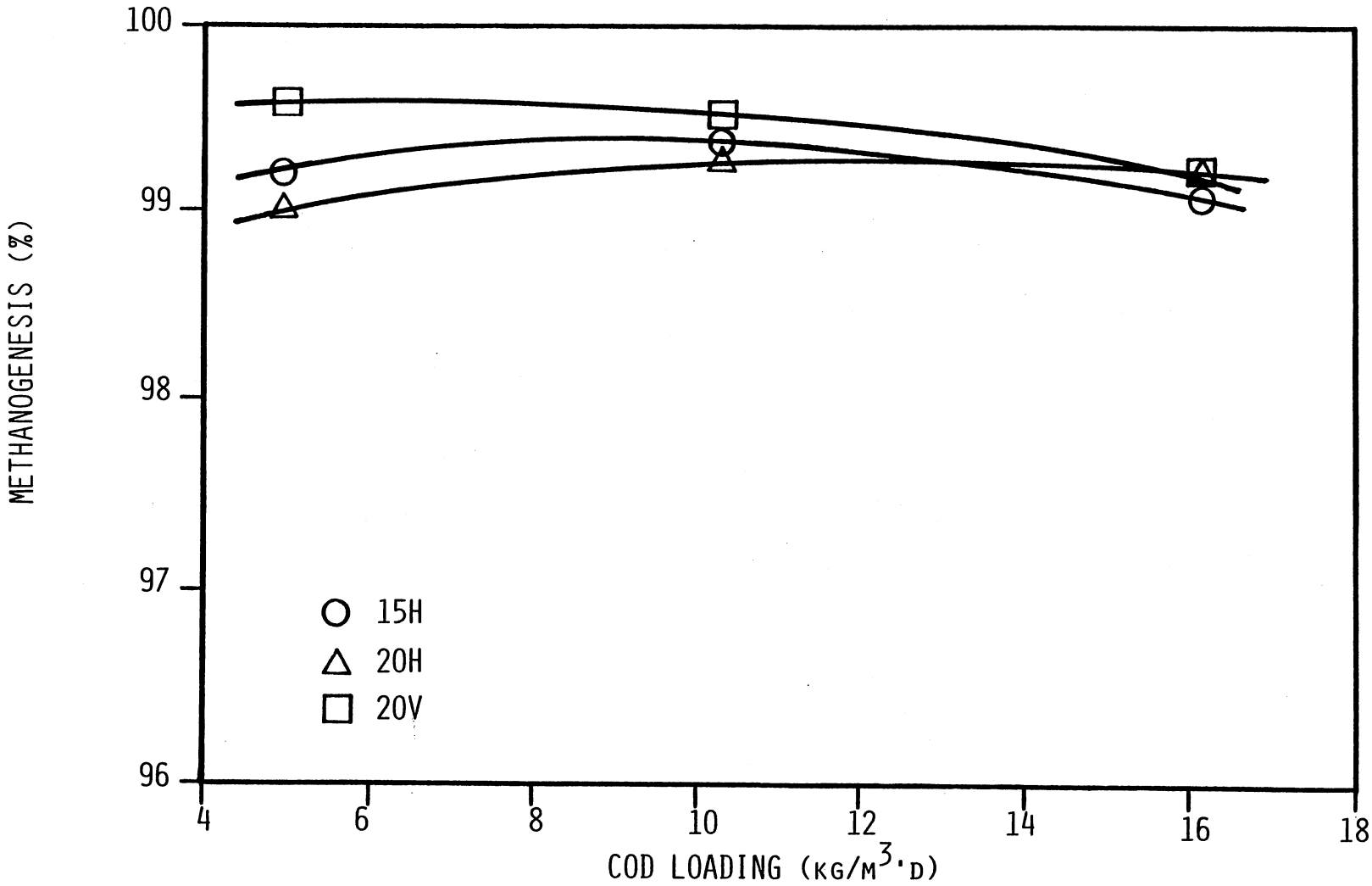

FIGURE 17. EFFECT OF ORGANIC LOADING ON METHANOGENESIS, USING MODIFIED EQUATIONS

particulate COD of 35,600 mg/L in the influent and 16,400 mg/L in the effluent. Applying van Velsen's equation to the same system results in a 66.0% hydrolysis efficiency. The modified equation differs significantly from the one used by van Velsen in that it does not assume that all gas and effluent soluble COD are a result of the hydrolysis of particulates. Since some of the gas and effluent soluble COD were produced without the benefit of particulate hydrolysis, the calculated efficiency of hydrolysis was lower when using the modified equation.

With respect to the modified acidogenesis equation, it was not assumed that all effluent VFA was a direct result of acidogenic reactions occurring within the anaerobic filters. The assumption concerning effluent VFA was made for the original equations and would be valid if the influent contained no VFA. However, the average composition of the influent used during Phase II included a VFA concentration of approximately 7,300 mg/L. Therefore, VFA that shows up in the effluent does not necessarily have to have been a result of acidogenesis in the anaerobic filter.

In developing the modified acidogenesis equation, the following factors were taken into account:

1. Particulate COD which has not been hydrolyzed can not serve as substrate to the acidogenic bacteria.
2. Only non-VFA soluble COD and hydrolyzed particulate COD can serve as substrate to the acidogenic bacteria.
3. Any non-VFA soluble COD in the effluent is acidogenic substrate which has not been utilized.

Applying the modified acidogenesis equation to the 10 day HRT data for the 15H anaerobic filter (refer to Appendix A for data values), the calculated efficiency of acidogenesis was 88.1%. Applying van Velsen's

equation to the same system yields an acidogenesis efficiency of 59.8%. Van Velsen's equation results in a lower efficiency mainly as a result of considering all influent compounds to be substrate for the acidogens.

The equation for acetogenesis was developed for this study since it is now strongly believed that a distinct group of bacteria (the acetogens) are responsible for oxidizing volatile acids with three or more carbons to form acetic acid (Bryant, 1979). To develop the acetogenesis equation, the following factors were taken into account:

1. Volatile acids with three or more carbons serve as direct substrate for the acetogenic bacteria. Any effluent VFA with three or more carbons is a result of acetogenic inefficiencies.
2. Neither unhydrolyzed particulate COD nor unoxidized non-VFA soluble COD can serve as substrate to the acetogenic bacteria.

Applying the acetogenesis equation to the 10 day HRT data for the 15H anaerobic filter (refer to Appendix A for data values), the calculated efficiency of acetogenesis was 99.8%. This extremely high rate of efficiency is reflected in the relatively low effluent concentration of C3 to C5 VFA's (46 mg/L). This indicates that, under the given conditions, the acetogenic bacteria were capable of metabolizing practically all available substrate.

The equation for methanogenesis was modified for many of the same reasons as were the other equations. Van Velsen's equation states that the efficiency of methanogenesis is equal to the percentage of influent (manure) that ends up as methane gas. Granted, all methane gas is produced by the methanogens. However, only a small portion of the influent in its original form serves as a direct substrate to the methanogens. As discussed previously, it is now strongly believed that only one- and two-carbon

compounds may serve as direct methane precursors. These precursors include acetic acid, formic acid, methanol, and carbon dioxide. Of these, only acetic acid and carbon dioxide are considered to play a major role in anaerobic digestion (Parkin and Owen, 1986).

With this in mind, the modified methanogenesis equation was developed based on the following factors:

1. Any acetic acid in the effluent is a result of methanogenic inefficiencies.
2. In the anaerobic process, all COD actually removed from the waste stream is done so in the form of methane gas (with the exception of very minor amounts of hydrogen and other reduced compounds). Therefore, the difference in influent and effluent total COD reflects the amount of COD removed by the methanogens.

Applying the methanogenesis equation to the 10 day HRT data for the 15H anaerobic filter (refer to Appendix A for data values), the calculated efficiency of methanogenesis was 99.2%. Applying van Velsen's equation to the same system yields a methanogenesis efficiency of 59.2%. The modified equation shows that the methanogens were capable of metabolizing practically all substrate available to them.

An examination of Figure 16 reveals that a sharp decline in the rates of acetogenesis occured around a loading of 10 kg COD/m^3·d. A similar decline in the rates of methanogenesis is not noted in Figure 17. This difference was due primarily to an accumulation of propionic acid in the anaerobic filters at the higher loadings. The 3-day HRT data presented in Appendixes B and C for the 20V anaerobic filter further illustrates the point. During the vacuum experiment (Appendix B), the effluent

concentration of C3 to C5 acids for the 20V filter increased from 19 to 1050 mg/L when the HRT was reduced from five to three days. Under the same conditions, however, the effluent concentration of acetic acid only increased from 149 to 228 mg/L. Similar results can be seen in Appendix C. These results indicate that the acetogens are more sensitive to organic overloads than are the methanogens.

In a report by Cohen (1983), the predominance of propionic acid during unstable anaerobic digestion is cited as a common occurrence. He states that propionic acid is a preferred electron sink product under low pH conditions and, once formed, is a relatively difficult product to degrade. As discussed previously, propionic and butyric acids are not known methanogenic substrates and must pass through acetogenesis before methane can be formed. Nevertheless, methanogenesis is often cited as being the rate-limiting step in anaerobic degradation. It is proposed that, in cases where methanogenesis is suspected of being rate-limiting, in actuality the rate-limiting step is acetogenesis. Rate-limitation due to acetogenesis would explain the common observations of propionic and butyric acids accumulating at a much faster rate than acetic acid during unstable conditions. The differentiation between acetogenesis and methanogenesis is encouraged in any future studies concerned with the identification of rate-limitation.

CHAPTER V

SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

An evaluation of several factors affecting the design and operation of anaerobic filters was performed. Operational and design factors were evaluated under a range of organic loading conditions using screened swine manure as a substrate. The operational factors examined were agitation, applied vacuums, and applied pressures. The design factors examined were reactor configuration (horizontal vs. vertical) and gas-to-liquid interface. In addition to these evaluations, the mechanism of rate-limitation was assessed and equations were developed to determine the efficiency of the individual biochemical steps involved in anaerobic degradation.

The following conclusions were reached:

1. Agitation was not beneficial to the anaerobic filters. The anaerobic microorganisms formed very weak attachments to the plastic support media and were readily detached during the turbulent conditions. Based on this study and others, the principle advantage of a plastic support system in anaerobic treatment is in physically impeding the direct exit of the microorganisms, and not necessarily in providing surfaces for attachment and growth.

2. In the range of 0.8 to 1.2 atm pressure, no significant effects on treatment efficiencies were realized due to changing pressures. It is possible that operating at pressures outside this range would have resulted

in improved treatment efficiencies, but the practicality of such operation on a full-scale must first be weighed.

3. The horizontally-oriented anaerobic filters were better capable of retaining biological solids than was the vertical unit. This improved retention of biological solids made the horizontal filters better capable of handling high organic loads than the vertical filter. Much of the improved solids retention in the horizontal filters was due to the spatial separation of gas turbulence and the effluent port.

4. Within the range of interfaces examined, the size of the gas-to-liquid interface had no effect on treatment efficiencies. However, the range of interfaces examined was relatively narrow and it still remains possible that a larger differential would result in major differences in treatment efficiencies.

5. Hydrolysis was rate-limiting up to an average organic load of 17 kg COD/m^3·d. The rate of acetogenesis declined readily at a load of approximately 10 kg COD/m^3·d whereas the rate of methanogenesis did not. Based on the results of this study and others, acetogenesis generally becomes rate-limiting before methanogenesis.

The findings of this research suggest several areas which warrant further investigation. These recommended areas of research are as follows:

1. An expanded investigation of the beneficial and detrimental effects of substrate sedimentation is recommended. Attention should be given to its effects on filtration, volatile solids destruction, channeling, and overall treatment efficiency.

2. Increased research with horizontal anaerobic filters is recommended. Various reactor lengths, media types, and substrates should

be examined. Comparison with vertical filters under extended operation (periods greater than one year) is also encouraged.

3. Methods of enhancing propionic acid degradation should be investigated. More attention should be given in the future to propionic acid accumulation rather than the accumulation of volatile acids in general.

4. The role which media has in anaerobic filters needs further study. Whether it is possible or not for anaerobic microorganisms to become firmly attached to support systems needs to be determined so that media can be designed accordingly.

BIBLIOGRAPHY

Bloodgood, D. E. and Anderson, D. R. "A study of the Effects of Negative Pressure on Sludge Digestion." Water and Sewage Works, **110**, 29 (1963).

Brumm, T. J. and Nye, J. C. "Dilute Swine Waste Treatment in an Anaerobic Filter." Proceedings of the 36th Purdue Industrial Waste Conference, 453 (1981).

Bryant, M. P. "Microbial Methane Production Theoretical Aspects." Journal of Animal Science, **48**, 193 (1979).

Cochrane, B. C. "A Review of the Analysis of Free Fatty Acids [C_2-C_6]." Journal of Chromatographic Science, **13**, 440 (1975).

Cohen, A. "Two-Phase Digestion of Liquid and Solid Wastes." Proceedings: Third International Symposium on Anaerobic Digestion, 123 (1983).

Coppinger, E., Brantigan, J, Lenart, J. and Baylon, D. Report on the Design and Operation of a Full-Scale Anaerobic Dairy Manure Digester, Report No. SERI/TR-312-471 (Solar Energy research Institute, Golden, CO, 1979).

Cordoba, P. R., Sanchez Riera, F. and Sineriz, F. "Treatment of Dairy Industry Wastewater with an Anaerobic Filter." Biotechnology Letters, **6**, 753 (1984).

DiLallo, R. and Albertson, O.E. "Volatile Acids by Direct Titration." Journal Water Pollution Control Federation, **33**, 356 (1961).

Finney, C. D. and Evans, R. S. "Anaerobic Digestion: The Rate-Limiting Process and the Nature of Inhibition." Science, **190**, 1088 (1975).

Finney, C. D., Evans, R. S. and Finney, K. A. The Fast Production of Methane by Anaerobic Digestion, Final Report, ERDA contract No. EY-76-C-02-2900 (1978).

Fynn, G. H. and Whitmore, T. N. "Retention of Methanogens in Colonised Reticulated Polyurethane Foam Biomass Support Particle." Biotechnology Letters, **6**, 81 (1984).

Grady, C. P. L. "Biodegradation: Its Measurement and Microbiological Basis." Biotechnology and Bioengineering, **27**, 660 (1985).

Grady, C. P. L. and Lim, H. C. Biological Wastewater Treatment, Marcel Dekker, Inc., New York (1980).

Hansson, G. and Molin, N. "End Product Inhibition in Methane Fermentations. Effects of Carbon Dioxide and Methane on Methanogenic Bacteria Utilizing Acetate." European Journal of Applied Microbiology and Biotechnology, **13**, 236 (1981).

Harper, S. R. and Pohland, F. G. "Recent Developments in Hydrogen Management During Anaerobic Biological Wastewater Treatment." Biotechnology and Bioengineering, **27**, 585 (1986).

Hashimoto, A. G. "Effect of Mixing Duration and Vacuum on Methane Production Rate from Beef Cattle Waste." Biotechnology and Engineering, **24**, 9 (1982).

Huysman, P., Van Meenen, P., Van Assche, P. and Verstraete, W. "Factors Affecting the Colonization of Non Porous and Porous Packing Materials in Model Upflow Methane Reactors." Biotechnology Letters, **5**, 643 (1983).

Jirka, A. M. and Carter, M. J. "Micro Semi-Automated Analysis of Surface and Wastewaters for Chemical Oxygen Demand." Analytical Chemistry, **47**, 1397 (1975).

Josephson, J. "Fixed-Film Biological Processes." Environmental Science and Technology, **16**, 380A (1982).

Kandler, O., Winter, J. and Temper, U. "Methane Fermentation in the Thermophilic Range." In: Energy from Biomass, 1st E. C. Conference, London, Applied Science Publishers, 472 (1981).

Kennedy, K. J. and van den Berg, L. "Anaerobic Digestion of Piggery Waste Using a Stationary Fixed Film Reactor." Agricultural Wastes, **4**, 151 (1982a).

Kennedy, K. J. and van den Berg, L. "Continuous vs Slug Loading of Downflow Stationary Fixed Film Reactors Digesting Piggery Waste." Biotechnology Letters, **4**, 137 (1982b).

Mangel, G., Villermaux, J. and Prost, C. "Methane Production Under Pressure by Fermentation of Waste Materials." European Journal of Applied Microbiology and Biotechnology, **9**, 79 (1980).

McCarty, P. L. "Anaerobic Waste Treatment Fundamentals. Part One. Chemistry and Microbiology." Public Works, **95**, 107 (September, 1964).

Messing, R. A. "Immobilized Microbes and a High-Rate, Continuous Waste Processor for the Production of High Btu Gas and the Reduction of Pollutants." Biotechnology and Bioengineering, **24**, 1115 (1982).

Metcalf and Eddy, Inc. Wastewater Engineering, McGraw-Hill, Inc., New York (1979).

Murray, W. D. and van den Berg, L. "Effect of Support Material on the Development of Microbial Fixed Films Converting Acetic Acid to Methane." Journal of Applied Bacteriology, **51**, 257 (1981).

Parkin, G. F. and Owen, W. F. "Fundamentals of Anaerobic Digestion of Wastewater Sludges." Journal of Environmental Engineering, ASCE, **112**, 867 (1986).

Person, H. L. "The Anaerobic Filter for Treating Liquid Swine Wastes." PhD Thesis, University of Minnesota (1980).

Pescod, M. B., Anderson, G. K., and Norton, T. S. "Treatment of Strong Organic Wastewater Using Aerobic and Anaerobic Packed-Cage RBC's." Proceedings: Second International Conference on Fixed-Film Biological Processes, 1315 (1984).

Podolak, P. L., Friedman, A.A., and LaGrega, M. D. "Effects of Reduced Partial Pressure on an Anaerobic Rotating Biological Contactor." Proceedings: Second International Conference on Fixed-Film Biological Processes, 1050 (1984).

Poels, J., Van Assche, P., and Verstraete, W. "Effects of Disinfectants and Antibiotics on the Anaerobic Digestion of Piggery Waste." Agricultural Wastes, **9**, 239 (1984).

Samson, R., van den Berg, L. and Kennedy, K. J. "Mixing Characteristics and Startupof Anaerobic Downflow Stationary Fixed Film (DSFF) Reactors." Biotechnology and Bioengineering, **27**, 10 (1985).

Speece, R. E. "Anaerobic Biotechnology for Industrial Wastewater Treatment." Environmental Science and Technology, **17**, 416A (1983).

Standard Methods for the Examination of Water and Wastewater, American Public Health Association, 14th Edition: Washington, D. C. (1976).

Steel, R. G. D. and Torrie, J. H. Principles and Procedures of Statistics, McGraw-Hill Book Company, Inc., New York (1960).

Stover, E. L., Gonzalez, R., and Gomathinayagam, G. "Anaerobic Fixed-Film Biological Treatment Kinetics of Fuel Alcohol Production Wastewaters." Proceedings: Second International Conference on Fixed-Film Biological Processes, 1625 (1984).

Tait, S. J. and Friedman, A. A. "Anaerobic Rotating Biological Contactor for Carbonaceous Wastewaters." Journal Water Pollution Control Federation, **52**, 2257 (1980).

van den Berg, L. and Kennedy, K. J. "Comparison of Advanced Anaerobic Reactors." Proceedings: Third International Symposium on Anaerobic Digestion, 71 (1983).

van Huyssteen, J. J. "Gas Chromatographic Separation of Anaerobic Digester Gases Using Porous Polymers." Water Research, **1**, 237 (1967).

van Velsen, A. F. M. "Anaerobic Digestion of Piggery Waste. 1. The Influence of Detention Time and Manure Concentration." Netherlands Journal of Agricultural Science, **25**, 151 (1977).

Wilkie, A., Faherty, G. and Colleran, E. "The Effect of Varying the Support Matrix on the Anaerobic Digestion of Pig Slurry in the Upflow Anaerobic Filter Design." In: Energy from Biomass, 3rd E. C. Conference, London, Applied Science Publishers, 531 (1983).

Wise, D. L., Cooney, C. L. and Augenstein, D. C. "Biomethanation: Anaerobic Fermentation of CO_2, H_2, and CO to Methane." Biotechnology and Bioengineering, **20**, 1153 (1978).

Young, J. C. and Dahab, M. F. "Effect of Media Design on the Performance of Fixed-Bed Anaerobic Filters." Proceedings: IAWPR Specialized Seminar on Anaerobic Treatment, 321 (1982).

Young, J. C. and McCarty, P. L. "The Anaerobic Filter for Waste Treatment." Journal Water Pollution Control Federation, **41**, R160 (1969).

APPENDIX A

AVERAGE COD VALUES FOR THE ATMOSPHERIC EXPERIMENTS OF THE PHASE II STUDY

10 Day Hydraulic Retention Time

	Influent	15H Eff	20H Eff	20V Eff
Total (mg/L)	50,100	19,800	21,200	16,300
Particulate (mg/L)	35,600	16,400	18,100	13,500
Non-VFA Soluble (mg/L)	6,980	3,110	2,840	2,680
C3 to C5 VFA (mg/L)	4,920	46	54	9
Acetic Acid (mg/L)	2,530	232	273	137

5 Day Hydraulic Retention Time

	Influent	15H Eff	20H Eff	20V Eff
Total (mg/L)	51,700	28,000	28,800	25,700
Particulate (mg/L)	38,900	24,800	25,500	22,800
Non-VFA Soluble (mg/L)	6,550	3,050	3,020	2,770
C3 to C5 VFA (mg/L)	3,960	68	187	27
Acetic Acid (mg/L)	2,260	146	147	120

3 Day Hydraulic Retention Time

	Influent	15H Eff	20H Eff	20V Eff
Total (mg/L)	48,500	29,900	28,800	29,700
Particulate (mg/L)	37,000	26,400	25,300	26,200
Non-VFA Soluble (mg/L)	4,160	3,010	2,890	3,110
C3 to C5 VFA (mg/L)	4,490	311	464	309
Acetic Acid (mg/L)	2,850	165	156	143

APPENDIX B

AVERAGE COD VALUES FOR THE

VACUUM EXPERIMENTS OF

THE PHASE II STUDY

10 Day Hydraulic Retention Time

	Influent	15H Eff	20H Eff	20V Eff
Total (mg/L)	49,900	20,700	21,400	18,900
Particulate (mg/L)	37,400	17,700	18,300	16,300
Non-VFA Soluble (mg/L)	5,180	2,660	2,630	2,410
C3 to C5 VFA (mg/L)	4,690	40	77	30
Acetic Acid (mg/L)	2,530	301	355	195

5 Day Hydraulic Retention Time

	Influent	15H Eff	20H Eff	20V Eff
Total (mg/L)	47,700	24,200	23,700	24,200
Particulate (mg/L)	36,700	21,600	21,000	21,800
Non-VFA Soluble (mg/L)	5,140	2,370	2,490	2,200
C3 to C5 VFA (mg/L)	4,120	22	29	19
Acetic Acid (mg/L)	1,810	192	193	149

3 Day Hydraulic Retention Time

	Influent	15H Eff	20H Eff	20V Eff
Total (mg/L)	51,400	29,300	27,900	32,800
Particulate (mg/L)	39,500	26,400	25,200	28,900
Non-VFA Soluble (mg/L)	3,130	2,570	2,390	2,700
C3 to C5 VFA (mg/L)	6,290	140	42	1,050
Acetic Acid (mg/L)	2,410	217	229	228

APPENDIX C

AVERAGE COD VALUES FOR THE

PRESSURE EXPERIMENTS OF

THE PHASE II STUDY

10 Day Hydraulic Retention Time

	Influent	15H Eff	20H Eff	20V Eff
Total (mg/L)	49,700	21,500	22,200	19,200
Particulate (mg/L)	35,600	18,800	19,400	16,700
Non-VFA Soluble (mg/L)	6,980	2,360	2,390	2,280
C3 to C5 VFA (mg/L)	4,580	34	42	20
Acetic Acid (mg/L)	2,520	301	285	201

5 Day Hydraulic Retention Time

	Influent	15H Eff	20H Eff	20V Eff
Total (mg/L)	51,900	30,000	30,200	27,600
Particulate (mg/L)	39,100	26,700	26,300	24,700
Non-VFA Soluble (mg/L)	6,170	2,780	2,950	2,570
C3 to C5 VFA (mg/L)	4,260	193	610	75
Acetic Acid (mg/L)	2,400	308	348	246

3 Day Hydraulic Retention Time

	Influent	15H Eff	20H Eff	20V Eff
Total (mg/L)	51,300	30,200	29,200	33,000
Particulate (mg/L)	37,600	26,600	25,900	28,600
Non-VFA Soluble (mg/L)	4,670	2,940	2,750	3,180
C3 to C5 VFA (mg/L)	5,930	471	375	1,090
Acetic Acid (mg/L)	3,030	164	149	173

VITA[2]

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