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**REDUCED GAS PRESSURE OPERATION
OF SLUDGE DIGESTERS: EXPANDED STUDIES**

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**REDUCED GAS PRESSURE OPERATION OF SLUDGE DIGESTERS:
EXPANDED STUDIES**

Final Report

Prepared for

**THE NEW YORK STATE
ENERGY RESEARCH AND DEVELOPMENT AUTHORITY**

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ABSTRACT

REDUCED GAS PRESSURE OPERATION OF SLUDGE DIGESTERS: EXPANDED STUDIES

Previous investigations strongly suggested that the municipal anaerobic sludge digestion process could be enhanced by reactor operation with subatmospheric headspace pressures. Enhanced solids destruction and methane production along with increased process stability were observed in these earlier studies. However, due to the small scale of the anaerobic reactors used (≈ 1.5 L), definitive steady-state measurements could not be obtained. These expanded studies were undertaken to verify and define the magnitude of the benefits that might be obtained with vacuum operation of sludge digesters. Four reactors (≈ 15.0 L) were fed municipal sludge at three different organic loading rates while being maintained with a 15-day solids retention time. One reactor had a constant headspace pressure of 1.02 atm; a second was maintained at 0.75 atm; and the remaining two reactors were operated for the majority of the day at 1.02 atm, and for part of the day with a 0.75 atm headspace pressure. Additional small-scale, batch experiments were performed to help identify controlling digestion mechanisms. The results of these expanded studies indicate that vacuum operation did not yield significant advantages over the organic loading range investigated (0.088 to 0.352 lb VSS/ft³·d).

Key Words: anaerobic treatment, municipal sludge, reduced headspace pressures, vacuum operations.

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ABBREVIATIONS

Alk'y	alkalinity (reported as calcium carbonate)	PCOD	particulate COD (TCOD minus SCOD)
atm	atmosphere	pH	standard unit of acidity
CaCO ₃	calcium carbonate	R	reactor
CH ₄	methane	RS-1	reactor system
COD	chemical oxygen demand	SCOD	soluble COD
CO ₂	carbon dioxide	S ⁻²	sulfide
d	day	SS	suspended solids
g	grams	SRT	solids retention time
GC	gas chromatograph	STP	standard temperature and pressure
HAc	acetic acid	TCOD	total COD
HRT	hydraulic retention time	TS	total solids
H ₂	molecular hydrogen	TVS	total volatile solids
H ₂ S	hydrogen sulfide	VFA or VA	volatile fatty acids (C ₁ through C ₆ only, reported as acetic acid)
L	liter	VSS	volatile suspended solids
lb	pound		
Metro	Metropolitan Treatment Plant (Syracuse, NY)		
MGD	million gallons per day		
mg	milligram		
mL	milliliter		
NH ₃ -N	ammonia nitrogen		

SUMMARY

Residue wastewater sludge is difficult and expensive to treat, stabilize and dispose of, often accounting for more than half the cost associated with municipal wastewater treatment facilities. Anaerobic digestion is the most common process used to minimize residual sludge volumes and organic content for facilities treating more than five million gallons per day of wastewater. Developing improved anaerobic digestion processes that minimize sludge solids to be disposed, generate additional energy-rich digester gases for economic use, and allow higher organic loadings of existing digester facilities were the goals of this research project.

Previous research sponsored by the New York State Energy Research and Development Authority strongly suggested that digester operations with subatmospheric headspace gas pressures would meet these goals. This earlier work, conducted with 1.5 liter model anaerobic digesters, indicated that a headspace pressure of 0.75 atm seemed to provide the "best" economic operation. However, due to the small scale employed, there were problems in interpreting the experimental results. The research described in this report was undertaken to verify the earlier results, to determine the mechanisms involved in the improved sludge digestion as a result of vacuum operation, and to evaluate a potential technique for retrofitting existing municipal sludge digesters.

Four experimental anaerobic reactors having liquid volumes of 15 or 18L were operated under steady-state conditions with 15-day solids retention times. One reactor served as

a control with its headspace gas pressure constantly maintained at 1.02 atm to simulate conventional digester operation. A second reactor was operated with a constant headspace pressure of 0.75 atm. The remaining two reactors were used to evaluate the effects of intermittent vacuum on sludge digestion by maintaining the headspace pressures at 1.02 atm for 23.5 and 23.0 hours per day respectively. During the balance of the day the two reactors were operated with a headspace pressure of 0.75 atm.

Thickened sludge, a mixture of primary and waste-activated sludge, was routinely obtained from the Metropolitan Treatment Plant (Metro) in Syracuse, New York to serve as raw feedstock for these experiments. Following initial studies which duplicated Metro's full-scale anaerobic digester loading patterns, feedstock sludge was concentrated by settling and/or centrifugation to provide higher organic loading rates. Feed solids ranged from about 2.6 to about 8.5 percent and the organic content ranged from about 35 g/L to 105 g/L of chemical oxygen demand. These feed-sludge loading conditions represented light, typical, and heavily loaded conditions for municipal sludge digesters.

Based on the results of the earlier research, enhanced solids destruction and methane generation rates on the order of ten to fifteen percent were anticipated for the reactors with reduced headspace pressures, especially for heavier organic loading conditions. The vacuum-assisted reactors did attain steady-state operating conditions more rapidly than the conventional 1.02 atm reactor following step changes in the organic loading patterns in these studies. In addition, there was strong, but inconclusive, evidence that feed solids were processed more rapidly during reduced headspace pressure operation for the two heavier loading conditions tested and that even higher organic loads might be used without inducing process failure. However, the steady-state performance of the four reactors was essentially identical for each of the three loading conditions tested. These

observations led to the unexpected conclusion that there are few benefits from operating municipal sludge digesters with reduced headspace pressure over the loading range investigated.

Section 1

INTRODUCTION

To treat, stabilize and dispose of wastewater sludge is difficult and expensive, often accounting for more than half the cost associated with municipal wastewater treatment facilities. Therefore, municipalities are constantly searching for cost-effective methods for reducing the volume and strength of sludge. Anaerobic sludge digestion is the most common process used to minimize sludge volume and organic content prior to final residue disposal for facilities treating more than five MGD of wastewater. Reasons for selecting an anaerobic digestion process include the potential for obtaining net energy production (as methane); sizable reductions in sludge mass and volume (30 to 50%); and production of reasonably odor- and pathogen-free materials for final disposal. However, many wastewater treatment facilities are currently overloaded and/or subject to episodic events that result in sludge processing failures. The research described in this report was undertaken to evaluate reduced digester headspace pressure operation as a promising low-cost method for increasing sludge destruction rates and improving energy yield for the anaerobic digestion process.

BACKGROUND

During the early and mid 1980's bench-scale experiments at Syracuse University demonstrated that high-strength, soluble, organic wastes could be treated more efficiently by anaerobic processes when reactor headspace gas pressures were reduced to less than atmospheric pressure. Both fixed-film and suspended-culture anaerobic processes were shown to convert organic substrates to methane under organic loading conditions that resulted in failure for systems operating with conventional headspace pressures (1.00-1.02 atm). Based on these studies, the New York State Energy Research and Development Authority (Energy Authority) sponsored research at Syracuse University to ascertain whether reduced headspace pressure would be beneficial for the anaerobic

digestion of municipal wastewater sludges (Energy Authority Agreement No. 924-ERER-ER-87). This project, co-sponsored by the Onondaga County Department of Drainage and Sanitation and Syracuse University, used mixtures of primary and waste-activated sludges obtained from the Metropolitan Treatment Plant (Metro), Syracuse, NY as feedstock for bench-scale anaerobic sludge digestion experiments with reduced headspace gas pressures. The experiments were conducted with four small (1.5L), semi-continuous flow reactors with headspace gas pressures maintained at 0.50, 0.75, 0.83 and 1.00 atm, respectively.

The results of these preliminary experiments were promising, especially at the higher organic loading rates. Organic solids destruction, measured as total chemical oxygen demand (TCOD) removed and volatile suspended solids (VSS) destroyed, was substantially improved as a result of reduced headspace pressure operation for heavy organic loading conditions. Similarly, methane production, another indicator of solids destruction, was significantly enhanced (15-20 percent), as a result of vacuum operation. It was concluded that digester operation with a headspace pressure of 0.75 atm represented the "best" compromise headspace pressure for methane generation, organic destruction, digester engineering and economics. These results were published as Energy Authority Report 90-20, Reduced Gas Pressure Operation of Sludge Digestion.

Because the small size of the experimental reactors limited sample volume and collection frequency, errors inherent with VSS measurements were suspected and there was concern about the accuracy of the VSS destruction data. If the findings of these preliminary investigations could be substantiated at a larger scale, then an opportunity for significantly improving the anaerobic sludge digestion process will have been demonstrated. New digesters, especially egg-shaped digesters, could be designed for negative headspace pressure operation with minimal changes in capital costs.

Unfortunately, most existing cylindrical anaerobic digesters would collapse if subjected to a 0.75 atm headspace pressure. Structurally retrofitting these existing digesters to withstand negative pressures would probably not be cost effective. However, as shown

in Figure 1.1c, existing digester systems might be equipped for partial vacuum operation with small side-stream reactors for continuously degassifying a fraction of the digesting sludge and returning the degassified sludge to the main reactor. If proven practical from a process perspective, the addition of inexpensive, small, side-stream, vacuum reactors to existing anaerobic treatment systems might be economically feasible.

The need to test the vacuum anaerobic sludge digestion process at a larger scale in order to substantiate previous findings served as the primary impetus for this project. Testing the concept of retrofitting existing digester systems with small, side-stream reactors served as an additional impetus for this project.

GOALS AND OBJECTIVES

The primary goal of this work was to demonstrate the benefits attainable with vacuum anaerobic sludge digestion at a scale that would encourage construction and operation of prototype demonstration units. Based on the results of the earlier studies, enhanced volatile suspended solids destruction and methane generation rates on the order of ten to fifteen percent were anticipated. A second major goal for these expanded studies was to evaluate the effects of intermittent vacuum application on the sludge digestion process. Another major goal of this work was to determine how and why vacuum operation benefits the anaerobic sludge digestion process. Specific project objectives included;

1. Development of reactor systems suitable for modelling reduced headspace pressure operations for anaerobic sludge digestion under "steady state" conditions;
2. Operating these reactor systems for the organic and solids loading ranges that are representative of municipal sludge digestion systems;
3. Development, operation and evaluation of reactor systems that simulate intermittent vacuum digestion; and
4. Conducting small-scale batch experiments that would help define the controlling mechanism(s) involved in anaerobic digestion.

A. Traditional Anaerobic Digester with
1.02 atm Headspace Pressure

B. Reduced Headspace Pressure
(Vacuum) Anaerobic Digester

C. Intermittent Reduced Headspace
Pressure Anaerobic Digester

FIGURE 1.1

ANAEROBIC SLUDGE DIGESTER SYSTEMS STUDIED.

Section 2

RESEARCH PROGRAM

RESEARCH PLAN OVERVIEW

Reduced headspace pressure treatment must demonstrate superior performance for volatile suspended solids (VSS) destruction, chemical oxygen demand (COD) destruction and methane (CH_4) generation to be considered attractive as an alternative to current sludge digestion processes. Enhancement of these rates by ten to fifteen percent would more than offset the increased construction costs for digester structures ($\approx 2\%$) and the cost of maintaining reduced headspace pressure in reactors. In addition, the system may be able to operate under organic loading conditions that normally would be considered toxic or inhibitory to conventional sludge digestion processes thus allowing digestion of larger volumes of sludge. This section provides an overview of the experimental system and the research plan employed during the project to ascertain the performance characteristics of reduced headspace treatment.

In order to meet the goals and objectives described in Section 1, data were obtained from four independent anaerobic digestion systems, each operated under four different organic loading conditions (called phases) during the 563 day research program. Based on the earlier, small-scale investigations, it was anticipated that major benefits for reduced headspace operation would be observed for organic loading conditions higher than those commonly employed for municipal sludge digestion. Sludge feedstock for these experiments was derived from thickened primary and secondary sludge mixtures obtained from the Metropolitan Treatment Plant (Metro) in Syracuse, New York. The Phase 1 (base case) organic loading rate (used from days 78 through 220) was designed to be the same as the average organic loading rate used at the full-scale Metro anaerobic digesters during the first 77 days of the project. Following completion of detailed studies for characterizing steady-state reactor performance, the organic loading rate was doubled to initiate the Phase 2 as shown in Table 2.1. At the completion of the Phase 2 studies, the

TABLE 2.1 RESEARCH SCHEDULE							
PHASE	STEADY STATE PERIOD (days)	SRT (days)	TARGET FEED COD (g/L)	AVERAGE FEED COD (g/L)	AVERAGE FEED SS (g/L)	AVERAGE FEED VSS (g/L)	PCOD VSS
Start-up	0-77	15	---	34.97	28.86	21.97	1.54
1	181-210	15	35.0	35.02	26.11	18.89	1.68
2	355-384	15	70.0	69.68	54.00	41.44	1.57
3	508-537	15	105.0	105.39	84.62	59.83	1.68
4	538-563	10	105.0	105.79	78.91	57.98	1.61

organic loading rate was increased to three times that of the Phase 1 base case. The four reactors were maintained with 15-day solids retention times (SRTs) during start-up and the first three loading conditions (phases) tested. A 15-day value is the minimum SRT normally recommended for conventional anaerobic sludge digestion facilities. During Phase 4, the reactor SRTs were purposely reduced to 10 days to stress the four anaerobic systems. The Phase 4 organic loading rate was about 4.5 times that of the Phase 1 loading rate.

One reactor system, hereafter referred to as RS-1, was operated with the conventional anaerobic digester headspace pressure of 1.02 atm throughout the study and served as the experimental control reactor. Another identical reactor system (RS-4) was operated with the headspace pressure continuously maintained at 0.75 atm during the entire study. The remaining two reactors were operated with the 1.02 atm conventional headspace pressures for most of each day and with a 0.75 atm headspace pressure for one half hour (RS-2) and one hour (RS-3) per day, respectively.

REACTOR SYSTEMS

Four independent reactor systems were constructed and maintained in a controlled temperature room at 35°C. Each reactor system included three major components, the reactor, the headspace gas pressure control regulators and the vacuum reservoir. Ancillary support systems included an attachable feed/sampling system and a portable vacuum pump for periodically evacuating the vacuum reservoirs. The reactor systems are shown schematically in Figures 2.1 and 2.2.

The reactors were five gallon glass carboys that had been carefully calibrated to contain a volume of 18.00 L (± 0.05 L) of liquid reactants. Fifty glass marbles were placed in each reactor to aid in manual mixing of the contents. A glass feed/sampling tube and a gas collection tube passed through No. 12 stoppers that sealed each reactor from the atmosphere. During Phase 2 experiments, foaming problems made it necessary to add surge tanks to prevent foam from being carried over and fouling pressure gages and

Reactor

- A. Valve, on-off
- B. Feed-Sample extraction tube
- C. Surge tank for foam control
- D. Condensed foam removal line
- E. Valve, on-off
- F. Gas sampling port with septum
- G. Three-way valve
- H. Water manometer for Reactor System 1, pressure gage for Reactor System 4 replaces G and H
- I. Gas pressure regulator
- J. Valve, on-off
- K. Pressure gage
- L. Vacuum reservoir
- M. Valve, on-off

FIGURE 2.1 SCHEMATIC FOR REACTOR SYSTEMS 1 AND 4.

- A. Valve, on-off
- B. Feed-Sample extraction tube
- C. Surge tank for foam control
- D. Condensed foam removal line
- E. Valve, on-off
- F. Three-way valve
- G. Gas sampling port with septum
- H. Three-way valve
- I. Water manometer
- J. Gas pressure regulator for 1.02 atm operation
- K. Valve, on-off
- L. Pressure gage
- M. Vacuum reservoir for 1.02 atm operation
- N. Valve, on-off
- O. Gas pressure regulator for 0.75 atm operation
- P. Valve, on-off
- Q. Pressure gage
- R. Vacuum reservoir for 0.75 atm operation
- S. Valve, on-off

FIGURE 2.2 SCHEMATIC FOR REACTOR SYSTEMS 2 AND 3.

pressure controllers. These foam surge tanks consisted of one or two liter side arm flasks and generally proved to be effective for eliminating foam problems.

Reactor System One (RS-1) served as the experimental control reactor and was operated with the headspace pressure maintained at 1.02 atm (six inches of water pressure) throughout the study. The reactor headspace pressure was monitored daily by reading the water manometer (H on Figure 2.1). The pressure regulator (Cole Parmer L-00909 Vacuum Controller), was adjusted so that when the reactor headspace pressure exceeded 1.02 atm, the regulator valve (Part I on Figure 2.1) would open and excess gas would flow to the vacuum reservoir (Part L) until the headspace pressure was again equal to 1.02 atm.

The volume of each vacuum reservoir was determined to the nearest 0.21 percent (≈ 45 mL). At the beginning and ending of each cycle (approximately 24 hours), the vacuum reservoir pressure gage (Cole-Parmer No.L-07371-01), was read to the nearest 0.02 in. Hg, allowing calculation of the volume of gas collected during the cycle. Based on the sensitivity of the pressure gage (0.25%) and the volume of the reservoir, it is believed that the gas produced during steady state operations could be measured to at least the nearest ± 1.2 percent of the values reported.

Reactor System Four (RS-4) was similar to RS-1 except that valve G and the water manometer H (Figure 2.1) were replaced with a pressure gage. RS-4 was continuously operated with a reactor headspace pressure of 0.75 atm.

Reactor Systems 2 and 3 were similar to RS-1 and RS-4 with the exception that reactor headspace pressure could be changed from 1.02 atm to 0.75 atm (and back again) by manually changing a valve (H in Figure 2.2). RS-2 and RS-3 were operated with the reactor headspace pressure maintained at 0.75 atm for 0.50 and 1.00 hours per day, respectively and with a headspace pressure of 1.02 atm for the balance of the day.

Daily Reactor System Operations

Routine daily maintenance procedures were designed to sustain each reactor system in an appropriate operating mode (temperature, headspace pressure and SRT), and to provide liquid and gas samples for monitoring sludge digestion. These procedures were followed seven days per week, at about the same time each day. The procedures described below are for RS-1 and RS-4 (Figure 2.1). Similar procedures were employed for RS-2 and RS-3. The only major difference in the operating procedures for RS-2 and RS-3 was that valve H (Figure 2.2) would be changed so that the reactors would be operated with a 0.75 atm instead of a 1.02 atm headspace pressure for the appropriate period of time (0.5 or 1.0 hours). This change was made about four hours after feeding.

Daily Maintenance Procedures (RS-1 and RS-4)

1. Reactor temperatures were recorded and corrections to the room temperature controller were made if necessary. Each reactor headspace pressure was checked.
2. The vacuum reservoir (L on Figure 2.1) was isolated from the system by closing valve J. Pressure gage K readings were recorded.
3. The pressure regulator (I) setting was checked against the manometer (H) reading or a pressure gage (not shown) and adjusted if necessary.
4. A portable vacuum pump was used to evacuate the vacuum reservoir (L) to about 0.1 atm. Valve M was closed and pressure gage K reread and the value recorded.
5. The gas collection system was reset by opening valves G and J.
6. Next, the reactors were shaken vigorously until the marbles in the reactor could be heard freely swirling. This manual mixing process required one to five minutes, depending on the reactor solids concentration and viscosity. Immediately following mixing, an appropriate volume of reactor contents was removed by pumping through the feed-sample line (B) into a sample collection flask (not shown).

7. Fresh feed, equal in volume to the sample removed, was pumped into the reactor, the feed valves closed and the reactor again shaken vigorously to assure complete mixing.
8. Each reactor was shaken several times during the ensuing reaction cycle to encourage complete mixing conditions in the reactor.

FEED SLUDGE PREPARATION

Source

Raw Metro sludge was obtained two or three times per week from the underflow of one of the three thickeners at the Metropolitan Treatment Plant in Syracuse, New York (Metro). These thickener units were designed to concentrate the solids contained in mixtures of primary and waste-activated sludges prior to feeding Metro's three primary anaerobic digesters. Project sludges were usually obtained from the underflow of the thickener having the highest suspended solids concentration as indicated by on-line solids meters. Samples were collected in five-gallon carboys and transported to the laboratory within 15 to 20 minutes of collection.

Upon arrival at the laboratory, the sludges were sieved through a coarse screen (U.S.A. Standard Sieve No.10 - 2.00 mm, (0.0787 inches)), to provide a uniform material that would serve as a feedstock. Samples of the screened, raw "Metro Sludge" were obtained for determining TCOD, SCOD, SS, VSS, TS, VS and pH values. The screened Metro Sludge was stored in a cold room ($\approx 5^{\circ}\text{C}$) until used for daily feed preparation.

Raw Metro Sludge Variations

Raw Metro sludge characteristics varied significantly throughout the study as shown in Figures 2.3, 2.4, 2.5, and 2.6. These variations reflected both seasonal changes in the influent wastewater characteristics at Metro and operational changes at Metro. For example, seasonal variations in the influent Metro suspended solids concentration due to

peak spring run-off occurred around project days 135 and 520 and are reflected in the Metro thickened sludge data which can be observed in Figure 2.4. It is interesting to note that the VSS concentrations were reasonably constant while the inert portion of the SS increased significantly at these times. The annual operations shutdown at a major industrial contributor to Metro resulted in first extremely low and then extremely high TCOD, SCOD, SS and VSS concentrations in Metro thickened sludge around project day 250 (Figures 2.3 and 2.4). Operational changes for the thickeners (e.g. flowrates, coagulant type and concentration), are believed to have directly contributed to the significant increase in the Metro sludge TCOD and suspended solids concentrations observed during days 420 to 530 (Figure 2.3). Figure 2.5 illustrates that the raw sludge pH varied from a low of about 5.7 to a high near 6.9. The reason for the low pH values during days 250-350 is not known but may be related to Metro experiments with chemicals intended to enhance settling. Figure 2.6 shows that the energy content of the VSS, measured as the PCOD/VSS ratio, varied by about 20 percent during the study. The significance of this parameter will be discussed later in this section. Thus, the characteristics of thickened Metro sludges were constantly changing throughout the project. In order to perform effective research it was necessary to use a feed sludge having reasonably consistent characteristics from day to day.

Metro sludge analyses obtained during the first 77 days of the project were used to develop the initial feed characteristics and anaerobic sludge digester loading conditions used for this project. Because both methane production and solids destruction can be related to total chemical oxygen demand (TCOD) destruction and Metro raw sludge TCOD values could be obtained within a few hours of sludge collection, TCOD was chosen as the primary digester loading parameter for these studies. During the 77-day start-up period, the raw Metro sludges contained an average of about 35,000 mg/L TCOD, as indicated in Table 2.2. This TCOD concentration was used as the target TCOD concentration for the remainder of the Phase 1 studies.

The start-up period (days 0 to 76) proved to be atypical compared to raw sludge characterization data obtained during the remainder of the project. As shown in Table

FIGURE 2.3 RAW METRO THICKENER SLUDGE TCOD AND SCOD.

FIGURE 2.4 RAW METRO THICKENER SLUDGE SS AND VSS.

FIGURE 2.5 RAW METRO THICKENER SLUDGE pH.

FIGURE 2.6 METRO THICKENER SLUDGE ENERGY DENSITY, PCOD/VSS.

TABLE 2.2
AVERAGE METRO RAW SLUDGE CHARACTERISTICS

PERIOD	DAYS	TCOD (mg/L)	SCOD (mg/L)	TSS (mg/L)	VSS (mg/L)	PERCENT VOLATILE (%)	PCOD VSS	pH
Start-up	0-76	34966	1045	28863	21968	76.1	1.54	6.54
Phase 1 Steady State	181-210	40709	1893	31804	23300	73.3	1.68	6.26
Phase 2 Steady State	355-384	38430	2483	29899	22898	76.6	1.57	6.19
Phase 3 Steady State	508-537	49314	2441	40994	29276	71.4	1.60	6.24
Phase 4	538-563	41771	2533	33004	24532	74.3	1.61	6.17
Overall	0-563	40411	2034	32865	24168	73.5	1.59	6.29

2.2, average TCOD, SS and VSS values were substantially below those observed during later periods. Of special interest was the low value for the particulate COD/VSS ratio (1.54) during the start-up period. This parameter represents the energy density of the raw feed volatile solids. Low values for this ratio suggest that VSS constituents are present in a partially oxidized state and hence are less likely to be amenable to biodegradation (fermentation) than VSS having higher PCOD/VSS ratios. Sludges having higher PCOD/VSS ratios presumably will undergo more complete destruction and yield more methane per unit mass destroyed. Observations supporting this hypothesis will be presented in Section 3. As a result of low strength Metro sludge during the start-up period, the COD loading rates should have been about fifteen percent higher for the remainder of the study.

Table 2.2 presents average values for the raw sludges obtained at Metro during critical project study periods. All Metro sludge data are presented in Appendix B as Table B1.

Daily Feed Sludge Preparation

During Phase 1 (project days 77 to 210) it was seldom necessary to concentrate the sludge collected at Metro to achieve the target TCOD value of 35,000 mg/L. Usually the sludge would require dilution with supernatant. However, during Phases 2 and 3, when the target feed TCOD concentrations were 70,000 and 105,000 mg/L respectively, it became necessary to concentrate raw Metro sludge solids to attain the desired feed TCOD concentrations. Attempts to utilize gravitational settling and several forms of membrane filtration for concentrating raw Metro sludge failed. It proved necessary to develop and use a batch centrifugation process to prepare feedstocks with the appropriate TCOD concentrations for Phases 2, 3, and 4.

On a daily basis, during Phases 2 and 3, sieved Metro sludge was poured into 500 ml. plastic bottles, and centrifuged in a Marathon 10K Centrifuge at 3,000 rpm (~ 2200g) for 12 minutes. The supernatant was poured off into a graduated cylinder, measured and retained for further use. The compressed sludge "pellet" was removed from the bottle

and transferred to a five gallon storage container. The process was repeated until a known volume of raw Metro sludge (12-18L) had been separated into the two phases. The percent volume of supernatant removed from the raw Metro sludge by centrifugation was recorded. Both supernatant and thickened sludge were stored at $\sim 5^{\circ}\text{C}$ until needed. The centrifuged sludge solids were deliberately "over-thickened" so that the TCOD exceeded the target feed concentration. Based on the total and soluble COD values determined for the raw Metro sludge and the measured volume of the centrifuged raw sludge "pellet", it was possible to estimate the amount of supernatant to be added back to the concentrated sludge solids to attain a feed sludge having the desired TCOD value.

Fresh feed was prepared daily. Samples of the feed were taken daily and analyzed for TCOD, SCOD and other parameters. Both the target TCOD and the average TCOD concentrations fed to the reactors for each phase are shown in Table 2.1.

ANALYTICAL MEASUREMENTS AND PROCEDURES

Growth and substrate removal kinetics for anaerobic treatment systems are difficult to measure, define and predict, compared to aerobic treatment systems. This is due to inherently slow microbial growth rates and the complex interactions between the different species of microorganisms involved. Slow growth rates make the establishment of "steady state" conditions time consuming and difficult to verify experimentally. For the purposes of this work, "steady state" conditions were achieved when day-to-day changes in any parameter were consistently less than $\pm$ five percent around a mean value for a period of at least two SRTs (30 days).

A specific volume of reactor liquor was removed daily and analyzed for the constituents shown in Table 2.3. An equal volume of feed containing the target TCOD concentration shown in Table 2.1 was introduced to the reactor in order to maintain the desired SRT. It was assumed that a once-per-day feeding regime followed by vigorous mixing would closely approximate a continuous flow reactor system for the 15-day SRTs employed in Phases 1, 2 and 3. One of the special studies, described in a subsequent section,

TABLE 2.3
REACTOR SAMPLING SCHEDULE

PARAMETER	FEED			REACTOR			OFF-GAS		
	Daily	Intermittent days	Daily Steady State	Daily	Intermittent Days	Daily Steady State	Daily	Intermittent Days	Daily Steady State
TCOD	••	--	--	•	--	--	--	--	--
SCOD	•	--	--	•	--	--	--	--	--
TS	•	--	--	•	--	--	--	--	--
TVS	•	--	--	•	--	--	--	--	--
TSS	•	--	--	•	--	--	--	--	--
TVSS	•	--	--	•	--	--	--	--	--
pH	•	--	--	•	--	--	--	--	--
NH ₃ -N	--	•	•	--	•	•	--	--	--
S ²⁻	--	--	--	--	•	•	--	--	--
Alkalinity	--	--	--	--	--	--	--	--	--
Volatile Acids (GC)	--	--	•	--	--	--	--	--	--
Volatile Acids (titration)	--	--	•	--	•	•	--	--	--
Gas Volume Produced	--	--	--	--	--	--	•	--	--
CH ₄ percent	--	--	--	--	--	--	•	--	--
CO ₂ percent	--	--	--	--	--	--	•	--	--
H ₂	--	--	--	--	--	--	•	•	•

1. GC analyses during Phases 1 and 2 only.
2. Titration analyses during Phases 2, 3 and 4
3. Intermittent means every other day or daily for part of a non-steady state period
4. Astrisks (•) indicate sampling frequency.

evaluated this assumption.

When the feed, reactor and off-gas analyses shown in Table 2.3 suggested that a reactor system was at or approaching steady state, the complete set of analyses shown in the Daily Steady State columns in Table 2.3 was begun. The analytical methods used for the analyses shown in Table 2.3 are described in Appendix A and the data presented in Appendix B represent the average of three replicate analyses for most parameters (exceptions were pH, alkalinity, ammonia nitrogen and sulfides).

Daily measurements of the parameters shown in Table 2.3 permitted calculations of COD and solids destruction rates as well as methane generation rates. These derived data served as the basis for comparing reactor performance under identical loading conditions.

SPECIAL STUDIES - METHODS

A series of "special" or side studies were conducted during the project to further investigate vacuum and conventional anaerobic sludge digestion. The first set of side studies involved intensive 24-hour gas production monitoring of the four reactors during each of the three steady-state periods. Other special studies used repetitive series of small batch reactors (120 mL serum bottles) to investigate a variety of conditions. The small batch reactors (Figure 2.7) were operated at 35°C with either a conventional (1.02 atm) headspace pressure or under a continuous (0.75 atm) reduced headspace pressure anaerobic digestion mode. Feed (if used) was added as 1/15 of the total liquid volume to simulate an initial SRT of 15 days. Mixing was provided by either a reciprocating mechanical mixer (considered to be continuous gentle mixing) or by manually shaking the serum bottles (considered to be a periodic intense mixing). Gas production was measured using a glass syringe for small volumes of gas (less than 100 mL) or by bleeding the gas into an inverted graduated cylinder filled with water (for gas volumes greater than 100 mL).

The first batch reactor experiments were used to investigate the response of Phase 1 digester sludge to an extended range of feed TCOD concentrations. The batch reactors were operated at 1.02 atmospheres and manually shaken. The batch reactors were kept in the temperature control room to assure that a constant temperature of 35° C was maintained.

A second set of batch reactor experiments was conducted to compare vacuum and conventional anaerobic sludge digestion as a function of feed TCOD loading and system mixing intensities. The batch reactor systems were constructed as illustrated in Figure 2.7. The continuously mixed batch reactors were maintained at 35°C using a water bath-shaker unit. The periodically mixed batch reactors were maintained at 35°C in an incubation oven.

The original research plan included a series of batch reactor experiments designed to evaluate the effects of vacuum operation on pH-stressed systems. These experiments proved unnecessary since pH, alkalinity, volatile acid alkalinity, molecular hydrogen and ammonia nitrogen values never exceeded normal operating values in the continuous flow reactors, even during heavily-stressed Phase 4 conditions. Each of these parameters are described in Section 3.

Phase 3 batch reactor side studies were used to compare vacuum (0.75 atm) to conventional anaerobic sludge digestion as a function of time. The batch reactors were mixed using the reciprocating mechanical shaker with the temperature maintained at 35°C using a water bath. The final series of batch reactor experiments was used to investigate the "endogenous decay" of Phase 3 digester sludge. The reactors were operated at 1.02 atmospheres and manually shaken. The temperature was maintained by placing the reactors in the temperature control room.

EXPERIMENTAL DIFFICULTIES

Several significant problems occurred during these studies that deserve special mention.

FIGURE 2.7 **SMALL SCALE BATCH
REACTOR SYSTEM.**

First, aperiodic air leaks into the reactor systems were both suspected and observed during the first 120 days of the project. Many corrective actions were attempted, but none was completely satisfactory until all glass valving was replaced with teflon valving on day 123. Thereafter the four systems were deemed to be air tight, long before the first two SRT "steady state" measurements were begun.

Reactor System One, the 1.02 atm control system, exploded on day 214. Severe foaming within the four reactors had been observed shortly after the Phase 2 studies (with the 70,000 mg/L TCOD feed) were initiated. The explosion was attributed to the build up of headspace gas pressure when foam transported solids plugged the gas lines. Based on subsequent gas production data, it is estimated that the headspace pressure may have reached four to five atm when the reactor vessel failed. Reactor System 2 was immediately converted to the new control reactor system by eliminating the one half hour per day vacuum period. A new RS-2 system was constructed seeded with excess sludge from the remaining three reactors and brought into operation over the next two weeks.

Excessive foaming became a significant problem for all four reactors during Phase 2. Corrective measures, in addition to repeatedly cleaning the lines and valves, consisted of adding surge tanks ahead of the pressure regulators to catch and trap the foam. While the installation of the surge tanks helped, it wasn't until the active reactor volume was reduced from 18 L. to 15 L. on day 285 that the problem was solved. The 3L increase in reactor headspace allowed for foam development without excessive carryover. This, of course, necessitated changing the sample and feed volumes in order to maintain a 15-day SRT. Additional foaming problems occurred during Phase 3 and were corrected in a similar manner before the "steady state" data were obtained.

Extreme problems with the gas chromatograph used for measuring reactor volatile acids were experienced during the project. Repeated service calls failed to rectify the problem and the GC failed permanently on day 406. Although not as precise, wet chemistry volatile acid alkalinity measurements were used for estimating volatile acids during the remainder of the project. Since the concentrations of volatile acids in the reactors never

approached levels reported to be inhibitory or toxic by the literature, the use of volatile acid alkalinity in lieu of specific volatile acid determinations was deemed appropriate for the purposes of the project.

CALCULATIONS

The data collected according to the schedule shown in Table 2.3 were processed using the equations presented in Table 2.4. All input data are shown in Appendix B. Daily data and information obtained from periods of "steady state" operation were averaged and are reported and described in Section 3.

TABLE 2.4
CALCULATIONS AND CONSTANTS

The following equations and constants were used to evaluate and compare experimental results. The subscript R implies a measurement of the reactor contents and the subscript Fd implies a feed characteristic. V_r is the reactor liquid volume (L) and the solids retention time (SRT) is in days. The subscript t indicates a measurement at time zero and t + 1 indicates the next measured value for the same parameter. All TCOD, SCOD, VSS and SS values are in units of g/L and are reported in Appendix B.

1. TCOD DESTROYED (g/d)

$$\text{TCOD destroyed} = [((V_R - V_R/SRT) \times \text{TCOD}_{R@t}) + ((V_R/SRT) \times \text{TCOD}_{Fd@t})] - [V_R \times \text{TCOD}_{R@t+1}]$$
2. SCOD DESTROYED (g/d)

$$\text{SCOD destroyed} = [((V_R - V_R/SRT) \times \text{SCOD}_{R@t}) + ((V_R/SRT) \times \text{SCOD}_{Fd@t})] - [V_R \times \text{SCOD}_{R@t+1}]$$
3. SUSPENDED SOLIDS DESTROYED (g/d)

$$\text{SS destroyed} = [((V_R - V_R/SRT) \times \text{SS}_{R@t}) + ((V_R/SRT) \times \text{SS}_{Fd@t})] - [V_R \times \text{SS}_{R@t+1}]$$
4. VOLATILE SUSPENDED SOLIDS DESTROYED (g/d)

$$\text{VSS destroyed} = [((V_R - V_R/SRT) \times \text{VSS}_{R@t}) + ((V_R/SRT) \times \text{VSS}_{Fd@t})] - [V_R \times \text{VSS}_{R@t+1}]$$

TABLE 2.4 (Continued)
CALCULATIONS AND CONSTANTS

5. PERCENT SUSPENDED SOLIDS REDUCTION^a

$$X = \frac{(1 - VSS_{Fd_{\theta t}} / SS_{Fd_{\theta t}})}{(1 - VSS_{R_{\theta t+1}} / SS_{R_{\theta t+1}})} - (1 - VSS_{Fd_{\theta t}} / SS_{Fd_{\theta t}})$$

$$\% \text{ SS reduction} = [(VSS_{Fd_{\theta t}} / SS_{Fd_{\theta t}}) - x] \cdot 100$$

where VSS/SS ratios are expressed in decimal form.

6. PERCENT VOLATILE SUSPENDED SOLIDS REDUCTION

$$\% \text{ VSS reduction} = [(VSS_{Fd_{\theta t}} / SS_{Fd_{\theta t}} - x) / (VSS_{Fd_{\theta t}} / SS_{Fd_{\theta t}})] \cdot 100$$

where x is calculated as shown in Equation 5

TABLE 2.4 (Continued)
CALCULATIONS AND CONSTANTS

7. TOTAL GAS PRODUCED

Given T_1 = Temperature ($^{\circ}$ K) at pressure reading P_1 , assumed constant for period P_o to P_1 .

P_o = pressure reading (in. Hg) at time zero

P_1 = next measured pressure reading (in. Hg)

V = volume of gas reservoir in L.

<u>Collection Vessel</u>	<u>Volume (L)</u>	<u>Collection Vessel</u>	<u>Volume (L)</u>
Reactor 1 (1.02 atm)	21.833	Reactor 3 (1.0 hr 0.75 atm)	22.113
days 0-214		1.02 atm	9.510
days 215-564	22.106	0.75	
Reactor 2 (0.5 hr 0.75 atm)		Reactor 4 (0.75 atm)	22.228
days 0-214	22.106	days 0-30	35.712
days 218-564	21.833	days 31-564	
0.75 atm	9.978		

TABLE 2.4 (Continued)

CALCULATIONS AND CONSTANTS

From the Ideal Gas Law $PV = nRT$
Gas collected in reservoir (L)

$$G_R = V \frac{(P_1 - P_o)}{T_1} * 9.129$$

Total Gas Produced (L)
Reactor 1, 4
Reactor 2, 3

$$\begin{aligned} TGP &= G_R \\ TGP &= G_{R_{1.02}} + G_{R_{0.75}} \end{aligned}$$

8. THEORETICAL METHANE PRODUCTION^b

0.35L CH₄ @ STP per g TCOD destroyed

9. VOLATILE ACID-ALKALINITY RATIO

$$VA/ALK'Y = \frac{\text{Total volatile acids as acetic acid, mg/L}}{\text{Total alkalinity as CaCO}_3, \text{ mg/L}}$$

TABLE 2.4 (Continued)

CALCULATIONS AND CONSTANTS

10. PERCENT TCOD DESTROYED (%)

$$(\%) \text{ TCOD destroyed} = (\text{TCOD}_t - \text{TCOD}_{t+\tau}) \times 100 / \text{TCOD}_t$$

11. PERCENT VSS DESTROYED (%)

$$(\%) \text{ VSS destroyed} = (\text{VSS}_t - \text{VSS}_{t+\tau}) \times 100 / \text{VSS}_t$$

- a. Metcalf and Eddy, Wastewater Engineering: Treatment, Disposal, Reuse, 2nd Ed., McGraw Hill 1979, pp. 618-619.
- b. Ibid, pg. 614

Section 3

EXPERIMENTAL RESULTS

Four independent anaerobic sludge digester systems were operated for more than 560 days to test the effects of continuous and intermittent reduced headspace pressure on solids destruction and methane generation. Organic and volumetric feed loads bracketing the solids and TCOD loads commonly used in municipal sludge digestion were tested in these studies. During most of the study (through day 538), the reactors were operated with a 15-day SRT. In general, the results were disappointing since no significant differences between the performance of the four reactors under any of the conditions tested were observed. This section presents an overview of the experimental results. All operating data are summarized and presented in Appendix B.

The following subsection describes response patterns that were common to the four reactor systems during the study. Succeeding subsections will describe results that are specific to each reactor as a function of the organic loading condition tested.

COMMON PATTERNS

Feed

Figures 3.1 through 3.4 illustrate the consistency of several feed characteristics during the project. Wide variations in day to day Metro feed characteristics occurred during the initial 76 days of start-up and are readily apparent in these four figures. The average TCOD concentration of the thickened sludge fed to Metro's anaerobic digesters during the start-up period was 34,966 mg/L. Therefore, 35,000 mg/L was chosen as the initial feed TCOD target for these studies. During Phase 1 (days 77 through 210), the feed TCOD concentration averaged 35,147 mg/L, very close to the target value of 35,000 mg/L. Similarly, the average TCOD concentrations during Phase 2 (70,595 mg/L for days 211 through day 384), and Phase 3 (105,232 mg/L during day 385 through day 537), were quite close to the target values of 70,000 mg/L and 105,000 mg/L, respectively. The more notable variations in suspended solids (Figure 3.2), volatile suspended solids (Figure 3.3), and total solids (Figure 3.4) concentrations reflect the variable nature of municipal treatment plant sludges.

Differences in the basic chemical characteristics of Metro sludge with time are shown in Figure 3.5 where the ratio of the concentration of particulate chemical oxygen demand (PCOD) to volatile suspended solids (VSS) is plotted against time. Higher values of this ratio indicate greater energy density of the organic solids. The ratio varied from a low

FIGURE 3.1 FEED SLUDGE TCOD AND SCOD.

FIGURE 3.2 FEED SLUDGE SUSPENDED SOLIDS.

FIGURE 3.3 **FEED SLUDGE VOLATILE SUSPENDED SOLIDS.**

FIGURE 3.4 FEED SLUDGE TOTAL SOLIDS.

FIGURE 3.5 ENERGY DENSITY OF FEED VOLATILE SUSPENDED SOLIDS.

of about 1.37 near the beginning of the project to a high of 2.0 during Phase 2. Since feed was prepared on a constant TCOD basis, a high value for this parameter corresponds to a relatively low value of feed VSS concentration.

Overall Performance

Inhibitory or toxic conditions for anaerobic digestion processes result in the reduction of VSS destruction and methane generation rates. Classical symptoms of inhibitory or toxic conditions resulting from organic overloading include abnormal pH ($\text{pH} < 6$ or $\text{pH} > 8$), decreasing alkalinity, high levels of ammonia nitrogen and/or sulfides along with rapid increases of CO_2 and H_2 in the off-gases. As described in the following subsections, these symptoms were not observed except as infrequent "blips" during the transition between loading rates. The four reactor systems were not loaded to failure during these studies and hence it is impossible to state definitively whether reduced headspace pressure operation would have ameliorated the toxic or inhibitory mechanisms associated with process overloading.

Cumulative TCOD and VSS destruction along with cumulative CH_4 generation are shown in Figures 3.6, 3.7 and 3.8. Because the cumulative values for each of these parameters for the four reactors are nearly identical, it can be concluded there was little difference in anaerobic treatment as a function of headspace pressure manipulation over the range of parameters tested. Although the differences (less than five percent) are insignificant from an engineering perspective, the data ordered themselves such that RS-4, the 0.75 atm reactor, demonstrated slightly better performance than the remaining three reactors for methane production and solids destruction. The sharp changes in the slopes on these figures are primarily due to changes in the influent feed concentration (days 211 and 384) and changes in reactor liquid volumes (days 285 and 538).

The data shown in Figures 3.6 and 3.7 indicate that TCOD and VSS destruction rates were slightly higher during Phase 1 than during the start-up period despite essentially identical average loading conditions. This may have been due to a somewhat more biodegradable raw metro sludge during Phase 1 as indicated by the higher PCOD/VSS ratio shown in Table 2.2.

Alkalinity And pH

Figure 3.9 illustrates pH values for RS-1, RS-4 and the daily feed. Feed pH variations were a function of the raw Metro sludge pH, the degree of concentration of the Metro sludge and the sludge storage time prior to feeding. The pH in RS-4 was generally 0.1

FIGURE 3.6 CUMULATIVE TCOD DESTRUCTION.

FIGURE 3.7 CUMULATIVE VOLATILE SUSPENDED SOLIDS DESTRUCTION.

FIGURE 3.8 CUMULATIVE METHANE PRODUCTION.

FIGURE 3.9 DAILY pH VALUES FOR FEED, RS-1 AND RS-4.

FIGURE 3.10 ALKALINITY FOR RS-1 AND RS-4.

to 0.2 units higher than in RS-1, probably as a result of CO₂ stripping under constant vacuum. The pH values of RS-2 and RS-3 were about the same as those observed for RS-1.

There was no appreciable difference in alkalinity (measured as CaCO₃) between RS-1 and RS-4 (Figure 3.10). Interestingly, both pH and alkalinity tended to rise as the organic loading was increased. Both increases would be useful if digester supernatant is to be nitrified prior to discharge to a receiving water.

Volatile Acids And Molecular Hydrogen

High reactor concentrations of volatile acids and high concentrations of molecular hydrogen in the product gases are usually indicative of ensuing methanogenic process failures. Based on the gas chromatograph volatile acids data obtained during Phases 1 and 2 and the volatile acid alkalinity data obtained during Phases 2 and 3, it does not appear that the reactors were ever operating near critical volatile acid concentrations (10,000 mg/L of acetic or butyric acid and/or 1000 mg/L for propionic acid at near-neutral pH's).

Figures 3.11 through 3.13 present volatile acid alkalinity data for days 270 through 560. The surges in volatile acids occurring near days 270, 390 and 540 were in response to rapid feed changes (Figures 3.1, 3.2, 3.3). The surges in volatile acids observed near days 260-280 occurred as a result of feed preparation errors on days 249 and 250 that occurred simultaneously with significant changes in the characteristics of the raw Metro sludge (Figures 3.1 through 3.5). The volatile acid peaks occurring near days 390 and 540 were in response to programmed feed changes on days 385 and 538.

Comparison of volatile acid data measured both by titration and gas chromatographic techniques for specific volatile acids during days 390 through 405 indicate that almost all of the volatile acid alkalinity spikes observed on Figures 3.11 through 3.13 are due to increases in acetic acid. It should be noted that RS-4, the 0.75 atm reactor, was least affected and that the two intermittent vacuum reactors were most affected by the rapid feed changes.

The susceptibility of an anaerobic process to volatile acid toxicity is frequently gauged by the ratio of volatile fatty acids (VFA reported as mg/L acetic acid) to the alkalinity (reported as mg/L CaCO₃). A limiting value of 0.4 is commonly used as an acceptable operating ratio. Higher values, approaching 1.0, suggest that the buffering system will be overwhelmed with hydrogen ions and that low pH will become a severe operating

FIGURE 3.11 VOLATILE ACID ALKALINITY, RS-1 (a) AND RS-2 (b).

FIGURE 3.12 RS-3 VOLATILE ACID ALKALINITY.

FIGURE 3.13 RS-4 VOLATILE ACID ALKALINITY.

FIGURE 3.14 HEADSPACE HYDROGEN CONCENTRATION AT 1.02 ATM (RS-1).

FIGURE 3.15 HEADSPACE HYDROGEN CONCENTRATION AT 0.75 ATM (RS-4).

problem as the VFA concentrations increase. The VFA/Alkalinity ratio did not exceed 0.1 during any of the steady-state periods investigated and hence VFA toxicity was not a problem.

Rapid changes in the concentration of molecular hydrogen (H_2) in digester off-gases can serve as a warning that volatile acids are accumulating more rapidly than they can be processed. While the H_2 levels measured during this study were well below levels of concern (about 1000 mg/L), the data shown in Figures 3.14 and 3.15 for RS-1 and RS-4 seem to suggest minor increases in H_2 that were concurrent with the volatile acid spikes observed in Figures 3.11, 3.12 and 3.13.

Ammonia Nitrogen And Sulfides

The destruction of proteins and other organic molecules in municipal sludges results in the release of ammonia and sulfides to solution, both of which can be inhibitory or toxic to anaerobic systems at high concentrations. As shown on Figures 3.16 and 3.17, solution ammonia-nitrogen levels approached 2500-3000 mg/L as a result of solids destruction during Phase 3. Although unlikely, some minor methane inhibition due to ammonia toxicity may have occurred at the slightly alkaline pHs (7.7-7.9) observed during Phase 3. As long as the total ammonia concentration stays below 3000 mg/L at near neutral pHs, the literature indicates that little or no inhibition will occur. This will be discussed further in a subsequent section. The NH_3 -N patterns in RS-1 and RS-4 were essentially identical although lower levels of ammonia might have been expected in RS-4 as a result of vacuum stripping of ammonia at the slightly alkaline pHs in the reactors.

Sulfide concentrations were well below inhibitory levels (100-200 mg/L as S^{2-}) throughout the entire study and reactor sulfide patterns were essentially identical for all four reactors. Figure 3.18 presents sulfide data for RS-1 and RS-4. Sulfide concentrations increased slightly as the mass loading and organic destruction rates increased from Phase 1 through Phase 3. Reduced solids destruction rates during Phase 4 resulted in lower sulfide concentrations in the reactors.

PHASE 1 RESULTS

Phase 1 activities were designed to test the four anaerobic reactor systems with organic loading conditions that were the same as those being used at Metro. The anaerobic digesters at Metro were designed for use with a 15-day SRT and the experimental systems were operated with 15-day SRTs throughout Phase 1. During the first 76 days

FIGURE 3.16 AMMONIA NITROGEN AT 1.02 ATM (RS-1).

FIGURE 3.17 AMMONIA NITROGEN AT 0.75 ATM (RS-4).

FIGURE 3.18 SULFIDE CONCENTRATIONS IN RS-1 AND RS-4.

FIGURE 3.19 FEED AND RS-1 TCOD CONCENTRATION DURING PHASE 1

of the project, the thickened sludge fed to the Metro anaerobic digesters averaged about 35 g/L TCOD. This value was used as the "target" for preparing the daily feed sludge used during days 77 through 210. As shown on Figures 3.1 and 3.19, the feed sludge preparation procedures employed were suitable for producing the desired feed TCOD concentration throughout Phase 1.

The microorganisms in each of the four reactor systems took much longer than anticipated to acclimate and approach "steady state" conditions. Data from RS-1 will be used to illustrate the slow approach to steady state conditions. Almost identical patterns were observed for the other three reactors. Daily data for each of the four systems can be found in Appendix B. Figure 3-19 demonstrates the slow decline of reactor TCOD values from about 21,000 mg/L on day 77 to an average of about 18,700 mg/L during the 30 day (2 SRT) "steady state" period (days 181 through 210). A similar decay pattern was observed for SCOD (Figure 3-20) with values declining from about 1180 mg/L to an average of 760 mg/L. Volatile suspended solids (Figure 3-21), total gas production (Figure 3-22) and daily methane production (Figure 3-23) also required a disappointing long period of time, approximately 100 days, to approach steady state.

Phase 1 steady state conditions began on project day 181 and lasted through day 210. Average values for feed and reactor system parameters during the 30 day period are presented in Table 3.1. Each reactor system was loaded with about 42g TCOD, 31g SS and 23g VSS per day. Although these loads simulated the actual loading at Metro during days 1-76, they are light loads by most anaerobic digester loading standards. For example, feed for high rate municipal digesters will typically contain 4 to 6 percent suspended solids in contrast to the 2.6 percent used during the Phase 1 steady state period. The volatile solids loading factor was about 0.088 lb/ft³·d, well below the typical 15 day SRT municipal digester loading range of 0.13 to 0.16 lb/ft³·d for 4 and 6 percent SS with a 15 day SRT.

As shown in Table 3.1, the four reactors yielded essentially identical performance regardless of headspace pressure conditions. The only exception was the unusually high volatile acid/alkalinity ratio of 0.06 for RS-1. This is thought to be an artifact of the way the acids were measured and is of little consequence since levels of concern occur only when this ratio exceeds 0.4.

PHASE 2 RESULTS

The primary purpose of the Phase 2 work was to investigate the effects of vacuum operation for organic loading conditions that were significantly higher than those

FIGURE 3.20 PHASE 1 SCOD VALUES FOR RS-1.

FIGURE 3.21 FEED AND RS-1 VSS CONCENTRATIONS DURING PHASE 1.

FIGURE 3.22 TOTAL GAS PRODUCTION FOR RS-1 DURING PHASE 1.

FIGURE 3.23 RS-1 METHANE PRODUCTION DURING PHASE 1.

TABLE 3.1
PHASE 1 STEADY STATE DATA¹
DAYS 181 to 210

PARAMETER	REACTOR				FEED ²
	1	2	3	4	
1. TCOD (g/L)	18.70	18.52	18.32	18.87	35.02
2. SCOD (g/L)	0.76	0.68	0.67	0.70	4.24
3. TCOD destroyed (g/L-d) ³	1.11	1.08	1.12	1.08	
4. SCOD destroyed (g/L-d)	0.24	0.24	0.24	0.23	
5. SS (g/L)	17.72	17.62	17.56	17.88	26.11
6. SS destroyed (g/L-d)	0.55	0.56	0.57	0.56	
7. VSS (g/L)	10.29	10.28	10.22	10.46	18.69
8. VSS destroyed (g/L-d)	0.58	0.57	0.59	0.57	
9. VSS/SS (%)	58.1	58.4	58.2	58.5	76.0
10. Percent SS reduction (%)	34.0	33.6	33.9	33.4	
11. Percent VSS reduction (%)	47.0	46.4	46.8	46.1	
12. TS (g/L)	19.12	19.06	19.02	19.23	28.28
13. VS/TS (%)	58.1	58.1	58.1	58.8	74.8
14. Total gas produced (L/L-d)	0.69	0.70	0.69	0.71	
15. CH ₄ produced (L/L-d)	0.46	0.46	0.45	0.47	
16. Percent CH ₄ (%)	67.3	66.8	66.5	67.1	
17. H ₂ (ppm)	202	197	215	179	
18. CH ₄ /TCOD destroyed (L/g)	0.42	0.42	0.41	0.44	
19. CH ₄ /VSS destroyed (L/g)	0.80	0.80	0.77	0.83	
20. VFA/Alkalinity (mg/mg)	0.06	0.02	0.01	0.01	
21. pH	7.39	7.39	7.39	7.50	6.32
22. NH ₃ -N (mg/L)	902	894	917	894	
23. S ⁻ (mg/L)	9.77	10.03	9.81	10.09	

1. The values shown are averages for the 30 day period.

2. 1.00L of sample were removed and replaced with fresh feed daily to maintain 15 day SRT

3. Total volume of reactor contents = 18.00L

employed for the "base case" Phase 1 study. Phase 2 began on day 211 when the target feed TCOD was doubled from 35,000 mg/L to 70,000 mg/L as shown on Figure 3.1. It was anticipated that this drastic step feed change would stress each of the four reactor systems and allow for a comparison of reduced headspace pressure effects on recovery patterns.

Volatile acid, molecular hydrogen and ammonia nitrogen all increased in response to the rapid doubling of the feed TCOD concentration as shown in Figures 3.11 through 3.17. However, the pH in the four reactors did not decrease as anticipated (Figure 3.9). The rapid change in feed strength resulted in the almost immediate generation of excessive quantities of foam in all four reactors. As previously described, this resulted in repeated plugging of gas lines and the explosion of one of the reactors. By day 300, following the installation of foam surge tanks and the reduction of the reactor liquid volumes from 18L to 15L, the foam problem was controlled.

The four reactors yielded almost identical TCOD, SS and VSS destruction patterns during Phase 2. Figures 3.24, 3.25 and 3.26 illustrate these patterns using RS-4 data. Figure 3.24 illustrates an almost ideal pattern for a step feed increase to a completely mixed reactor, with the peak TCOD concentration occurring about three SRTs following the change (day 256). A slow decrease in TCOD concentration occurred from a peak value of 48g/L to about 39g/L over the next 100 days. A similar decay pattern was observed for suspended solids (Figure 3.26).

Phase 2 steady state conditions were assumed to exist from days 355 through 384 when reactor operating parameters varied by less than ± 5 percent around a mean value for the two SRT period. Average operating data for the four reactors during this period are presented in Table 3.2. Daily data for the entire period can be found in Appendix B.

During the Phase 2 steady state operating period, the feed strength averaged about 70g/L TCOD, 54g/L SS and 41 g/L VSS (Table 3.2). These values are typical for municipal anaerobic digester loadings and the calculated volatile solids loading factor of 0.172 lb/ft³·d is identical with that recommended for design with a 15 day SRT.

The data in Table 3.2 indicate that the four reactors provided essentially identical treatment results during the Phase 2 steady state period. Therefore, it can be concluded that there are no significant benefits to be gained by operating anaerobic digesters at a headspace pressure of 0.75 atm under typical municipal digester loading conditions.

FIGURE 3.24 PHASE 2 FEED AND RS-4 TCO CONCENTRATION.

FIGURE 3.25 PHASE 2 FEED AND RS-4 TOTAL SUSPENDED SOLIDS CONCENTRATION.

FIGURE 3.26 PHASE 2 FEED AND RS-4 VOLATILE SUSPENDED SOLIDS CONCENTRATIONS.

TABLE 3.2
PHASE 2 STEADY STATE DATA¹
DAYS 355 to 384

PARAMETER	REACTOR				FEED ²
	1	2	3	4	
1. TCOD (g/L)	38.30	37.93	38.13	38.91	69.68
2. SCOD (g/L)	2.51	2.43	2.46	2.70	6.30
3. TCOD destroyed (g/L-d) ³	2.15	2.14	2.10	2.10	
4. SCOD destroyed (g/L-d)	0.25	0.26	0.25	0.23	
5. SS (g/L)	36.17	35.68	35.27	35.60	54.00
6. SS destroyed (g/L-d)	1.24	1.26	1.28	1.28	
7. VSS (g/L)	23.07	22.58	22.28	22.54	41.44
8. VSS destroyed (g/L-d)	1.25	1.27	1.29	1.31	
9. VSS/SS (%)	63.8	63.3	63.2	63.3	76.7
10. Percent SS reduction (%)	35.8	36.7	36.9	36.6	
11. Percent VSS reduction (%)	46.7	47.8	48.1	47.7	
12. TS (g/L)	37.39	37.03	36.86	37.17	55.75
13. VS/TS (%)	64.4	64.1	64.0	64.2	
14. Total gas produced (L/L-d)	1.38	1.39	1.40	1.45	
15. CH ₄ produced (L/L-d)	0.90	0.91	0.92	0.91	
16. Percent CH ₄ (%)	64.9	65.5	65.6	62.5	
17. H ₂ (ppm)	140	148	163	164	
18. CH ₄ /TCOD destroyed (L/g)	0.42	0.42	0.44	0.43	
19. CH ₄ /VSS destroyed (L/g)	0.72	0.71	0.72	0.69	
20. VFA/Alkalinity (mg/mg)	0.05	0.05	0.05	0.05	
21. pH	7.48	7.51	7.52	7.59	6.00
22. NH ₃ -N (mg/L)	1738	1822	1844	1816	273
23. S [*] (mg/L)	21.72	20.69	21.19	22.46	

1. The values shown are averages for the 30 day period.
2. 1.00L of sample were removed and replaced with fresh feed daily to maintain the 15 day SRT
3. Total Volume of reactor contents = 15.00L

PHASE 3 RESULTS

The Phase 3 work was initiated to evaluate the effects of vacuum operation under organic loading conditions that were substantially higher than those commonly employed for anaerobic sludge digestion. Phase 3 began on day 385 when the feed TCOD concentration was increased from about 70,000 mg/L to about 105,000 mg/L - about three times the concentration fed the Metro digesters during the start-up period. A one day step change was again used in anticipation that one or more of the microbial systems would be stressed significantly. As in Phase 2, only relatively minor changes were observed for pH, volatile acids and molecular hydrogen concentrations (Figures 3.9 through 3.15). However, as shown on Figures 3.16 and 3.17 the ammonia nitrogen concentrations were approaching levels considered to be inhibitory, about 3000-3500 mg/L of $\text{NH}_3\text{-N}$ at pH 7.0. Each of the four digestion systems responded with almost identical patterns for all parameters during Phase 3.

Both feed preparation and the feeding process were especially difficult to accomplish during Phase 3. The feed, consisting of 8.5 percent solids, had to be forced into the reactor with a grease gun apparatus. As shown on Figure 3.27, feed TCOD concentrations varied somewhat more on a day-to-day basis than in previous study periods. However, the reactor TCOD concentration in RS-4 was remarkably consistent during the steady state period. A similar pattern was observed for VSS in RS-4 (Figure 3.28) and for each of the other reactors. Figure 3.29 shows a typical erratic pattern for total gas production. Similar gas production patterns were observed for all reactors during all phases of the study. Missing gas production data (for example day 456) occurred when gas lines plugged with foam. The installation of larger foam surge tanks solved the problem. Methane production data were surprisingly consistent during Phase 3, however (Figure 3.30). The reactor feed contained about 105g/L of TCOD, 85g/L of SS and about 60g/L VSS (Table 3.3) during Phase 3. The volatile solids loading factor was about 0.352 lb.VS/ft³d, about thirty percent higher than the value recommended for use with a 15-day SRT.

The data in Table 3.3 represent average values for the 30 day steady state period. These data seem to suggest that RS-4, operating with the headspace pressure constantly maintained at 0.75 atm, performed marginally better than the standard 1.02 atm reactor. However, the difference in COD and solids destruction and methane generation rates are too small to be of economic significance.

FIGURE 3.27 PHASE 3 FEED AND RS-4 TCOD.

FIGURE 3.28 PHASE 3 FEED AND RS-4 VSS CONCENTRATION.

FIGURE 3.29 RS-4 TOTAL GAS PRODUCTION DURING PHASE 3.

FIGURE 3.30 RS-4 METHANE PRODUCTION DURING PHASE 3.

TABLE 3.3
PHASE 3 STEADY STATE DATA¹
DAYS 508 to 537

PARAMETER	REACTOR				FEED ²
	1	2	3	4	
1. TCOD (g/L)	57.40	56.11	55.45	55.90	105.39
2. SCOD (g/L)	7.07	7.68	6.98	6.59	10.59
3. TCOD destroyed (g/L-d) ³	3.34	3.38	3.47	3.37	
4. SCOD destroyed (g/L-d)	0.27	0.20	0.27	0.31	
5. SS (g/L)	56.94	56.41	56.19	56.72	84.62
6. SS destroyed (g/L-d)	1.86	1.95	1.88	1.85	
7. VSS (g/L)	31.22	30.71	30.76	30.99	59.83
8. VSS destroyed (g/L-d)	1.91	1.98	1.94	1.92	
9. VSS/SS (%)	54.8	54.4	54.7	54.6	70.7
10. Percent SS reduction (%)	35.1	35.7	35.3	35.4	
11. Percent VSS reduction (%)	49.7	50.5	49.9	50.1	
12. TS (mg/L)	59.32	58.93	58.77	58.87	87.33
13. VS/TS (%)	55.9	55.7	55.9	55.9	
14. Total gas produced (L/L-d)	2.13	2.12	2.14	2.21	
15. CH ₄ produced (L/L-d)	1.28	1.29	1.29	1.30	
16. Percent CH ₄ (%)	60.2	60.7	60.2	58.8	
17. H ₂ (ppm)	147	160	149	144	
18. CH ₄ /TCOD destroyed (L/g)	0.38	0.38	0.37	0.38	
19. CH ₄ /VSS destroyed (L/g)	0.67	0.65	0.66	0.68	
20. VFA/Alkalinity (mg/mg)	0.09	0.12	0.09	0.09	
21. pH	7.73	7.74	7.75	7.85	6.01
22. NH ₃ -N (mg/L)	2805	2893	2859	2859	468
23. S* (mg/L)	54.39	59.48	57.02	56.67	

1. The values shown are averages for the 30 day period.
2. 1.00L of sample were removed and replaced with fresh feed daily to maintain 15 day SRT
3. Total volume of reactor contents = 15.00L

PHASE 4 RESULTS

Phase 4 experiments were initiated to assess the effects of subatmospheric operation on organically overloaded systems. On day 538, three of the reactor systems were shocked by reducing the active volume from 15L to 10L while maintaining the same feeding regime used for the Phase 3 studies. This resulted in a 10-day SRT for RS-1, RS-3 and RS-4. Reactor System 2 was maintained as a 15-day SRT system to provide seed microorganisms for additional batch experiments. Data were collected from day 538 through day 563 when experimentation was stopped for budgetary reasons.

Similar response patterns were observed for the three reactor systems. For example, reactor TCOD concentrations for RS-1 (Figure 3.31) and RS-4 (Figure 3.32) both show increasing trends. A similar pattern was observed for VSS (Figure 3.33). However, both total gas production (Figure 3.34) and methane production (Figure 3.35) decreased with time. RS-1 and RS-3 showed similar trends for VSS and gas production. After 25 days of operation with a 10-day SRT it was clear that the three systems had not yet reached steady state.

The data reported in Table 3.4 represent the average data for the 25 days of record and should not be interpreted in the same manner as the three sets of "steady state" data previously presented. It is clear that the biological systems were being stressed and had not yet reached steady state conditions. All daily data are presented in Appendix B. Based on the averaged data, RS-4 was only marginally more efficient than the remaining two reactor systems for both TCOD and VSS destruction as well as CH_4 generation. Whether this pattern would have continued is unknown.

SPECIAL STUDIES

A series of "special" or side studies were conducted during the duration of the project to further explore the advantages of reduced gas pressure operation on sludge digesters, to possibly reveal the controlling mechanisms behind vacuum anaerobic digestion, and to help explain the results obtained with the main reactor systems. These studies included detailed 24-hour monitoring of the reactors during each of the steady-state periods, and the use of small batch reactors (120 mL serum bottles) for use in evaluating a number of parameters.

24-Hour Gas Monitoring

As described in Section 2, the four reactor systems were maintained with a single daily

FIGURE 3.31 PHASE 4 - INCREASING TCOD IN RS-1.

FIGURE 3.32 PHASE 4 - INCREASING TCOD IN RS-4.

FIGURE 3.33 PHASE 4 - INCREASING VSS IN RS-4.

FIGURE 3.34 PHASE 4 - DECREASING GAS PRODUCTION IN RS-4.

FIGURE 3.35 PHASE 4 - DECREASING CH₄ PRODUCTION IN RS-4.

TABLE 3.4
PHASE 4 DATA¹
DAYS 538 to 563

PARAMETER	REACTOR				FEED ²
	1	2	3	4	
1. TCOD (g/L)	57.79	NA	56.71	57.41	105.79
2. SCOD (g/L)	6.58		6.25	6.10	12.31
3. TCOD destroyed (g/L-d) ³	4.74		4.80	4.77	
4. SCOD destroyed (g/L-d)	2.67		2.72	2.70	
5. SS (g/L)	55.71		55.32	55.25	78.91
6. SS destroyed (g/L-d)	2.39		2.41	2.40	
7. VSS (g/L)	32.55		32.06	32.11	57.98
8. VSS destroyed (g/L-d)	2.52		2.53	2.54	
9. VSS/SS (%)	58.4		58.0	58.1	73.5
10. Percent SS reduction (%)	29.4		29.9	30.0	
11. Percent VSS reduction (%)	43.9		44.7	44.6	
12. TS (g/L)	57.93		57.52	57.76	82.54
13. VS/TS (%)	59.3		58.9	59.0	73.5
14. Total gas produced (L/L-d)	2.88		2.91	3.04	
15. CH ₄ produced (L/L-d)	1.85		1.87	1.90	
16. Percent CH ₄ (%)	63.9		64.3	62.4	
17. H ₂ (ppm)	154		153	178	
18. CH ₄ /TCOD destroyed (L/g)	0.390		0.390	0.398	
19. CH ₄ /VSS destroyed (L/g)	0.734		0.739	0.748	
20. VFA/Alkalinity (mg/mg)	0.090		0.093	0.088	
21. pH	7.78		7.81	7.90	5.99
22. NH ₃ -N (mg/L)	2531		2622	2535	64.3
23. S ⁻ (mg/L)	47.6		46.6	43.9	

1. The values shown are averages for the 25 day period.
2. 1.00L of sample was removed and replaced with fresh feed daily to maintain the 10 day SRT
3. Total volume of reactor contents = 10.00L

batch feeding schedule and were mixed by vigorous manual shaking at least twice per day. While continuous feeding and mixing would have been preferable, suitable laboratory-scale pumps and mixers were not available. For example laboratory suitable pumps for adding an eight percent feed slurry continuous at a rate of about 0.8 mL/min are not commercially available. Externally driven mechanical mixers had proven unreliable and frequently leaked air in previous reduced headspace pressure experiments. Internal magnetically driven mixing systems had also proven unsatisfactory for mixing the viscous solids slurries anticipated for the higher organic loading rates. Therefore a batch feeding schedule and manual mixing techniques were incorporated into the research plan. It was assumed that the vigorous manual mixing (sufficiently intense so that marbles contained in the reactors could be heard swirling around) along with the additional mixing provided by gas evolution would approximate continuous mixing conditions. It was also assumed that a single daily feeding would closely approximate continuous flow conditions for a system having a 15-day SRT. To evaluate the adequacy of these assumptions, each reactor was monitored intensively for gas production and percent methane for a 24-hour period once during each of the three steady-state periods. This involved taking gas production readings every hour, followed by vigorously mixing each reactor and sampling the headspace biogas for percent methane. All data are presented in Appendix C.

As expected, gas production was clearly proportional to the organic loading as illustrated by the RS-4 data shown in Figure 3.36. The relatively flat, straight line portions of these curves (time > 12 hours) represent constant gas production rates, most likely resulting from the endogenous decay of microbial cells. The initial steeply curved portions of the traces indicate immediate and rapid gas production following the introduction of fresh feed. There are no signs of either substrate inhibition or substrate induced toxicity in the data shown in Figures 3.36 through 3.38.

The rate of gas production was not constant over the 24 hour period between successive feedings as shown by the changing slopes of the cumulative gas production curves for the four reactors on days 211, 376 and 527 (Figure 3.37). [Note that each of three sets of curves has a different ordinate scale.] Peak gas production rates occurred three to six hours after feeding and were about 1.5 to 2 times greater than the average hourly value. Methane production tracked total gas production although the percent methane dropped by about 10 percent during the first few hours following feeding as CO₂ production increased. (Figure 3.38). Since the daily percent methane test was usually conducted during the minimum methane generation period, it is possible that the actual production of methane gas may have been somewhat greater than that reported in Tables 3.1 to 3.4.

FIGURE 3.36 GAS PRODUCTION IN RS-4 DURING 24 HOUR STUDIES.

FIGURE 3.37 COMPARISONS OF REACTOR GAS PRODUCTION DURING 24 HOUR STUDIES.

Figure 3.37 provides additional insight into the effects of reduced headspace pressure on sludge digestion. Since each reactor was thoroughly mixed once-per-hour during these experiments and all other physical conditions (temperature, liquid volume, etc) were identical for each reactor, differences in gas production and substrate utilization can be attributed to differences in headspace pressure. The Phase 1 data shown on Figure 3.37 illustrate that for lightly loaded systems, headspace pressure had virtually no effect on gas production during the initial nine to ten hour period following feeding; fresh substrate was being converted to gas at the same rate in each of the four reactors. However during the remaining endogenous decay portion of the 24-hour cycle, the 0.75 atm (RS-4) reactor produced about 10 percent more gas than the 1.02 atm (RS-1) reactor. Phase 2 results were similar to the Phase 1 results in that maximum gas production occurred during the first 9 to 10 hours of the 24-hour cycle (Figure 3.37). However, by ten hours after feeding, RS-4 (0.75 atm) had produced about 22 percent more total gas and methane than the 1.02 atm reactor. However, by the completion of the 24-hour cycle, the conventional 1.02 atm reactor had caught up and produced about 90 percent as much gas as the 0.75 atm reactor. The Phase 3 experiments repeated the gas production pattern of Phase 2 in that about two thirds of the 0.75 atm reactor gas production occurred during the initial 10-hour period. By this time, the 0.75 atm reactor had produced about 22 percent more gas than the 1.02 atm reactor. However, by the end of the 24-hour cycle, the net gas production from the two reactors was essentially equal.

The intense hourly manual mixing along with the incidental mixing resulting from gas evolution should have maintained completely mixed conditions during the 24-hour experiments shown on Figure 3-37. As described earlier, symptoms indicating biological stress due to overloading (e.g. low pH or high ammonium and sulfide levels) were not at inhibitory or toxic levels during any of the twelve, 24-hour experiments. The essentially identical gas production rates observed during the first 10 hours of the Phase 1 experiments for all four reactors indicates that 0.75 atm operation did not enhance gas production by enhancing feed solubilization under conventional organic loading conditions. Had more soluble feed been available in the 0.75 atm reactor, RS-4 gas production would have exceeded that of RS-1 during the first few hours of the Phase 1 experiments. This was clearly not the case. However, vacuum operation significantly enhanced gas production during the first ten-to-twelve hours in the more heavily loaded Phase 2 and Phase 3 studies as shown on Figure 3.37.

By the process of elimination, it is likely that reduced headspace gas pressure improved gas generation rates by accelerating the removal of gaseous end products from solution that would otherwise interfere with substrate transport to active microorganisms and/or waste and enzyme transport from bacterial cell surfaces to the bulk solution. There is

FIGURE 3.38 PERCENT CH₄ IN OFF-GAS FOLLOWING FEEDING.

some evidence to support this hypothesis. Normally, heavily loaded anaerobic systems generate high levels of volatile acids and CO_2 , both of which lower the pH and inhibit methane production. As shown on Figure 3.9, the pH in RS-4 was always about 0.1 to 0.2 pH units higher than that in RS-1, most likely due to gas stripping of CO_2 from solution. Thus there is some evidence, albeit not conclusive evidence, to support the hypothesis that reduced headspace pressure operation enhances gas production by removing deleterious materials from solution.

Figure 3.38 additionally illustrates one effect of placing RS-2 and RS-3 under sudden, temporary reduced headspace pressure. Partial vacuum conditions were established in RS-2 and RS-3 about four hours after feeding. The rapid decrease in percent methane for these reactors at about four hours after feeding was due to the sudden release of carbon dioxide from the liquid to the gas phase.

Additional evidence that reduced headspace gas pressure operation improved the anaerobic digestion process under high organic loadings can be seen in Figures 3.37 and 3.39. For Phase 3 conditions, RS-4 produced 50 percent of its daily gas output in about 6.5 hours, RS-2 and RS-3 in about 7.5 hours and RS-1 in about 8.5 hours. Furthermore, by nine hours after feeding, RS-4, RS-3 and RS-2 had produced 22, 19 and 15 percent more gas (and methane) respectively than RS-1. At 24 hours the differences were significantly less (except for RS-2). Again it is important to note that the reactors were intensively mixed every hour during these 24-hour studies in contrast to a typical project day when the reactors were mixed several times during the first six to nine hours and then allowed to stagnate overnight until just before sampling when the contents were again vigorously mixed.

The data shown in Figure 3.37 further illustrate that the mode of feeding (i.e. batch feeding) clearly affected reactor performance and invalidated the assumption that once-per-day feeding could simulate continuous flow conditions, even for a 15-day SRT. Under ideal, continuous-flow conditions the rate of gas production would have been constant, yielding straight lines for the 24-hour cycles. Discrepancies from the ideal were most pronounced for the lightly loaded Phase 1 experiments and least for the four heavily loaded Phase 3 experiments. These discrepancies may represent unused microbial capacity to process additional raw feed under continuous flow conditions. If proven true, the steeper initial slopes of the 0.75 atm reactor data for Phase 2 and 3 shown on Figure 3.37 suggest that reduced headspace pressure operations could result in significant improvement in gas generation and VSS destruction rates when compared to conventional 1.02 atm digester operation.

FIGURE 3.39 DIFFERENCES IN CUMULATIVE GAS PRODUCTION COMPARED TO CONTROL (DAY 526).

Following the 24-hour gas monitoring experiment on days 526 and 527, RS-2 experienced a system imbalance for project days 527 to 533 as indicated by erratic gas production and high volatile acids values (Appendix B). The reasons for these observations are unknown, but the change in the routine mixing operation due to the side experiment may have been a contributing factor.

Long Term Batch Digestion Studies

A series of small 1.02 atm batch reactor experiments were conducted to determine the response of Phase 1 acclimated sludges to various organic loadings (Table C-2). Feed aliquotes having target TCOD values of 0, 1, 2, 3, and 4 times the Phase 1 base TCOD value of 35g/L were placed in the serum bottles at a ratio of 1/15th of the total liquid volume. The balance of the liquid volume (14/15) consisted of Phase 1, 15 day SRT sludge from RS-1. The batch reactors were operated in a conventional (1.02 atm) anaerobic digester mode with periodic gas production monitoring. The reactors were then tested at the end of the experiment (365 days) for residual COD and solids contents.

Figures 3.40 and 3.41 illustrate that gas production was essentially proportional to the feed strength. Furthermore, these data demonstrated that the batch reactors would not fail biologically even when presented with a slug TCOD feed of 127,000 mg/L. This information was used in the decision to step change the organic loadings for the reactors systems between the different phases of the project. These Phase 1, long-term batch experiments (Table C2) demonstrated that the ultimate TCOD biodegradability of the Metro sludge was about 65 percent.

Phase 2 Batch Reactor Experiments

Another set of batch reactor experiments were initiated near the end of Phase 2 to determine the effects of mixing on the vacuum and conventional sludge digestion processes. One set of reactors was mechanically shaken continuously and the other manually shaken twice per day (Table C-3). The most significant findings are illustrated in Figures 3.42 through 3.45. Figure 3.42 demonstrates that reduced headspace pressures resulted in significantly greater volatile suspended solids (VSS) destruction (10-25 percent) over the range of organic loads tested regardless of the mixing conditions employed. Figures 3.42 and 3.43 illustrate the different results due to continuous low intensity mixing (i.e. a mechanical oscillating shaker) and periodic high intensity mixing (i.e. vigorous hand shaking). Surprisingly, the aperiodic high intensity mixing resulted in greater VSS destruction and gas production (5 to 10 percent) than was obtained with continuous gentle mixing (Figures 3.42 and 3.43). This suggests that the periodic mixing

FIGURE 3.40 EFFECT OF INITIAL FEED STRENGTH ON LONG-TERM BATCH DIGESTION.

FIGURE 3.41 EFFECT OF FEED TCOD ON CUMULATIVE GAS PRODUCTION AFTER 161 DAYS.

FIGURE 3.42 EFFECTS OF MIXING, VACUUM AND INITIAL VSS CONCENTRATION ON 15 DAY VSS DECAY.

FIGURE 3.43 MIXING INTENSITY EFFECTS ON 15 DAY GAS PRODUCTION IN 1.02 ATM REACTORS.

FIGURE 3.44 EFFECTS OF FEED SLUDGE TCOD ON CH_4 IN BATCH SYSTEMS.

FIGURE 3.45 EFFECTS OF FEED TCOD ON GAS PRODUCTION IN BATCH SYSTEM.

of the four large reactors did not limit VSS destruction and gas production. This may be an important factor in interpreting the Phase 3 results because of the difficulty in manually mixing the systems and the significant degree of foaming that occurred.

These side experiments further revealed a direct relationship between percent methane and organic loading as shown in Figure 3.44. The percent methane in the off gas decreased from about 68 percent to about 56 percent as the feed TCOD concentration increased, at least during the first 15 days of digestion. However, Figure 3.45 indicates a direct "linear" relationship between total cumulative gas production and the initial TCOD loading after 15 days of incubation. Figure 3.45 also illustrates two distinctly different gas production regimes for these 1.02 atm batch experiments. The constant gas production rate indicated by the parallel straight-line portions of the curves can be attributed to endogenous decay of the initial 15 day SRT seed sludge. The early initial steeper curved portions of the lines result from the processing of the different quantities of feed sludge initially added to the bottles. Based on the data in Figures 3.44 and 3.45 it can be shown that net methane production increased for the higher feed TCOD concentrations even though Figure 3.44 shows lower percentages of methane in the off-gas. As a result of unexpected system stability at the higher loading levels, it was impossible to investigate vacuum anaerobic sludge digestion under near-failure conditions using the batch reactor experiments.

Phase 3 Batch Side Studies

Near the end of Phase 3, two series of batch reactor experiments were conducted to compare vacuum and conventional anaerobic sludge digestion for high organic loading rates. These experiments consisted of two runs, one lasting for 20 days (Table C-4) and a short-term experiment of 48 hours (Table C-5). Samples (i.e. identically prepared serum bottle systems) were periodically analyzed for COD and solids content. The results of these studies are illustrated in Figures 3.46 through 3.49. No significant benefits were observed for vacuum anaerobic sludge digestion during these studies. This may be a result of using inadequate, low intensity mixing with the very high Phase 3 solids concentrations employed.

"Endogenous Decay" Of Phase 3 Sludges

At the end of Phase 3, a series of serum bottle experiments were initiated to investigate the "endogenous decay" of the digesting sludge. Over a 56-day period, the bottles were routinely monitored for total gas production and percent methane. The digesting sludge was periodically analyzed for COD and solids content. The result of these studies are

FIGURE 3.46 PRESSURE EFFECT ON TCOD DESTRUCTION IN BATCH SYSTEM.

FIGURE 3.47 PRESSURE EFFECT ON VSS DECAY IN BATCH SYSTEM.

FIGURE 3.48 SHORT TERM VSS DECAY IN BATCH SYSTEM.

FIGURE 3.49 SHORT TERM TCOD DECAY IN BATCH SYSTEM.

FIGURE 3.50 BATCH ENDOGENOUS DECAY TCOD EXPERIMENTS.

FIGURE 3.51 BATCH ENDOGENOUS DECAY VSS EXPERIMENTS.

FIGURE 3.52 BATCH ENDOGENOUS DECAY GAS PRODUCTION.

presented in Table C-6 and illustrated in Figures 3.50 through 3.52. By allowing the 15-day SRT suspension an additional 56 days for biodegradation, the percent TCOD destruction increased by about 20 percent (Figure 3.50) with roughly an additional 6L total gas (65 percent CH₄) per liter of reacting sludge (Table C-6). As shown on Figure 3.51 VSS decreased by about 23 percent. These figures illustrate typical endogenous decay curves. It is interesting to note that the amount of methane produced per unit of TCOD destroyed increased to an approximate value of 0.45L/g from the almost standard value of 0.38L/g observed during the Phase 3 steady-state period. This may be due to the intensive mixing in the serum bottles compared to the mixing procedure employed with the five-gallon carboy reactors.

Batch Ammonia and Sulfide Toxicity Studies

As previously indicated, both ammonia and sulfide can be inhibitory or toxic to anaerobic sludge digestion processes. Sulfide concentrations at 200 mg/L and ammonium concentration of 3,000 mg/L (at pH 7.2) can be tolerated with little negative effects. As shown in Figures 3.16 - 3.18 these limits were not exceeded during the study. However, because the Phase 3 ammonium levels were approaching the limit, a series of batch serum bottle experiments were conducted to investigate both sulfide and ammonium toxicity potential.

Phase 3 sludge from the 1.02 atm reactor was buffered to pH 7.4 with a phosphate buffering system spiked with various concentration of NH₄⁺ (from NH₄Cl) or S⁼ (from Na₂S), and incubated at 35° for fourteen days. One series of bottles was incubated with the headspace pressure constantly maintained at 0.75 atm and a second series of bottles incubated so that the headspace pressure was always at 1.02 atm or higher (Figure 2.7).

The initial in-bottle NH₄⁺ concentrations ranged from 2550 mg/L for the Phase 3 control sludge to more than 9500 mg/L. Results from both experimental systems were essentially identical. Net gas production following fourteen days of incubation for the positive pressure experiments was not inhibited until the initial NH₄⁺ concentrations exceed 6500 mg/L. Similarly, TCOD and VSS destruction were not inhibited in either the positive or reduced headspace pressure systems until the initial NH₄⁺ concentration exceeded 6500 mg/L. Based on these results, it is concluded that ammonium toxicity was not a problem during the Phase 3 portion of the study.

A similar series of experiments was conducted with the initial sulfide concentrations ranging from 25 mg/L (Phase 3 control) to about 425 mg/L. Again, the 0.75 atm and 1.02 atm reactors yielded similar results. The 14-day cumulative gas production was not

inhibited until the initial sulfide concentrations exceeded 125 mg/L. Neither fourteen day TCOD nor VSS destruction were inhibited by initial sulfide concentrations of 125 mg/L. Only minor effects were observed at 224 mg/L regardless of headspace pressure. Since the sulfide concentrations were always less than 100 mg/L (Figure 3.18) it can be concluded that sulfide toxicity was not a factor in these studies.

Section 4

CONCLUSIONS

Previous studies had strongly suggested that municipal anaerobic sludge digester performance could be significantly enhanced if operated with reduced headspace gas pressures. This project was undertaken to verify the findings of the previous work and to identify the biological and/or physical mechanisms that might result in improved sludge management. It was anticipated that the current studies would conclusively demonstrate that vacuum operation would enhance sludge destruction and methane generation rates on the order of ten to fifteen percent compared to conventional systems under heavily loaded conditions. Unfortunately, these goals proved unattainable, at least over the range of operating parameters investigated.

The solids destruction and methane generation data shown in Tables 3.1, 3.2 and 3.3 for TCOD loading conditions of about 0.7, 1.0 and 1.3 times those typically used for municipal sludge digesters do not indicate significant improvement for vacuum assisted operation. Only very minor improvements in TCOD and VSS destruction resulted from reduced headspace pressure operation. Vacuum operation improved SCOD destruction by about 15 percent for the heavily loaded Phase 3 conditions (Table 3.3) and similar trends were suggested by the Phase 4 work (Table 3.4). However, the data shown in Figures 3.36 through 3.39 strongly suggest that reduced headspace pressure systems can be operated successfully at higher organic loading rates than conventional anaerobic digesters. During the Phase 3 experiments, the 0.75 atm reactor (RS-4) had completed virtually all gas production (excluding that due to endogenous decay) within 16 to 18 hours of feeding (Figures 3.36 and 3.37) while the 1.02 atm reactor required about 22 to 23 hours to generate the same quantity of gas. The Phase 4 experiments were initiated with a 10-day SRT to test the hypothesis that reduced pressure operation would prove more beneficial with a higher organic loading rate. The preliminary data shown in Table 3.4 suggest that vacuum operation may be beneficial for more heavily loaded systems. Since the reactor systems had not attained steady-state when the project was stopped for budgetary reasons, these observations and findings cannot be considered complete.

Several hypotheses can be offered as to why these expanded studies failed to replicate the findings of the earlier work. First, as described above, the organic loads employed may not have been high enough to demonstrate the benefits of reduced headspace pressure operation for anaerobic digestion despite the use of an organic loading rate three times higher than that employed at the local municipal digester. Next, of course, is the possibility that the earlier work was in error due to the inadequate number of samples

available for analysis. Third is the possibility that reactor mixing was inadequate. Batch experiment data (Figures 3.42 and 3.43) and the fact that the reactors were not manually mixed from about 8 pm until 8 am the following day, suggest that inadequate mixing may have been the cause for the disappointing results observed. However, the regular vigorous mixing during the major parts of the gas-producing day (10 to 12 hours after feeding) coupled with additional mixing due to gas production (up to three volumes per volume per day) and the experimental evidence shown in Figures 3.42 and 3.43 suggest that the aperiodic mixing employed was not a major limitation in this study.

It was originally assumed that a once-per-day feeding schedule would adequately simulate a continuous feed system when the reactor was operated with a 15-day SRT. Based on the 24-hour gas production studies, this assumption was obviously in error. As shown in Figure 3.37, the bulk of the gas production was completed within 12 hours following feeding, even for the heavily loaded Phase 3 Systems. It is unlikely that the percentages of COD destruction and biogas production would have been significantly improved under continuous-flow conditions, because the systems were underloaded as demonstrated by the unused reaction capacity shown in Figure 3.37. It should be noted that gas production was enhanced by vacuum operations during each of the three twenty-four hour studies. However, the data in Figure 3.37 indicate that the once-per-day feed equivalency assumption was not valid and that all four systems could probably have been loaded at higher organic rates prior to failure.

Regardless of the reason(s), the data collected in this study did not demonstrate significant engineering advantages for vacuum-assisted anaerobic sludge digestion over the organic loading range investigated. To be significant, operating parameters such as volatile suspended solids destruction and methane production would have to be improved by at least 15 percent.

APPENDIX A

APPENDIX A

ANALYTICAL PROCEDURES

This project required many repetitive analyses as indicated in Table 2.3. Unless otherwise noted, all analytical procedures, explicitly followed those described in Standard Methods For the Examination of Water and Wastewater 17th Editions, APHA, 1989.

SPECIAL PROBLEM - GAS ENTRAINMENT IN SAMPLES

Early in Phase III, numerous small gas bubbles were observed to be trapped in reactor sludge samples obtained for TCOD, SS and other analyses. This phenomena was not observed during Phases I and II. The gas bubbles, held in the sludge matrix, obviously altered the true volume and liquid density of the sludge. Therefore, it was necessary to develop a method to determine the magnitude of the trapped sludge gases to permit appropriate correction.

The following procedure was developed and was used from day 465 (2/21/92) through day 563 (5/29/92):

1. Each reactor was intensively shaken before samples (1.00 L) were removed by evacuation into sample collection bottles;
2. The sample collection bottle was shaken intensively followed by removal of a 50 mL sample with a wide-tip transfer pipet;
3. The outside of the pipet was cleaned and the 50 mL sample was discharged into about 50 mL of distilled water in either a 200 or 250 mL volumetric flask. A sludge "pellet" would form in the flask as the pipet was emptied;
4. The pipet was gently raised to the water surface and rinsed with distilled water, avoiding disturbance of the sludge pellet;
5. Next sufficient distilled water was carefully added to the flask, without disturbing the sludge pellet, to fill the flask;

6. The volumetric flask was stoppered, shaken vigorously and placed in an ultrasonic bath for about 50 seconds. This procedure resulted in the release of numerous gas bubbles from the sludge which rose to the liquid gas interface in the neck of the volumetric flask. The distance from the calibration line on the volumetric flask to the new liquid/gas interface was measured and recorded. An additional volume of the original reactor sample was added to the flask to return the gas-liquid interface to the calibration mark. The additional volume was recorded and served as the basis for daily correction factors.

This procedure provided a means for correcting sludge samples for entrapped or entrained gases prior to performing volume dependent analyses.

In general, the volume of gas entrapped in the sludge remained fairly constant although there were fluctuations from day to day for a given reactor. It was also observed that RS-4 had the least volume of trapped gas bubbles, as expected, due to the applied vacuum keeping its sludge less saturated with gas.

FILTRATION/SUPERNATES

The soluble fractions of feed sludge and reactor contents were obtained by centrifugation of samples for 15 to 20 minutes at ~2000 g. Supernate for the alkalinity, sulfide and ammonia tests were used without filtration. For the COD test it was filtered through a 0.45 μm glass fiber filter (Gelman type A/E)

pH

An Orion 701 A Ionalyzer equipped with a combination electrode was used for pH determination. The unit was standardized against purchased buffer solutions. Special efforts were made to process reactor samples as soon as possible to avoid pH changes due to CO_2 loss to the atmosphere. Values were recorded to the nearest 0.01 pH units.

COD SAMPLING/DILUTING PROCEDURES

Sludge was transferred from well shaken reactors into evacuated sampling bottles. As soon as possible aliquots were taken for the TCOD test. The sample bottles were shaken gently and samples withdrawn into a 50 mL wide tip pipet. The contents of the pipet were drained into a 500 mL volumetric flask and sludge adhering to the inside for the pipet was washed into the flask with distilled water. The process was repeated daily for all reactors and for feed sludges.

The flask contents were brought to volume with distilled water, and then transferred to a 1 L beaker containing a magnetic stir bar and agitated vigorously. Two 50 mL portions were removed and transferred to an appropriate size volumetric flask.

During the course of the project as the TCOD rose (from Phase II to Phase III for example) it was necessary to increase the dilution of the COD samples in order to use the linear portion of the calibration curve for this test. The volume of the second volumetric flask increased from 500 mL to 1000 mL; increasing dilution from 1:50 to 1:100. Feed sludge, with a higher COD, was diluted 1:100 to 1:200.

The sample was again brought to the mark with distilled water. The diluted samples were again placed in a 1000 mL beaker and vigorously stirred while three 10 mL portions were removed and transferred to tubes containing the COD oxidant solution.

CHEMICAL OXYGEN DEMAND (COD)

Both total (TCOD) and soluble (SCOD) chemical oxygen demand were determined using a modification of standard methods 5220 D. "CLOSED REFLUX, COLOROMETRIC METHOD". Potassium acid phthalate dilutions were prepared to provide a series of standards containing from 0 to 900 mg/L COD. A typical standard curve had a linear regression analysis coefficient of $r^2 = 0.998$. All samples (total and soluble) were diluted with distilled/deionized water so that the measured absorbance would fall near the center

of the linear range of standard. Culture tubes (25 x 250mm OD, Corning 9826) equipped with teflon-faced bakelite screw caps were used as both the reaction vessel and cuvette.

Each tube contained 6 mL of digestion/oxidant solution (potassium dichromate, and mercuric sulfate in dilute sulfuric acid), 10 mL of TCOD/SCOD sample, and 14 mL catalyst solution (silver sulfate in concentrated H_2SO_4). The tubes were capped, shaken vigorously and heated for 3 hours at 130°C . After cooling to ambient temperature, absorbance was measured at 600 nm. All samples were prepared and assayed in triplicate. The maximum error associated with this method was estimated as about $\pm 1.8\%$.

ALKALINITY AND VOLATILE ACIDS

The samples required for alkalinity determination were obtained at the same time as samples for COD, pH, etc, as soon as possible after withdrawal from the reactors. Depending on the stage of the project, two to three 50 mL conical plastic centrifuge tubes were filled with sludge, capped and centrifuged at 3,000 rpm $\approx$ (2,000g) for 25 minutes to remove solids that would interfere with the test. All samples were processed within two hours of collection. Standard Methods procedure 2320B Titration Method using an Orion 701A Ionalyzer with a combination pH electrode was used for this determination. The titration was carried out using 0.1N H_2SO_4 to the preselected pH of 4.3. The volume of acid required was recorded and reported as equivalent CaCO_3 .

Following day 200, the later portion of the project, the solution was further utilized to obtain volatile acid alkalinity for estimating volatile acid concentrations. Additional 0.1N H_2SO_4 was added to the alkalinity sample until a pH of 3.3 to 3.5 was reached. The solution was heated, with stirring, until a gentle boil was attained. The boiling was continued for 3-5 minutes, the solution covered and allowed to cool. Next, the solution

was titrated with 0.1N NaOH to a pH of 4.00 and the required volume noted. It was then titrated to a pH of 7.00 and the total amount of base used was recorded. The first volume of base was subtracted from the total and volatile acid alkalinity (as mg. CaCO_3/L) was calculated. In order to transform volatile acid alkalinity (as mg CaCO_3/L) to volatile acids (mg/L) as acetic acid) the proceeding volume was simply multiplied by 1.5. Values obtained by this method have an average deviation of 2.47% and a standard deviation of 3.30%.

This method was obtained from the Operations Manual: Anaerobic Sludge Digestion (EPA 4530/9-76--001) by C. Zickefoose and R.B. Joe Hayes, Office for Water Program Operations; US EPA Washington, DC. The theory behind these procedures is discussed in detail by R. DiLallo and O.E. Albertson in the Journal of Water Pollution Control Federation, 33 (4) 356-365, 1961.

VOLATILE ACIDS BY GAS CHROMATOGRAPHY (G.C.)

Twenty mL of sludge (reactor or feed) was acidified with 1 mL of 50% (v/v) H_2SO_4 and the liberated volatile fatty acids were extracted into 10 mLs of diethyl ether. After centrifugation (3,000 rpm/5min) to break the emulsion the ether layer was pipetted off and stored in a tightly capped vial over Na_2SO_4 .

The volatile acids in the sample were assayed by gas chromatography on a Perkin Elmer Sigma 2 instrument. Conditions for extraction and assay are largely devised from "Packed Column GC Analysis of Volatile Fatty Acids From Anaerobic Fermentation" (GC Bulletin 748H) Supelco Inc. The column used was a 1/4" by 6' stainless steel column packed with 15% SP-1220/1% H_3PO_4 on 100/120 Chromosorb WAW. (Supelco) Operating temperature for the column was 135°C, GC injectors were maintained at 160°C. The detection method used was thermal conductivity.

The sample size interjected into GC was generally 40 μ L. The area under each peak was compared to that produced from a purchased standard solution containing 1 milliequivalent per 100 mL of each of the organic acids known to be found in the extract. The amount of acid was corrected for the efficiency for the extraction process. The maximum error associated with this measurement depends on which volatile acids is being measured and its concentration. The maximum error is about 11% of the value reported for acetate, 6% for propionate and 3% for butyrate.

SULFIDE

The supernate obtained by centrifugation of digester sludge was analyzed for sulfide by an iodometric titration. (Standard Methods 4500-S²-E). Standard sodium thiosulfate solution was prepared and standardized by method 4500-O.C 2d and/or 4500-C1 B. Standard Methods estimates that in clear waters the end point should be observable within 1 drop which is equivalent to 0.4 mg/L in a 50 mL sample. As our samples were strongly colored, the error for sludge is higher, but the relative error will be smaller due to the high concentration of sulfide in our samples.

AMMONIA

The supernate from each reactor and the feed sludge was analyzed for ammonia using a modification of standard Method 4500-NH₃F (Ammonia-Selective Electrode Method). The electrode used was an Orion 95-12 with a Beckman 3500 pH meter (with a mv scale). The electrode had a usable range of 0.01 to 17,000 ppm NH₃ or 0.01 to 14,000 ppm N.

Since the supernate of the reactor sludge (as well as the feed sludge) contained surfactants, which can penetrate the gas-permeable membrane of the electrode, it was necessary to use a modification suggested by the Orion instruction manual. In this

method the electrode is inserted through a hole drilled in the screw cap of a 25 x 250mm pyrex culture tube. A gas tight seal is ensured by a neoprene O-ring gasket. The supernate was placed in the tube to a pre-determined mark and made strongly basic (pH > 11) with 5 N NaOH, containing 0.05 N EDTA, in 10:1 H₂O:MeOH. The ammonia content in the gas phase above the solution is then determined. The closed tube forms an air tight system whose gas phase is saturated with water vapor and has a partial pressure of NH₃ in equilibrium with the solution.

A calibration curve was prepared, using this technique, with standard solutions of NH₄Cl in Water. The concentrations of the standard solutions varied during the course of the project in order to bracket the rising ammonia concentrations of the sludge. In the last stages of the project the concentration range of the standards was from 1,000 to 3,500 mg/L in 500 mg/L steps. Standard Methods reports a mean standard deviation of 1.32 mg N/L when concentrations were in the 10.2 to 34.7 mg N/L (12.9% to 3.8%) range. At the much higher concentrations in the present system the percentage error was probably lower.

SOLIDS TESTS

Three replicate samples of 8 ml were analyzed for total solids using the standard Methods Procedure 2540B (Total Solids dried at 103°-105°C). The procedure for total suspended solids was Standard Methods 2540D (Total Suspended Solids Dried at 103-105°C) The residual samples from methods 2540B and C (after weighing) were ignited in an oven at 550°C as in Method 2540E (Fixed and Volative Solids Ignited at 550°C). The fixed total solids and fixed suspended solids values thus obtained were subtracted from the corresponding total solids and total suspended solids to obtain total volatile solids and suspended volatile solids.

As mentioned in the section dealing with the COD test it became necessary during the later phases of the project to dilute samples. It also became necessary to correct the

samples for the presence of trapped gas bubbles as previously described.

METHANE AND CARBON DIOXIDE

Biogas was analyzed for percent methane using a Series 150 Thermal Conductivity gas chromatograph (Gow-Mac Instrument Company, Bridgewater, NJ). The biogas was separated into methane, carbon dioxide and an impurity (e.g. N₂, H₂) gas components by an 8 foot by 1/4 inch diameter stainless steel column containing Porapak Q (80/100 mesh). The unit was operated at 50°C with helium carrier gas at 60 mL/min. A 6.0 mL volume of purchased methane and carbon dioxide reference standard (67% and 30% respectively by volume) was injected periodically during the analysis of the biogas, and the detector signal recorded on a strip chart recorder. The areas of the methane and carbon dioxide standard peaks were determined. A detector correction factor based on the ratio of methane to carbon dioxide standard peak areas was used to adjust the recorded biogas sample peaks based on a sample volume of 6 mL. The possible errors associated the methane determinations are ± 5 percent of the reported values.

HYDROGEN ANALYSES

Biogas was analyzed for molecular hydrogen using a model 12 Microlyzer (Quintron Inc., Milwaukee, WI). This instrument provided a direct reading in parts per million of hydrogen gas. The instrument was calibrated using 15 mL sample volumes of purchased hydrogen standard (100 ppm or 200 ppm, balanced with air). The biogas hydrogen concentration was determined by directly injecting 15mL of biogas directly into the instrument. The calibration of the instrument was then rechecked using the hydrogen standard. The possible errors associated the determination of the hydrogen concentration are ± 5 percent of the reported value.

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