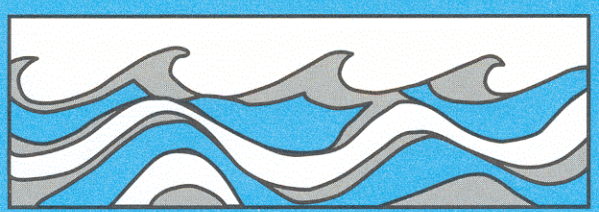
University of Washington
Department of Civil and Environmental Engineering

HIGH RATE ANAEROBIC TREATMENT OF EVAPORATOR CONDENSATE FROM SPENT PULPING LIQUORS

Mark M. Benjamin
John F. Ferguson
Joseph L. McCarthy
Neil L. Ricker



Water Resources Series
Technical Report No.92
February 1985

Seattle, Washington
98195

Department of Civil Engineering
University of Washington
Seattle, Washington 98195

HIGH RATE ANAEROBIC TREATMENT OF EVAPORATOR CONDENSATE FROM SPENT PULPING LIQUORS

Mark M. Benjamin
John F. Ferguson
Joseph L. McCarthy
Neil L. Ricker

Water Resources Series
Technical Report No. 92

February 1985

HIGH RATE ANAEROBIC TREATMENT OF EVAPORATOR CONDENSATE FROM SPENT PULPING LIQUORS

Mark M. Benjamin
John F. Ferguson
Joseph L. McCarthy
Neil L. Ricker

Departments of Chemical and Civil Engineering
University of Washington
Seattle, Washington 98195

PROJECT NO. B-084-WASH
Agreement No. 14-31-0001-0256

Project Period January 1979 - October 1983

Final Technical Completion Report

Submitted to

The State of Washington Water Research Center
and
Bureau of Reclamation
U.S. Department of Interior
Washington, D.C. 20240

March 1984

ACKNOWLEDGEMENTS

The work upon which this report is based was supported by funds provided by the U.S. Department of the Interior, Office of Water Research and Technology, as authorized under the Water Research and Development Act of 1978. The Office of Water Research and Technology has since been terminated effective August 25, 1982, by Secretarial Order 3084 and its programs transferred to other bureaus and offices in the Department of the Interior. The Matching Grants program was among those transferred to the Bureau of Reclamation.

DISCLAIMER

ABSTRACT

A study of the anaerobic treatment of several pulp and paper waste streams has demonstrated the degree of organic removal and concomitant methane production possible at varying organic loading rates. Evaporator condensate from the sulfite pulping process can be treated alone or with waste from the caustic extraction stage of bleaching. The neutralization requirement for those waste streams has been evaluated theoretically and empirically; toxicity and biodegradability of wastes and individual compounds have been evaluated in batch anaerobic bioassays. Pulse loading studies were conducted. Sulfur in the evaporator condensate has been shown to be partially reduced to sulfide and to reduce COD removal efficiency and methane production. Preliminary cost estimates for application of anaerobic treatment in a packed bed system have been completed for sulfite and kraft process evaporator condensates.

KEYWORDS

Anaerobic treatment, pulp and paper waste, anaerobic degradation, biodegradability, toxicity, acclimation, furfural, guaiacol, toxicity assay, evaporator condensates, treatment, waste treatment, costs, fermentation, methane.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF FIGURES (cont.)

LIST OF FIGURES (cont.)

LIST OF FIGURES (cont.)

LIST OF TABLES

LIST OF TABLES (cont.)

GENERAL INTRODUCTION

Anaerobic treatment of industrial water for energy recovery, water reuse, and waste water treatment has been identified as a major area of technological development. Among many candidate industries, the pulp and paper industry ranks high because of the large amounts of degradable organics. Evaporator condensates from pulping of wood are particularly attractive waste streams for anaerobic treatment because of the high concentration of simple, degradable organic compounds, the low concentrations of salts, and the warm temperature of the wastes. In 1978, a group of 6 companies formed a consortium to support a study of anaerobic treatment of sulfite and kraft process evaporator condensates to be conducted in the Civil and Chemical Engineering Departments at the University of Washington. Also in that year matching funds were obtained from the Office of Water Research and Technology. After the first year, Georgia Pacific made substantial additional funds available for additional anaerobic studies and for investigation of aerated lagoon treatment which could be used following anaerobic pretreatment. An amendment and extension of the original project was granted from the Office of Water Research and Technology, and additional grants were also made by Weyerhauser, Scott Paper and ITT-Rayonier.

The project involved participation of four faculty investigators, whole or partial support for nine master's degree candidates, one Ph.D. candidate, and participation of numerous student helpers. The project was organized around these students' research projects, and the principal results are incorporated in the theses and publications that have been completed.

The graduate students and the studies undertaken in chronological order are:

Mark Buggins, (1981) MSE Civil Engineering
Study of treatability of sulfite evaporation condensate at high organic loading rates and low hydraulic detention time. Parallel studies of synthetic wastes continuing acetate, methanol and furfural. Investigations of biological growth yield and nitrogen and phosphorus requirements for anaerobic treatment.

Sandra L. Woods, MSCE, (1980) Ph.D. candidate, Civil Engineering
Study of toxicity and biodegradability of major constituents of pulping condensates to anaerobic microorganisms using batch bioassay technique.

Peter Haggarty, MSChE (1980), Chemical Engineering.
Experimental investigation of anaerobic treatment of sulfite waste and completion of preliminary process design and cost estimates.

Brian J. Eis, MSCE (1982), Civil Engineering
Study of limiting factors in high rate treatment of sulfite condensate. Investigation of role of sulfur in toxicity, methane yield and neutralization. Study of neutralization by sodium hydroxide, sodium carbonate, and calcium hydroxide and the role of effluent recycle in neutralization requirement.

David Nitchals, MSCE (1983), Civil Engineering.
Study of treatment of sulfite condensates combined with caustic extraction stage, bleaching waste. Study of toxicity of caustic extract waste, its biodegradability and its use in neutralizing sulfite evaporation condensate.

Colin Felton, MSChE (1983) Chemical Engineering
Study of process dynamics in anaerobic rotating disc reactor receiving an acetate, methanol feed.

Mike Kuenzi, MSCE (1983), Civil Engineering
Study of effect of pH on performance of aerated lagoon system.

Mark Poling, MSE candidate, Civil Engineering.
Study of anaerobic treatment of kraft evaporator condensate at high organic loadings. Investigate biodegradability and toxicity of kraft condensates using anaerobic batch bioassays.

Theodore Pooler MSCE (1983), Civil Engineering
Development of mathematical model of anaerobic fixed film treatment, incorporating mass transport and biodegradation of sequentially used organisms in biofilm with sequented reactor incorporating advection with dispersion of longitudinal direction.

Complete titles of student theses and papers are listed in Appendix A.

Theses are available from University of Washington Library, and non-thesis masters' reports from the Environmental Engineering and Science Program, Department of Civil Engineering, University of Washington.

This completion report consists of papers prepared for publication. They are presented as chapters, dealing with the treatability of sulfite evaporator condensate, toxicity and biodegradability of its constituent, neutralization requirements, and fate and effects of sulfur in anaerobic treatment. Dynamic response of a reactor treating waste constituents, preliminary cost estimates for the application of anaerobic treatment to sulfite and kraft process condensates, and combined treatment of caustic extraction stage and bleach plant effluent with sulfite evaporator condensate complete the topics addressed in these papers.

CHAPTER 1

TREATMENT OF SULFITE EVAPORATOR CONDENSATE WITH AN ANAEROBIC REACTOR[1,2]

Mark M. Benjamin
John F. Ferguson
Mark E. Buggins

ABSTRACT

A study has been underway since 1979 evaluating the use of submerged media anaerobic reactors (SMAR's) to treat sulfite evaporator condensate (SEC). SEC from a calcium bisulfite mill and synthetic SEC have been both treated at an organic loading of 16 kg COD/m^3-day and a detention time of 7 hours, achieving 79% to 90% reduction in COD. A yield coefficient of 0.09 g cells/g COD removed has been calculated, and the balance of the removed COD is stoichiometrically converted to CH_4. Toxicity from sulfur compounds, furfural, or trace organics has not been a problem. Partial neutralization of the feed is necessary, as are the additions of nitrogen, phosphorus, and some trace nutrients. The process produces methane with a significant energy value. In addition, when used as pretreatment, it reduces the energy needed for aerobic treatment.

1. Presented at TAPPI Environmental Conference, New Orleans, LA, April, 1981.

2. Published in TAPPI, 65, 96-102, 1982.

Anaerobic treatment of concentrated soluble organic wastes has not heretofore been practiced widely in the pulp and paper industry but appears to be an economically attractive alternative for the future. Anaerobic treatment has several recognized advantages over aerobic treatment, including low sludge production, generation of methane, and low nutrient requirements. It might have been adopted long ago were it not for equally recognized disadvantages, including the requirement of relatively long detention time with resulting high capital costs, susceptibility to and very slow recovery from process upsets, and effluent unsuitable for direct discharge or in-process reuse.

While these disadvantages represent legitimate concerns, recent research on the microbiology of anaerobic fermentation has led to a better understanding of the environmental requirements of anaerobic bacteria and of the fermentation reactions they mediate. Many unexplained process upsets are now understood, and in most cases specific remedial measures can be prescribed for process overloading, temperature, pH, or toxicant upsets. Research on toxicity, acclimation, and removal of toxic substances has been especially important in expanding the application of anaerobic treatment process. For example, research has shown that solutions of 1-2 g/L phenolics are treatable, and that anaerobic microorganisms are not inhibited by sulfide at concentrations as high as 0.5 g/L (6, 10). These solutions were considered toxic and untreatable by anaerobic processes, according to the conventional wisdom of a few years ago. Another important result of recent process research is that anaerobic treatment processes can operate successfully at much higher organic loading rates than was previously thought possible. Maximum reported loadings have increased from about 3 kg BOD/m^3-day to 15 kg BOD/m^3-day in the past 15 years (2,3,5,7,11). The reasons for this increase are probably related to the use of novel reactor designs and a better

understanding of microbiological and environmental requirements. Process detention times are much lower than in the past, significantly reducing capital costs.

Increasingly stringent effluent requirements and high purchased-energy costs for waste treatment have made wastewater processing an important concern at every pulp mill. Anaerobic pretreatment of concentrated waste streams can offer a very substantial reduction in the cost of purchased energy for a typical plant.

We have conducted research to assess the feasibility of anaerobic treatment for evaporator condensates from the sulfite (calcium base) and kraft pulping processes. Specific objectives included developing operation and design criteria and evaluating the overall effect of such treatment on other plant waste processes. In this paper, studies of the treatability of sulfite evaporator condensate (SEC) are reported, emphasizing the effects of various process parameters on treatment efficiency.

Start-up and rate of increasing loadings

The first two reactors were put into operation in July 1979. Initial influent to these reactors was synthetic SEC at a loading of 0.32 kg COD/m^3-day. This influent was 60% neutralized with NaOH and contained no added trace nutrients. The reactors were kept at 35 ± 2°C. Recycle flow was at about 10 L/hr, and influent flow depended on the organic loading and waste strength. The detention time (based on influent plus recycle flow) varied from 1.9 to 1.5 hours. After successful steady-state operation at 1 kg/m^3-day, the loading was increased by between 20% and 50% with inconsistent results. At times the reactors would operate successfully for several days at the higher rate and then fail for no apparent reason. The decision was made

to add a suite of trace nutrients to the influent and to increase the amount of alkalinity added to the feed solution such that the alkalinity added equalled the acid in the feed. After these changes, the loading rate was increased by between 25% and 100%/week without reactor failure. In some cases there was a transient (less than one day) deterioration in reactor performance, but in no case was remedial action required. Two additional reactors were started readily under this regimen in early 1980.

We did not definitely determine whether the increased alkalinity, increased trace nutrients, some other factor, or some combination of factors was critical in allowing us to increase organic loading steadily and to avoid reactor failures. Nevertheless, the successful operation of all 4 reactors for the past 1-1/2 years indicates that SMAR's treating SEC can be brought on-line at an initial loading of 1 kg COD/m^3-day and that the loading can be increased at a rate of 50%/week until it reaches at least 16 kg/m^3-day (in 8 weeks). Further experimentation may allow startup to proceed considerably faster.

Two reactors were st rted up with synthetic SEC and then converted to industrial SEC by succes e volumetric replacement with industrial feed in increments of 10% or 25%. The changeover process was completed in approximately six weeks.

Results

Data characterizing overall reactor performance (COD removal efficiency, methane production, etc.) and specific aspects of the process (e.g., removal of individual substrates) for eight steady-state trials are presented in Table 1. In most trials the effluent organics could be accounted for by organic acids (largely acetic) and suspended solids (>90% volatile, largely cells).

Table 1. Summary of results from 8 steady-state trials

Feed type	Synthetic SEC				Industrial SEC			
Loading rate, kg COD/m^3-day	1.0 60	1.6 100	3.2 200	16.0 10000	1.0 60	1.6 100	3.2 200	16.0 10000
Detention time, hours	120	70	36	7	142	84	36	7
COD_{total}, mg/liter	350 (93% red.)	86 (98% red.)	360 (92% red.)	400 (92% red.)	410 (93% red.)	420 (90% red.)	490 (90% red.)	1050 (79% red.)
$BOD_{5,total}$, mg/liter	170 (94% red.)	13 (99% red.)	121 (96% red.)	---	87 (97% red.)	130 (96% red.)	180 (94% red.)	480 (84% red.)
Organic acids mg/liter acetic	280	50	250	---	150	180	80	---
Total suspended solids, mg/liter	26	25	27	96	110	138	123	70
pH	6.9	7.6	7.7	7.6	7.6	7.3	7.2	7.2
Normalized gas production, liter gas/g COD fed	0.42	0.33	0.36	0.34	0.38	0.39	0.42	0.39
Gas analysis, % CH_4	69	87	87	---	76	86	73	72

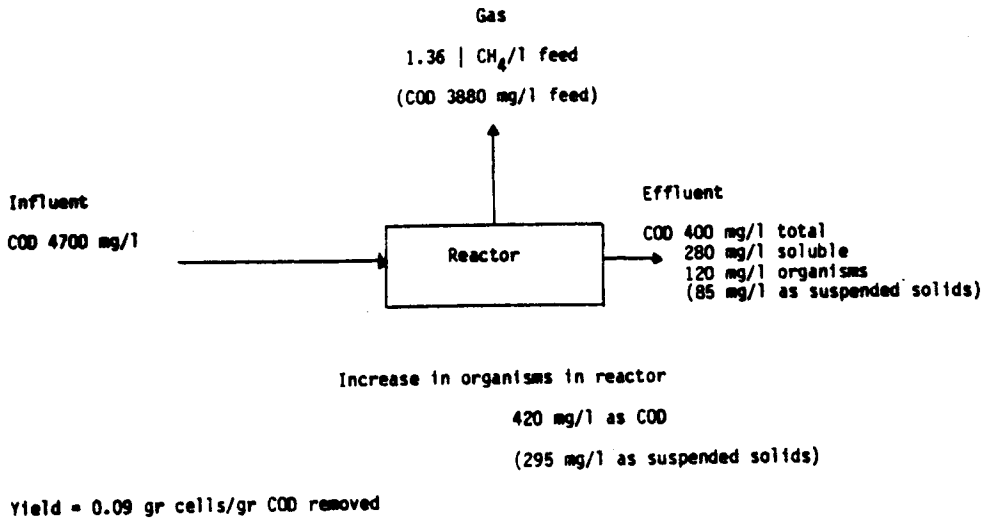
The pH values, except for the first trial, were uniformly high in the effluent as well as throughout the reactor at all times.

COD Removal

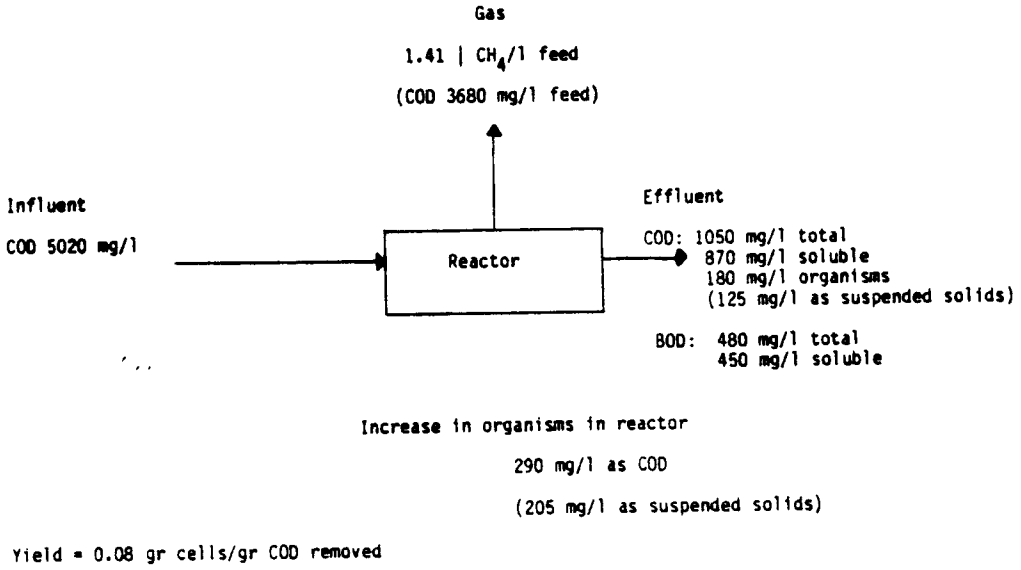
Balances on organic COD in reactors treating synthetic and industrial SEC at high loadings are shown schematically in Fig. 1. Possible fates for influent COD include appearance in the effluent as soluble COD, conversion to methane, or synthesis into biomass which may remain in the reactor or appear as suspended solids in the effluent. The COD of the influent, the soluble and total COD of the effluent, and the COD equivalent of the methane can be measured directly. Particulate COD in the effluent is computed by subtracting the soluble from the total. Since there is no net oxidation in the reactor, the COD in the influent must all be accounted for by COD in one of the exit streams or retained in the reactor. Thus a COD balance can be used to estimate the COD converted to biomass and retained. This COD balance applies to organic consitutents and ignores the effect of sulfur compounds. The reactions of sulfur are not yet well understood in the process, but the total amount of sulfur is small and would cause only minor changes in the values calculated.

For instance, according to Fig. 1b, when industrial condensate is treated at a loading of 16 kg/m^3-day, the COD converted to cells is that not found in the gas phase or in a soluble form in the effluent, while the COD removed and metabolized is the influent minus the soluble effluent values. Using a typical value of 1.4 mg COD/mg cells, the yield coefficient in the reactor can be computed:

$$Y = \frac{COD_{in} - COD_{s,\,eff} - COD_{CH_4}}{COD_{in} - COD_{s,\,eff}} \div 1.4 \quad (1)$$



(a)



(b)

Figure 1. COD balances from 2 steady-state trials: (a) synthetic condensate at 16 kg/m^3-day, (b) industrial condensate at 15 kg/m3-day.

The yield coefficients calculated in this way are 0.08 and 0.09 for the industrial and synthetic SEC, respectively, which are typical values for anaerobic growth.

The retention of cells is computed from the total productions ($Y \times COD_{in}$) minus the particulate COD in the effluent. For the particular flow scheme of our reactors, from 97% to 60% of the cells synthesized have been retained in the reactor, with higher fractions during start-up and lower fractions later.

Overall, COD removal was $\geq$ 90% for all trials except the highest loading of industrial SEC. Generally, removal efficiency was less for industrial SEC than for synthetic SEC and decreased with increasing loading for both types. COD removal efficiency depends on a number of factors besides loading, including hydraulic characteristics of the reactor, trace nutrient additions, alkalinity, etc. Thus the data should be regarded as feasible efficiences showing general tends rather than as definitive limits for these loadings.

Effluent suspended solids and sludge production

The net yield coefficient calculated by attributing to cell growth all COD except that measured as methane or soluble effluent COD gives values that are lower by a factor of 5 than those found in aerobic treatment. The values (0.08 to 0.1) seem high compared with other aerobic treatment studies and may be biased, since measurement errors in gas production and sulfur contributions to effluent COD would probably result in overestimates of the COD converted to cells. Nonetheless, a substantial amount of biological cellular material is produced in the reactor. The efficiency of the reactors in retaining produced biomass varies between 60% and 100% depending on organic and hydraulic loading and on the operating history of the reactor. In a full-scale application of

this process, periodic wasting of cells will be necessary, but the amount of sludge produced will be small compared with aerobic processes.

The major nutrients required for biological processes are nitrogen and phosphorus. Based on literature values for N and P requirements of bacteria, no more than 8% N and 1% P should be assimilated into cellular biomass. For a yield coefficient of 0.09, calculated requirements are 7.2 kg of N and 0.9 kg of P per 1000 kg of COD removed. Measured values are somewhat lower: 6 kg of N and 0.2 kg of P per 1000 kg of COD, much lower than comparable ones for aerobic processes.

Methane Production

The preceding sections have shown that most of the COD in the feed is converted to methane, with smaller amounts appearing in the effluent or accumulating as cellular material in the reactor. The theoretical maximum yield of methane (in the absence of any net growth in biomass) is 0.35 L of CH_4/g COD removed. Assuming 5-10% of the COD removed was converted into biomass retained in the reactor, the measured value of 0.33 ± 0.02 L CH_4/g COD removed is in excellent agreement with theory.

The methane produced represents a source of energy available to displace purchased fuel at a mill. The value of this energy is computed in four ways in Table 2, which is based on current natural gas energy values in the Northwest. While the amount of energy is not large compared with total mill usage, it could significantly reduce the amount purchased from outside sources.

The COD removed in anaerobic treatment also reduces energy requirements for aerobic wastewater treatment. Cost of energy for aerations to treat SEC is approximately of the same magnitude as the value of methane produced. Thus

Table 2. Calculations of methane production and its value for SMAR treatment of SEC

Calculation	Conventional Unit	SI Units
COD basis:		
5.6 ft^3/lb COD x 0.92 x 960 BUT/ft^3 x 10^{-5} term/BUT x 0.42 $ therm =	0.19 $ lb COD	0.42 $/kg COD
Flow basis (5000 mg/liter COD):		
0.019 $/lb COD x 5000 mg/liter x (lb/million gal)/(mg/liter)	810 $/million gallon	0.21 $/$m^3$
Pulp production basis (50 lb BOD/ton)		
0.019 $/lb COD x 50 =	0.97 $/ton	1.07 $/1000 kg
Annual for 1000 ton/day mill:		
0.97 $/ton x 1000 ton/day x 350 day/yr	340,000 $/yr	

the net shift in purchased energy for a mill may be approximately twice the values indicated in Table 2.

Study of process limitations

In developing a process, several apparent loading limits may be then successfully exceeded by making relatively simple changes in operating procedures. For instance, in the particular case of a SMAR treating SEC, loading limits may appear; when the concentration of a required trace constitutent limits growth rate; when pH or organic acid concentration in the influent reaches a level inhibitory to the organisms near the inlet; when loss of organisms in the effluent equals their growth rate in the reactor; or when affected by one or more of a myriad of other causes. Adjustments, such as chemical additions to the influent or changes in the reactor configuration, may overcome these problems and allow much greater loading rates. Clearly, rational choices about how to proceed when an apparent loading limit is reached require a fundamental understanding of the processes occurring in the reactor; treating the reactor as a "black box" could lead to wasted effort or even premature abandonment of a viable process.

Pulse loading tests

Proper performance of any biological reactor depends on an effective coupling of the biological processes with the hydraulic flow pattern. We have conducted a series of tests to provide information about the internal flow pattern in our reactors, and the response of the reactors to the types of influent changes to be expected in a pulp mill. A step or spike change in the influent was imposed, and the reactor response was monitored as a function of time at several locations in the reactor. The chemicals used in these tests

were an inert tracer (LiCl), an easily degradable organic (acetic acid), and a potentially toxic mixture or organics and inorganics (fermented spent sulfite liquor).

LiCl pulse test. In this test, a spike dose of 0.64 g LiCl was injected into a reactor treating synthetic SEC under the following conditions: Q = 2.16 L/hr; R = 10.6 L/hr; L = 16 kg COD/m^3-day. The reactor void volume in the absence of any bacterial growth was 19 L, yielding a mean hydraulic residence $\theta_H = V/Q = 8.8$ hr. The hydraulic residence time for one pass through the reactors was $\theta_H' = V/(R + Q) = 1.5$ hr. Lithium is presumed not to interact with any component of the reactor and can therefore be used as a tracer for the water mass entering the reactor.

In an ideal plug-flow reactor, the lithium spike would move upward through the column and appear sequentially at ports. Part of the lithium would then exit, and the remainder would be recycled and act as a new spike input at $t = \theta_H' = 90$ min. In any real reactor, the lithium spike will "spread out" with time because of molecular diffusion and bulk mixing of the fluid. In a SMAR, bulk mixing is enhanced by gas bubbles formed from the fermentation reactions. Particularly in the upflow SMAR, mixing is expected to be quite efficient since most of bubbles form near the bottom (the region of highest substrate concentration and therefore greatest microbial activity) and pass through the entire water column before collection.

That mixing was quite efficient in the laboratory SMAR is shown by the appearance of a Li peak in the effluent long before the single-pass detention time θ_H' (Fig. 2). The slow decrease in Li concentration after the initial peak is more characteristic of a completely mixed reactor than a plug-flow reactor. The vertical gradient of Li was completely eliminated at about 40 minutes after the spike. The short delay before any Li appears in the

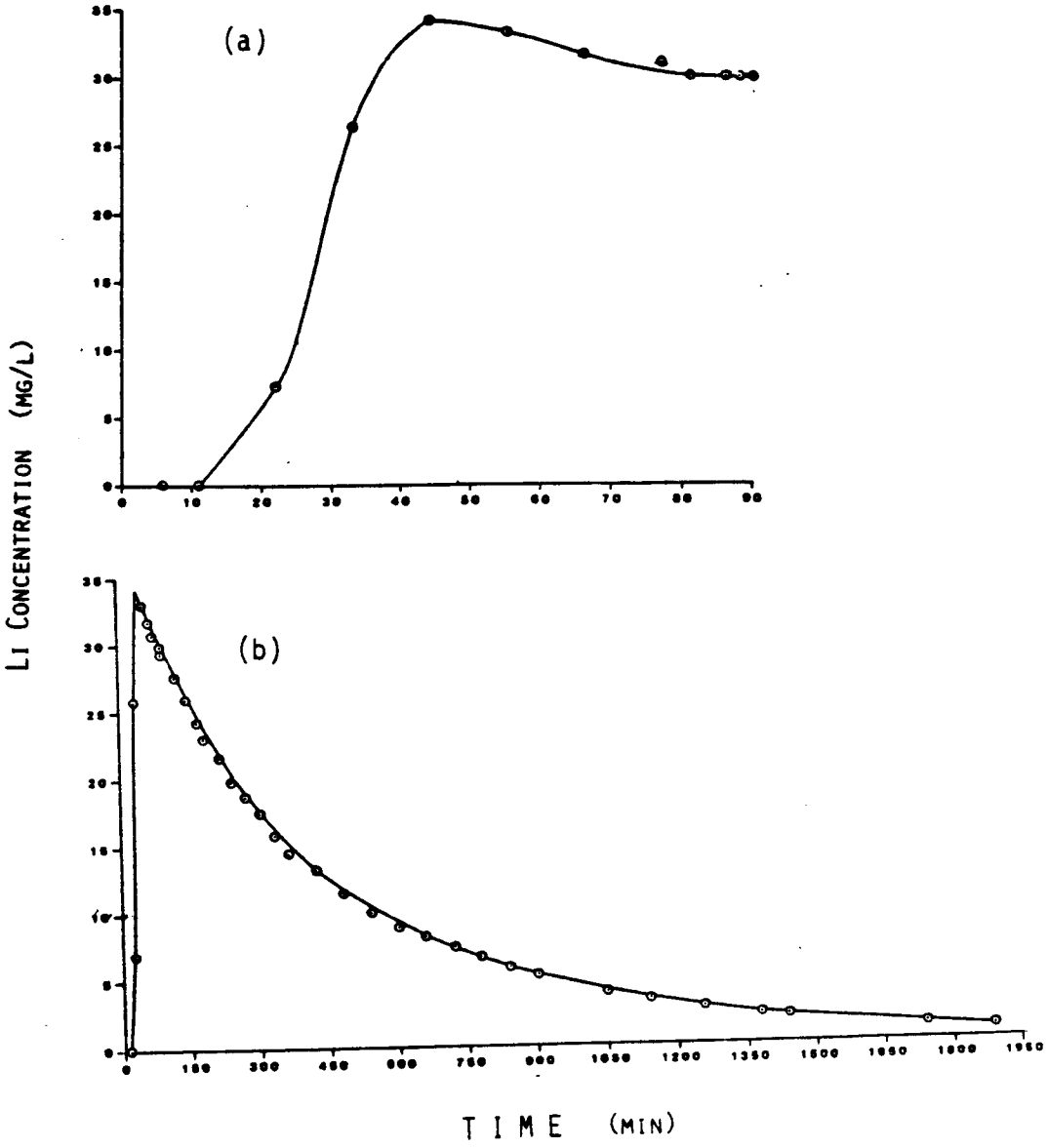


Figure 2. Lithium chloride pulse test effluent concentration vs. time: (a) concentration during the first 1.5 hr., (b) concentration during 30 hr.

effluent indicates the existence of at least a small reactor section which does not mix completely with the rest of the reactor. This section is undoubtedly at the bottom of the reactor where bubbles are first forming.

The mean residence time of Li in the reactor computed from these data is 8.84 hours (Fig. 2b). This value agrees within experimental error with θ_H', indicating that during 8 months of operation the reactor's void volume was not significantly decreased by growth of biomass or deposition of nonbiological solids.

It is likely that COD removal is a function of flow pattern in the reactor. For example, the most efficient COD removal that may be expected in a system with a plug-flow component could be attained by either converting the reactor to a downflow or a horizontal flow system, by reducing the recycle rate, or by reducing mixing by gas bubbles. On the other hand, a well-mixed reactor has the advantage of rapidly diluting any inhibitory or toxic component in the influent. In any case, tracer experiments such as this can be used to quantify the degree of mixing in the reactor and to help construct models of the overall process, which can then be used in subsequent design analyses.

Acetic acid steps input test. The effect of rapid fluctuation in waste strength was simulated by a step increase influent acetic acid concentration to one reactor. The step was from 3.0 to 4.0 g/L acetic acid, representing a 22% increase in total influent COD, and was applied for 1.5 hours to a reactor receiving synthetic SEC under the following conditions: Q = 0.52 L/hr; R = 11.4 L/hr; L = 3.2 kg COD/m^3-day; θ_H = 3.6 hrs; θ_H' = 1.5 hr. An amount of NaOH sufficient to neutralize all the extra acetic acid was added to the influent concomitantly. The data collected included COD and pH at each port and total gas production (Table 3). Consider the COD profile represented by

Table 3. COD and gas production data from acetic acid pulse test

Sample port, height in cm	Time t, hr 0	0.5	1.0	1.5	2	3	4	5	24
	Soluble COD, mg/L								
A, 15 cm	160	180	200	210	150	140	150	180	150
B, 45 cm	140	120	120	140	90	100	130	150	120
C, 75 cm	110	80	110	100	80	80	100	140	100
D, 105 cm	110	70	90	80	70	80	100	110	80
E, 120 cm	80	70	80	80	70	70	80	100	80
	Gas production rate, liter/hr								
All	---	0.86	1.02	1.12	1.10	1.01	0.94	1.02	0.88

the circles in Fig. 3, which describes operation at t = 0 (before the step increase) or t = 24 hr (after return to normal). If the recycle flow mixed completely with the fresh feed solution, the overall influent COD would be 265 mg/L. The COD values at Port A are significantly lower than this because of the combination of rapid substrate uptake in the lower part of the reactor and rapid mixing with the more dilute solution in the rest of the reactor, as discussed earlier. The small but steady decrease in COD as the condensate proceeds up the reactor is consistent with the model of a plug-flow reactor with high dispersion.

The reactor's response to the step increase in influent COD was a rapid and efficient fermentation of the extra substrate. The conversion of the extra acetic acid to methane and bicarbonate was so efficient that the COD increase was never even detected at any port above Port A. The nominal hydraulic detention time between the influent and Port A was 11 minutes and that between Ports A and B was 22 minutes. The results demonstrate dramatically that the microbial population near the influent port was not inhibited by the change in influent composition. In fact, the microorganisms metabolized all the extra substrate immediately, indicating that they were far from a condition of substrate saturation. Independent confirmation that essentially none of the extra acetate "leaked" through the reactor to the effluent was provided by measurement of gas production for 24 hours after the start of the test. The increase in gas production subsequent to the step increase was consistent with the 100% reaction of the added acetic acid.

The information gained from this experiment is important for two reasons. First, it suggests that variations in waste strength typical of sulfite mills do not upset the SMAR under the conditions tested. Of course, the results may be different for SMAR's operated at much higher organic loading rates, or if

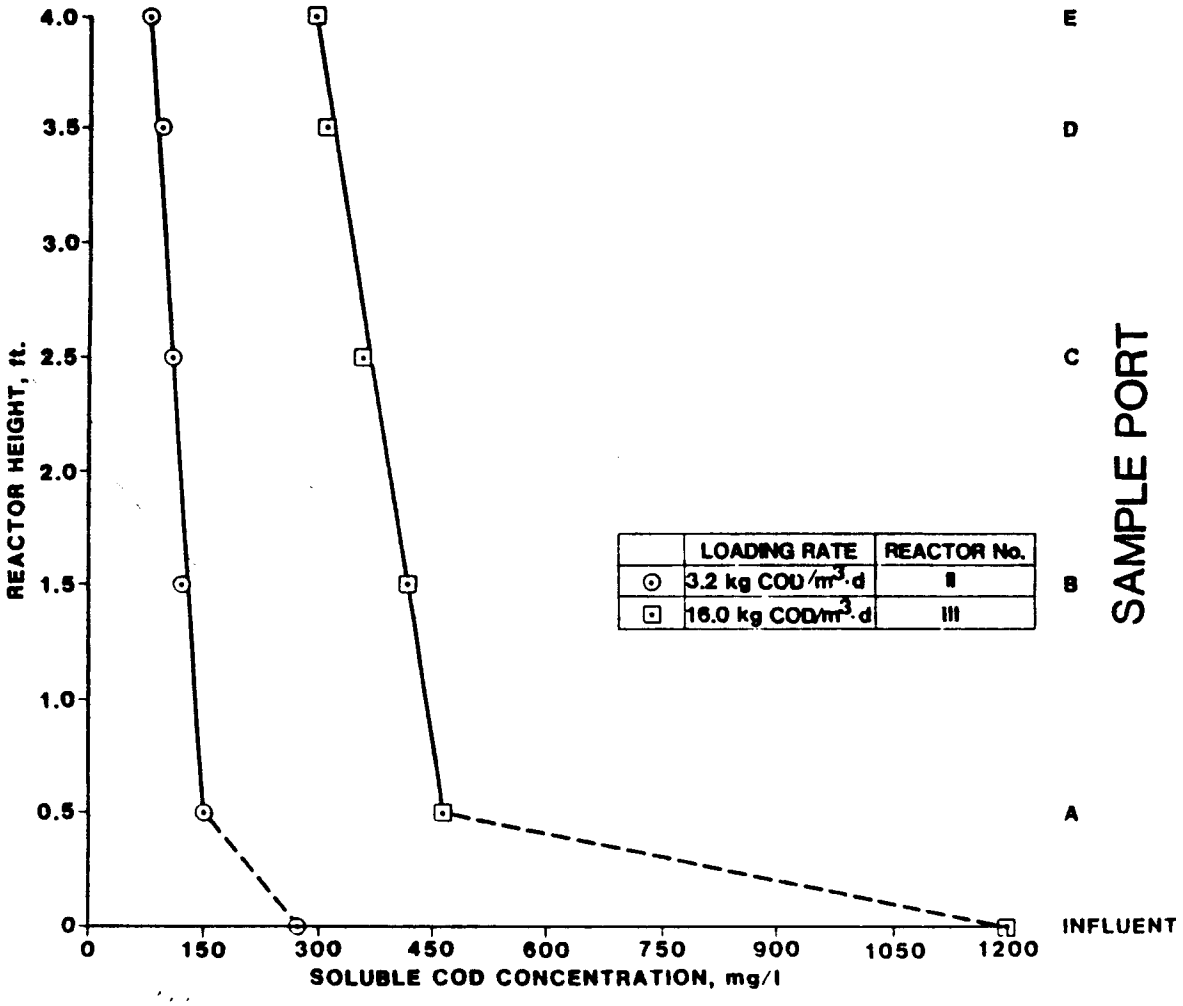


Figure 3. Steady-state COD profiles from reactors used in step (circles) and pulse (boxes) loading tests.

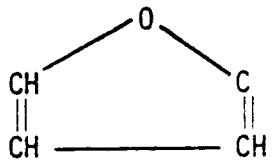
the increase in acetic acid is not balanced by an equivalent increase in base added. Secondly, the apparent complete utilization of added substrate in the lower portion of the reactor suggests that very high substrate removal rates are being achieved in this section. Utilization at the bottom of the reactor, utilization expressed as kg COD removed/m^3-day, is probably much higher than the average rate, based on total reactor volume. By mixing or feeding at several ports, it may be possible to increase the rate throughout the reactor and thereby treat wastes at a much greater organic loading than at present.

Pulsed loadings of spent sulfite liquor. At an operating pulp mill, spent sulfite liquor (SSL) may be mixed with SEC intentionally during washdown of the evaporator or unintentionally as a result of process upset. Both organic and inorganic constituents of SSL present potential toxicity problems. The magnitude of such problems was assessed in two pulse loading tests in which fermented SSL was added directly to a laboratory SMAR treating industrial SEC under the following conditions: Q = 2.5ℓ/hr; R = 10.1ℓ/hr; L = 16 kg COD/m^3-day; $\theta_H^{'}$ = 7.4 hr; $\theta_H^{'}$ = 1.5 hr. The SSL used in these tests contained 50% solids. Total SSL solids added were 10 g and 100 g, added over periods of 1 minute and 10 minutes, respectively. In both cases, total gas production increased when the SSL was added, indicating not only a lack of inhibition or toxicity but also partial metabolism of the SSL. Daily gas production during 10 days of steady operation preceding these tests was 4.60 ± 0.39 (1)L/day. Assuming the gas to be 80% methane and the BOD of this SSL to be 0.16 g/g, approximately 7 L of gas would be produced by complete fermentation of 100 g of SSL solids. The actual increment in gas production following addition of 100 g of SSL solds to the reactor was ∿ 3.5 L, so approximately 50% of the BOD in the SSL was converted to methane. While these calculations are very rough, they do indicate that when SSL mixes with SEC,

SMAR performance does not deteriorate. Some metabolism of SSL occurs even in SMAR's unacclimated to SSL.

Metabolism of specific compounds in SEC

Analysis for specific compounds in the effluent is an important tool in understanding the reactions, performance, and ultimately the limits of the process. The bulk of the COD in SEC is comprised of acetic acid, methanol, and furfural. The major metabolic pathways for anaerobic degradation of acetic acid and methanol have been studied extensively by other workers[1]. A reasonable fermentation pathway for furfural is shown in reaction[10].



$$\xrightarrow{} CHO + 4H_2O \xrightarrow{} 2CH_3COOH + CO_2 + 2H_2 \qquad (2)$$

Measurements of these 3 compounds in the laboratory SMAR's treating industrial SEC indicate that all are degraded efficiently in the reactor. Analysis of acetic acid and furfural in the influent and effluent streams indicates that approximately 85% of the furfural and $\geq$ 95% of the acetic acid are metabolized in the trials with > 90% COD removal. Assuming that all the COD in the effluent, other than that accounted for as acetic acid or furfural, is methanol, a conservative estimate of 97% methanol degradation can be made. In reality, much of the COD attributed to methanol in this calculation is probably due to metabolic by-products, so that actual methanol removal efficiency is > 97%. A schematic representation of these relationships is presented in Fig. 4.

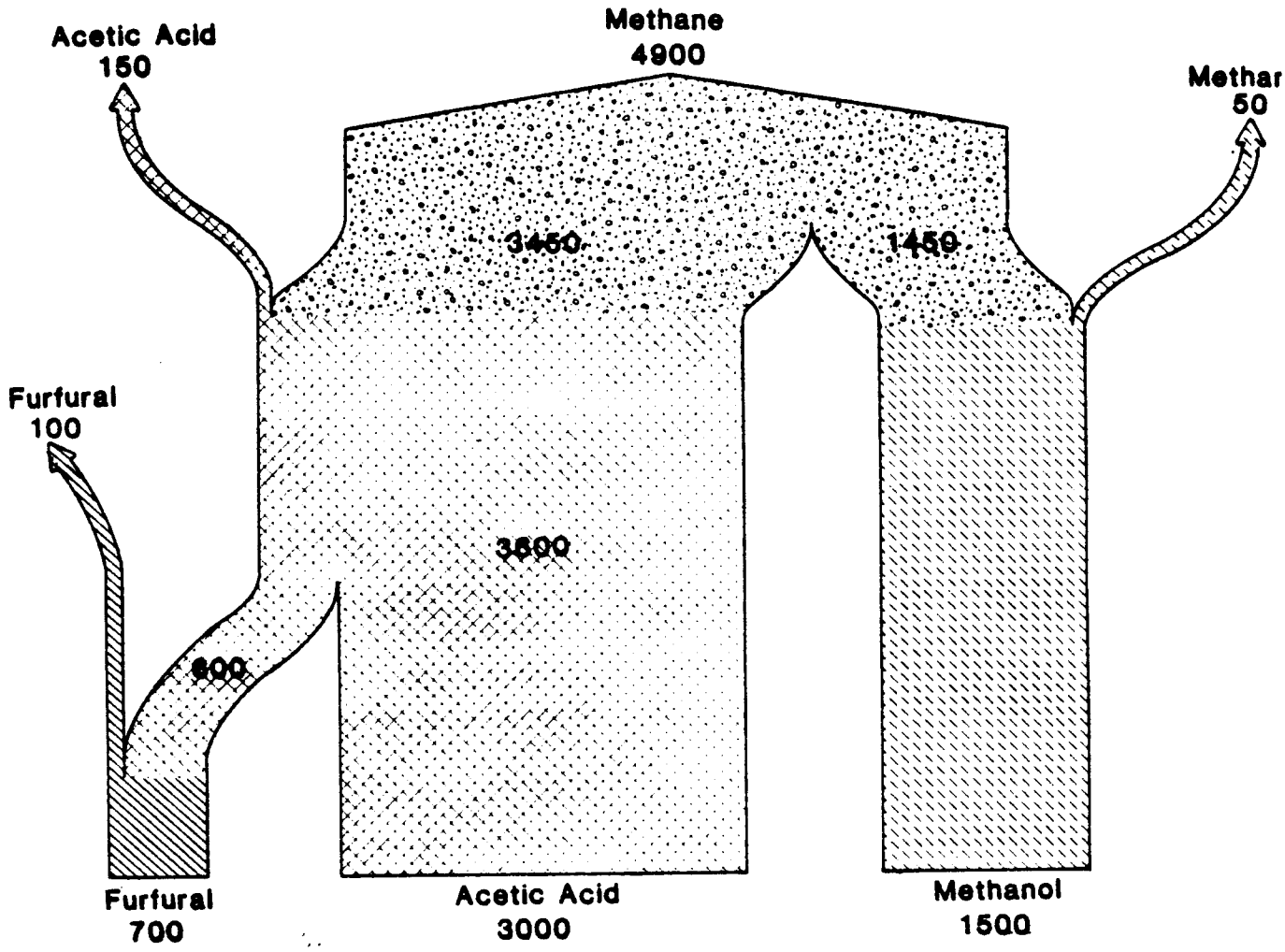


Figure 4. Schematic methane fermentation pathways based on COD balance for conversion of furfural, acetic acid, and methanol.

The fate of sulfur in the process has not been elucidated. The industrial condensate contains about 0.25 g/L sulfur in a variety of forms, including free and loosely combined SO_2, SO_4^{2-}, and sulfonates. The sulfur may be reduced by sulfate-reducing bacteria and immobilized as sulfides or elemental sulfur. Preliminary measurements indicate about 50% removal of total sulfur. Reactions of sulfur in the industrial SEC are not extensive enough to affect the COD balances significantly. However, SO_2 concentrations as high as 0.5g/L as S have been reported in SEC[4] and could be a significant part of the effluent COD.

Effluent quality

Our studies thus far have focused on demonstrating the feasibility of SMAR treatment of SEC. The goal has been to remove most of the COD from SEC with concomitant production of methane. The effluent from this process is of dramatically better quality than the influent, but is still not suitable for direct discharge at a receiving water because of odor and residual concentrations of oxygen-demanding substances, inorganic salts, and particulate matter (Table 4). Preliminary short-term studies indicate that the sulfide odor can be removed and COD reduced 10% to 15% by aeration. In these tests the effluent was from a SMAR treating industrial SEC at 16 kg COD/m^3-day, and aeration was for 10 minutes. Additional removal of COD and some nutrients may be accomplished by pumping the effluent to an aerobic treatment system treating other in-plant waste streams. Alternatively, filtration of the SMAR effluent may make it acceptable for reuse within the plant in a process which can tolerate water with relatively high dissolved-solids concentrations. The trade-off between the costs of further treatment to bring the water to reusable quality versus the benefits of reuse would

Table 4. Effluent characteristics for industrial and synthetic SEC from reactors at COD loadings near 16 kg/m^3-day

Characteristic	Industrial condensate	Synthetic condensate
COD_{total}, mg/L	490	360
$COD_{soluble}$, mg/L	280	280
BOD_{total}, mg/L	190	120
$BOD_{soluble}$, mg/L	120	N.A.
Total suspended solids, mg/L	112	46
Total dissolved solids, mg/L	3650	3630
Conductivity, μmhos/cm	5.98	6.30
Alkalinity, mg/L as $CaCO_3$	3100	3000
pH	7.2	7.7
Color, Pt units	7.8	< 5
Turbidity, NTU	69	18
Orthophosphate, mg/L as P	12.0	11.5
Total phosphorus, mg/L as P	14.5	12.3
NH_3-N, mg/L as N	170	160
Total iron, mg/L	2.4	0.1
Soluble iron, mg/L	0.0	0.0

differ from plant to plant. In balancing these costs and benefits, one should remember that the concentrations of inorganic constituents in the effluent presented in Table 4 represent worst-case conditions. The SMAR's have had excess additions or inorganic nutrients and alkalinity to ensure that bacterial growth was not nutrient limited. It is likely that alkalinity can be reduced by 30 to 60% and trace nutrient concentrations can be reduced by 50 to 90% without adversely affecting reactor performance.

One other option that should be considered is redesigning the present reactors, or, similarly, designing a second stage of anaerobic reactors with the specific goal of producing a high-quality effluent. This option may be particularly desirable since the present effluent already contains high alkalinity and all required trace nutrients. Factors that limit the quality attainable with anaerobic treatment are not satisfactorily established, but recent work suggests that anaerobic treatment is capable of producing effluent approaching the quality of most aerobic systems.[3]

Materials and Methods

Studies were conducted using 4 laboratory-scale synthetic media anaerobic reactors (SMAR's) fed either a synthetic condensate, clean evaporator condensate from the calcium bisulfite mill of the Georgia Pacific Corp. in Bellingham, Wash., or a mixture of the two. The reactors illustrated in Fig. 5, have a length of 120 cm and a diameter of 14 cm. They are packed with plastic cylindrical media with high specific surface areas and greater than 90% void volume; the void volume is approximately 19 liters in each reactor. The reactors are housed in refrigerator cabinet incubators, adapted to maintain internal temperatures between 25° and 40°C to a range of ± 2°C. Feed pumps, recycle pumps, gas meters, and collection bottles are external to the

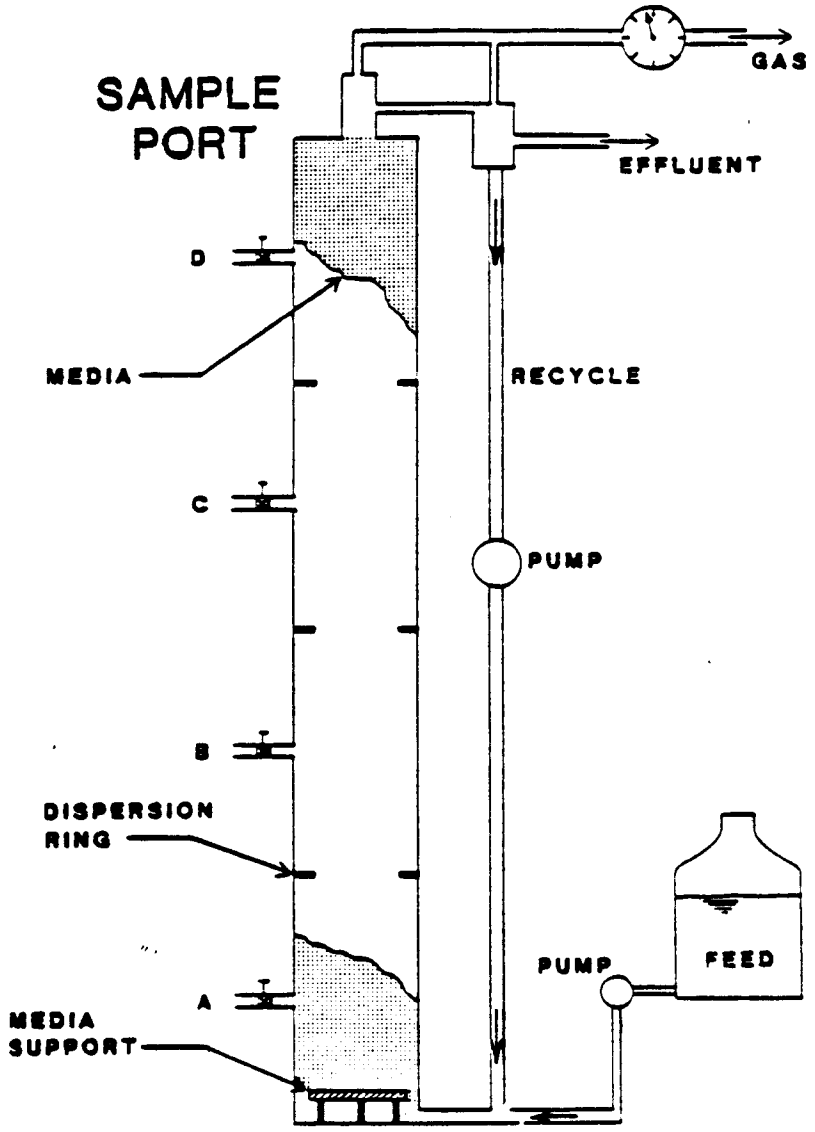


Figure 5. Schematic diagram to a submerged media anaerobic reactor (SMAR).

incubators. Connections are with lucite and tygon tubing, painted black to discourage growth of photosynthetic bacteria.

The characteristics of the two feed solutions are presented in Table 5. The synthetic condensate was made up in tap water using reagent-grade chemicals. Nitrogen, phosphorus, trace metals, and trace organic nutrients were added to the feed solutions in concentrations sufficient to assure that they would not limit biological growth. Acetic acid and dissolved SO_2 (in the industrial condensate) depress the feed pH to below 3. Much of the acidity is destroyed and bicarbonate alkalinity is produced by microbial acetate fermentation or sulfite reduction.

A stable pH above 6.8 is required to maintain a healthy microbial population in the reactor, and this condition can be achieved by providing adequate buffer capacity (typically 24 to 70 meq/L alkalinity). During most of this study, the feed solution was neutralized, and buffer capacity was provided by adding 66 meq/L base (48 meq/L NaOH, 18 meq/L $NaHCO_3$). This neutralization resulted in pH values above 6.8 throughout the reactors, effluent pH values above 7.2, and effluent alkalinities of approximately 60 meq/L.

The reactors were started in 1979 and 1980 using digesting sludge from the METRO treatment plant at West Point in Seattle. The organic loadings to the reactors were slowly increased in steps, allowing time for acclimation and growth of adapted populations. When stable operation was reached at a loading, a 5-day intensive sampling period was conducted to assess reactor performance at that loading rate. A total of 8 such tests are reported in this paper. The data collected included chemical oxygen demand (COD) of the influent; total and soluble COD, BOD, total and volatile suspended solds, pH, alkalinity, and volatile acids in the effluent; gas volume, and gas

Table 5. Major constituents in calcium bisulfite evaporator condensate and in synthetic feed

	Feed type			
	Synthetic SEC		Typical SEC (calcium base)	
Component	mg/liter	mg/liter as COD	mg/liter	mg/liter as COD
Acetic acid	3000	3200	3000	3200
Methanol	1000	1500	800	1200
Furfural	0	0	400	670
SO_2(aq) as S	0	0	250	125

composition. In other trials, conductivity, color, turbidity, ultraviolet absorption spectra, dissolved solids, phosphate, nitrogen, and iron were measured.

Summary

The treatment of sulfite evaporator condensate by an anaerobic process has significant advantages compared with aerobic biological treatment. This study has demonstrated the feasibility of such treatment and has dispelled some concerns about toxicity, reactor size, and other issues that militate against process adoption. Specific findings are as follows:

- Anaerobic treatment of SEC is practicable at loadings of at least 16 kg m^3-day, achieving about 85% removal of BOD.
- The submerged-media anaerobic filter, containing plastic media and with recycle flows greater than the influent flow rate is a practical reactor configuration.
- Methane production is proportional to COD removal and equals 0.33 L CH_4/gr COD removed.
- Biological sludge production is at most 0.09 g cells/g COD removed. Nitrogen and phosphorus requirements will not exceed 7.2 kg of N and 0.9 kg of P per 1000 kg COD removed. Measured values to date are significantly lower.
- Partial neutralization of the condensate is required.
- The effluent quality is not suitable for direct discharge.

There are many questions that require further study, including the fate of specific constitutents, the influence of reactor design or loadings and performance, the minimal requirements for neutralization and nutrient additions, and proper operating procedures to waste sludge and maintain stable

operation. The results to date are encouraging and merit development of the process on a pilot scale as well as serious consideration of the process for sulfite mills.

REFERENCES

1. Gaudy, A.F., and Gaudy, E.T., Microbiology for Environmental Engineers and Scientists, McGraw-Hill, New York, 1980.

2. Lettinga, G., Industrial Wastes, 25(1): (1979).

3. Mueller, J.A. and Mancini, J.L., Proceedings, 30th Purdue Industrial Waste Conference, May 1975.

4. Ruus, L., Svensk Papperstid., 67: 221 (1964).

5. Shea, T.G., et al., EPA Report 660/2-74-074, July 1974.

6. Suidan, M.T., Cross, W.M., Fong, M., Calvert, J.W., J. Environmental Engineering Division, ASCE 107: 563 (1981).

7. Switzenbaum, M.S., and Jewell, W.J., JWPCF, 52(7): 1953 (1980).

8. Van Den Berg, L., Proceedings, 35th Purdue Industrial Waste Conference, May 1980.

9. Witt, E.R., Humphrey, S.J., and Roberts, T.E., Proceedings, 34th Purdue Industrial Waste Conference, May 1979.

10. Yang, J., Parkin, G.F., and Speece, R.E., "Recovery of Anaerobic Digestion after Exposure to Toxicants," Final Report, U.S. D.O.E. Contract No. EC-77-S-02-4391, 1979.

11. Young, J.C., and McCarty, P.L., Proceedings, 22nd Purdue Industrial Waste Conference, p. 559, 1967.

CHAPTER 2

ANAEROBIC TOXICITY AND BIODEGRADABILITY OF PULP MILL WASTE CONSTITUENTS EXPOSED TO ANAEROBIC BACTERIA[1,2]

Mark M. Benjamin
Sandra L. Woods
John F. Ferguson

ABSTRACT

Batch bioassays have been conducted to characterize the response of methanogenic bacteria to several constituents of sulfite evaporator condensate. The results can be grouped into three ranges with increasingly severe consequences to anaerobic reactors: a low concentration, no effect range; a medium concentration range where methanogenesis is temporarily interrupted or slowed down, but may return to normal; and a high concentration range where methanogenesis is permanently inhibited. In some cases the toxicant was metabolized when present in the lower concentration ranges. There was also evidence that mechanisms other than fermentation to methane were significant in accounting for removal of the toxicants from solution. Organisms acclimated to low concentrations of a toxicant are better able to withstand a shock load of that toxicant than are unacclimated organisms.

1. Presented at IAWPR Specialized Seminar on "Anaerobic Treatment of Wastewater in Fixed Film Reactors," Copenhagen, Denmark, June 1982.

2. Accepted for publication in Water Research.

INTRODUCTION AND BACKGROUND

As anaerobic treatment is used increasingly for industrial wastes that may contain high concentrations of toxic or nondegradable compounds, there is a need for methodology to evaluate and characterize the factors controlling toxicity, removal, and degradation of these compounds. This paper presents the results of such a study of sulfite evaporator condensate, a wastewater produced during the evaporative concentration of spent wood pulping liquors in the acid bisulfite process.

Batch Assays of Anaerobic Toxicity and Biodegradability

Anaerobic toxicity assays (ATA) and biological methane potential (BMP) tests, developed initially by Hungate[5] and modified by Miller and Wolin[7] and Owen, et al.,[9] can be used to screen a waste for potential toxicity and degradability. These bioassays can also be used to determine the concentration at which particular compounds exhibit toxicity and the length of time required for a microbial population to acclimate to them.

The ATA is a batch procedure intended to provide reproducible assay conditions where toxicant concentration is the only parameter varied. In this test an active methanogenic culture is fed some easily degradable compounds and various concentrations of the potential toxin. A decrease in the rate of methane production with increasing concentration of the test compound is indicative of toxicity. In BMP tests the same procedure is followed but no easily degradable compounds are added, so methane production can be interpreted as a direct measure of the potential for the test compound to be used as a sole carbon source for methanogenesis.

Interference with metabolism of methanogenic cultures can manifest itself in several different ways in these tests. If the test compound is extremely toxic, it may kill all the organisms responsible for at least one step in the metabolic sequence. In this case methanogenesis cannot resume unless the toxic compound is removed or detoxified, e.g. by dilution or by reactions which lower its activity in the aqueous phase, such as sorption or complexation. Then the solution can be re-inoculated with organisms which can carry out all the transformations of the killed populations.

In a slightly less severe situation, the test compound may totally or partially inhibit microbial metabolism. In the former case biological activity ceases until the compound is removed from the system or is detoxified. If the compound does not completely inhibit metabolism, some bacterial activity will continue. The culture may eventually detoxify or acclimate to the compound, allowing a return to the same specific metabolic rate as in the absence of toxicant. Alternatively, methanogenesis may proceed at a lower specific rate than in the absence of toxicant.

If the toxicant can be degraded to methane by the culture after some acclimation period, the evidence of toxicity in an ATA may be either a decreased initial gas production rate or a lag period before gas production begins. In either case, the toxic effects should diminish with time, and the ultimate gas production will reflect the additional gas generated by utilization of the test compound.

One other possible result of the ATA's is that fermentation of the spike may proceed without any effect of the test compound. This may occur with or without any utilization of the test compound, and would be apparent if gas production was equal to or greater than that in the controls at all times after inoculation.

Several of the above responses have been reported by Parkin, Speece, and co-workers (Chou, et al.;[3] Yang, et al.;[13,14] Parkin and Speece[10]) who have studied the response and recovery of methanogens exposed to numerous organic and inorganic toxicants. They have observed a decreased rate of gas production in some cases and a temporary total cessation of gas production in others. The duration of the period of no gas production generally increases with toxicant concentration. The most interesting result of this work is that in almost all cases where severe toxicity occurs, the organisms eventually acclimate to the toxicant and gas production returns to its pre-exposure rate. They conclude that the reputation which anaerobic bacteria have acquired of being very sensitive to toxicants is ill-deserved.

The observed effect of a given toxicant may be much more complex than the previous discussion implies. First, the effect will clearly depend on toxicant concentration. In addition, multiple populations of microorganisms are likely to be involved in mediating the complete degradation of a single compound, and the effect of the toxicant may be different on each species. Nevertheless, the description above is useful as a conceptual model and to describe the dominant response of a mixed culture to a specific toxicant.

Characteristics of Sulfite Evaporator Condensate

Sulfite evaporator condensate (SEC) is a wastewater with a high, soluble COD (4,000-7,000 mg/l). In a pulp mill SEC represents approximately 15% of the wastewater flow, but it can contain 30% to more than 50% of the BOD_5 of the total pulp mill effluent. The predominant organics in the waste are short-chain acids and alcohols and furfural, an aldehyde derived from pentose dehydration. These slightly volatile organics can readily be measured by gas

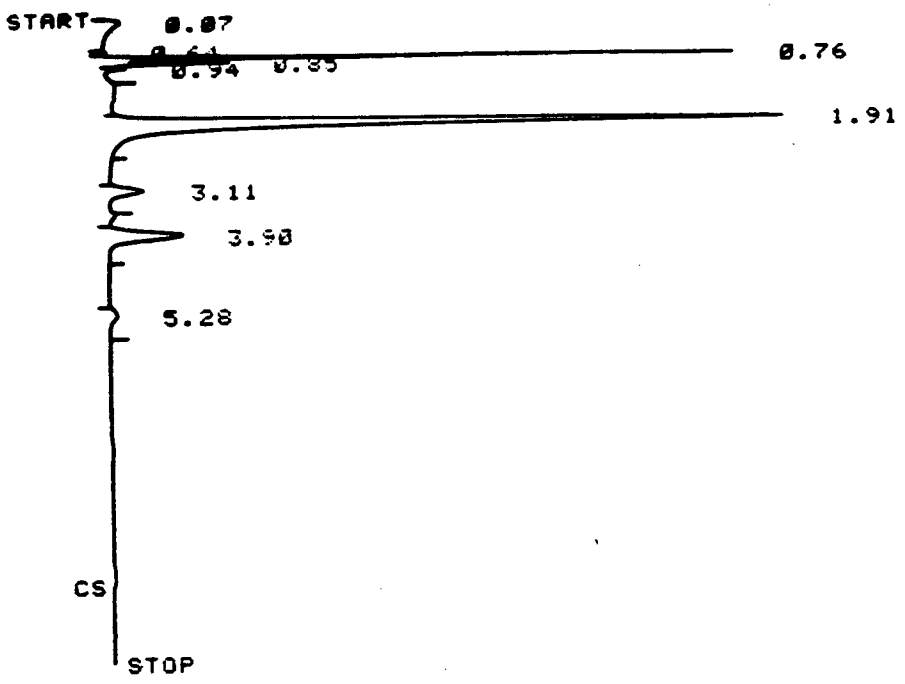
chromatography (Fig. 6). Acetic acid and methanol contribute 70% to 80% of the COD in the condensate.

In addition to volatile acids and alcohols, SEC contains potentially toxic minor constituents including terpenes, aldehydes, ketones, phenols, and sulfur bearing compounds. The number and concentration of these compounds in SEC are functions of several variables including the species of tree being pulped, the conditions of the pulping process and contamination with other process streams.

The results presented here describe the response of mixed methanogenic cultures to individual toxicants (furfural, guaiacol, p-cymene, eugenol, limonene, and difurfuryl disulfide) expected to be present in SEC, and to a sample of industrial SEC. The inocula for the tests were either "acclimated cultures" taken from a reactor which had been treating industrial SEC for 8 months or "unacclimated cultures" taken from a reactor fed a synthetic condensate containing acetic acid, methanol and nutrients. This work is part of a larger study to determine the treatability of SEC and the fate of potentially toxic compounds in anaerobic reactors.[1,2,4]

METHODS

BMP assays and ATA's were conducted according to the method of Owen et al.[9] A defined media was prepared from stock solutions of resazurin (a redox indicator to detect oxygen contamination), sodium sulfide (to provide a reducing environment), and nutrients and vitamins added to deoxygenated deionized water. Two hundred ml of seed inocula were taken from reactors treating synthetic or industrial SEC and added to 1800 ml of defined media. The test compound, media, and inocula were anaerobically transferred to serum bottles



RT min	Compound	Concentration mg/l
0.75	Methanol	730
0.85	Ethanol	≈ 100
1.94	Acetic Acid	3750
3.17	Propionic Acid	150
3.95	Furfural	225
5.40	Butyric Acid	≈ 50

(10% SP-1200/1% H_3PO_4 on 80/100 Chromsorb W AW, 6ft x 4mm ID; column temp.: 130°C; injector: 200°C; FID temp.: 200°C; flow rate: 40 ml/min nitrogen; 1 microliter sample)

Figure 6. Typical gas chromatograph and composition of industrial sulfite evaporator condensate.

which had been purged of oxygen. The bottles were capped and in the ATA's, a solution containing 105 mg acetic acid and 16 mg methanol was injected. The bottles were then allowed to equilibrate to 35°C for 1 hour before gas measurements were begun. The volume of gas produced in each bottle was measured periodically by displacement of the barrel of a lubricated syringe,[8] and methane in the gas was determined by gas chromatography. All tests, including blanks which contained no toxicant, were run in triplicate.

Volatile acids, alcohols, and trace organics were analyzed using a Hewlett Packard 5840A gas chromatograph with a flame ionization detector. A 6 foot by 2 mm ID glass column packed with 10% SP 1220/1% H_3PO_4 (Supelco, Inc.) was used for the separations. The analyses were run isothermally at 130° C. The detector and injection port were held at 200° C. The carrier gas was 40 ml/min nitrogen and a 1 microliter sample was injected directly onto the column.

Blanks

The mean gas production for 38 blank ATA samples (containing the easily degradable spike but no test compound) was 53.6 ml (s.d. 8.6 ml) of which approximately 87% (47 ml) was CH_4. This value is 91% of the theoretical value (58.9 ml) predicted based on complete utilization of the spike and a yield coefficient of 0.06 grams cells per gram COD.[6] The 53.6 ml represents the cumulative gas production after all available substrate had apparently been utilized, i.e., after several days of zero gas production. In all the blanks, most of the gas production occurred over a 2 to 5 day period. This period started immediately after inoculation with unacclimated seed, but did not start for 5-15 days with acclimated seed. The lag period for these latter cultures was always consistent ($\pm$ 1 day) for bottles inoculated at the same

time (Fig. 7). The lag period in the tests with acclimated organisms was apparently associated with some insult to the reactor (e.g., a spike of some toxicant in the feed) just prior to collection of the organisms. Since organisms from both reactors (receiving synthetic and industrial feed) were transferred to the bottle tests over several weeks using the same technique and since only those receiving industrial feed displayed a lag in the bottle tests, it is unlikely that the lag was an artifact of the inoculation procedure.

In the discussion, the effects of test compounds are always based on a comparison with a blank inoculated at the same time as the test bottle. Methane production in the test bottles is compared to the blank value and to the total potential methane production assuming the test compound is fermented along with the spike. Degradation of the test compound to methane is indicated if gas production in a test bottle is significantly greater than in bottles with an equivalent spike and media but none of the test compound.

Furfural

Furfural is present in SEC at concentrations ranging from 10 to 1280 mg/l.[12] In five condensate samples from Georgia Pacific's mill in Bellingham taken over a 5 month period, the mean furfural concentration was 274 mg/l (range 179 to 471 mg/l; s.d. 113 mg/l). To determine the effects of furfural on methanogenic cultures, triplicate ATA's were run with furfural concentrations of 10 to 5800 mg/l with unacclimated and acclimated cultures.

Unacclimated anaerobic organisms exposed to furfural responded in several of the ways noted above (Fig. 8). When 120 mg/l furfural was added to a test bottle, methanogenesis proceeded at the same rate as in the blanks. The amount of gas that would have been produced by degradation of furfural was

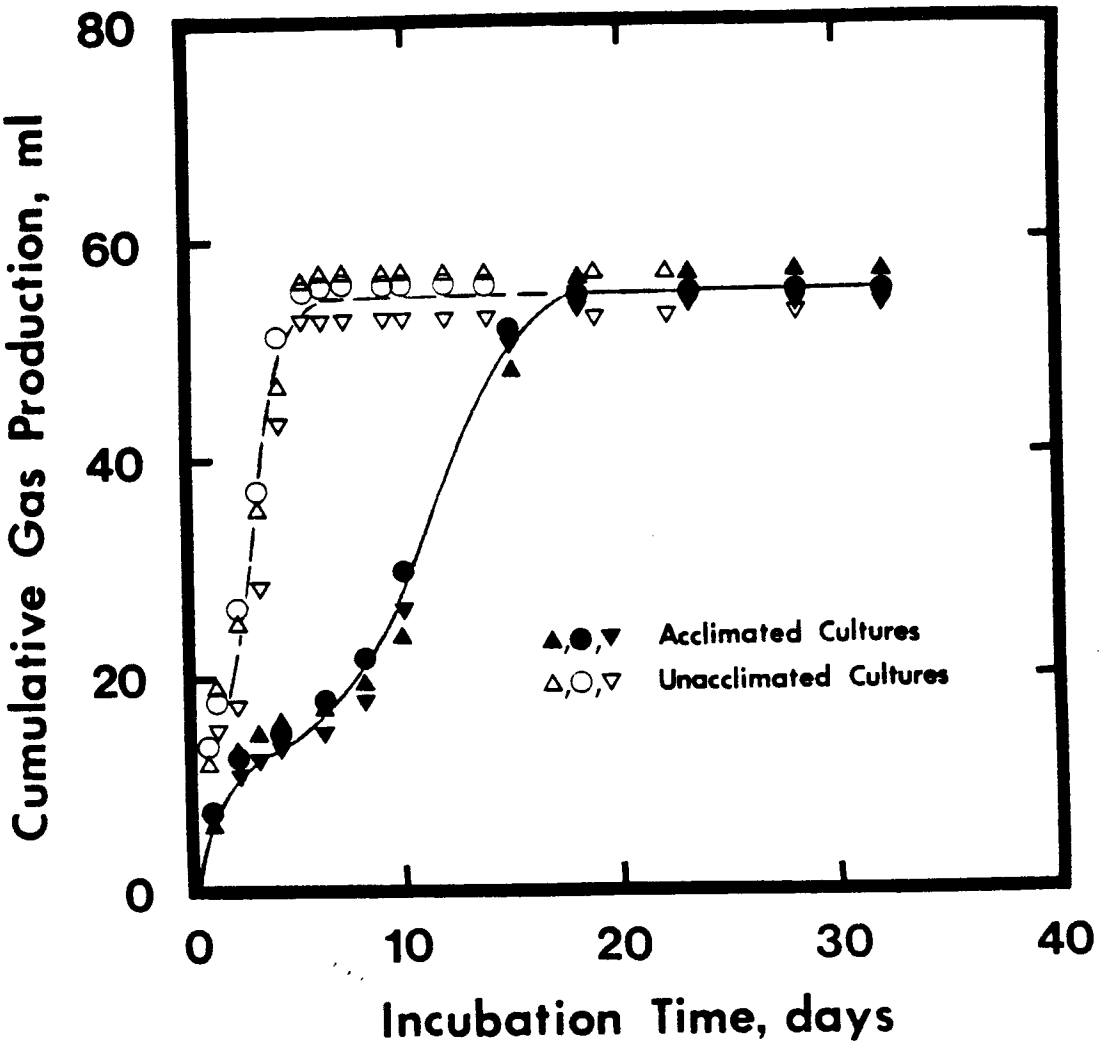


Figure 7. Typical replicate blanks using inocula acclimated and unacclimated to industrial SEC.

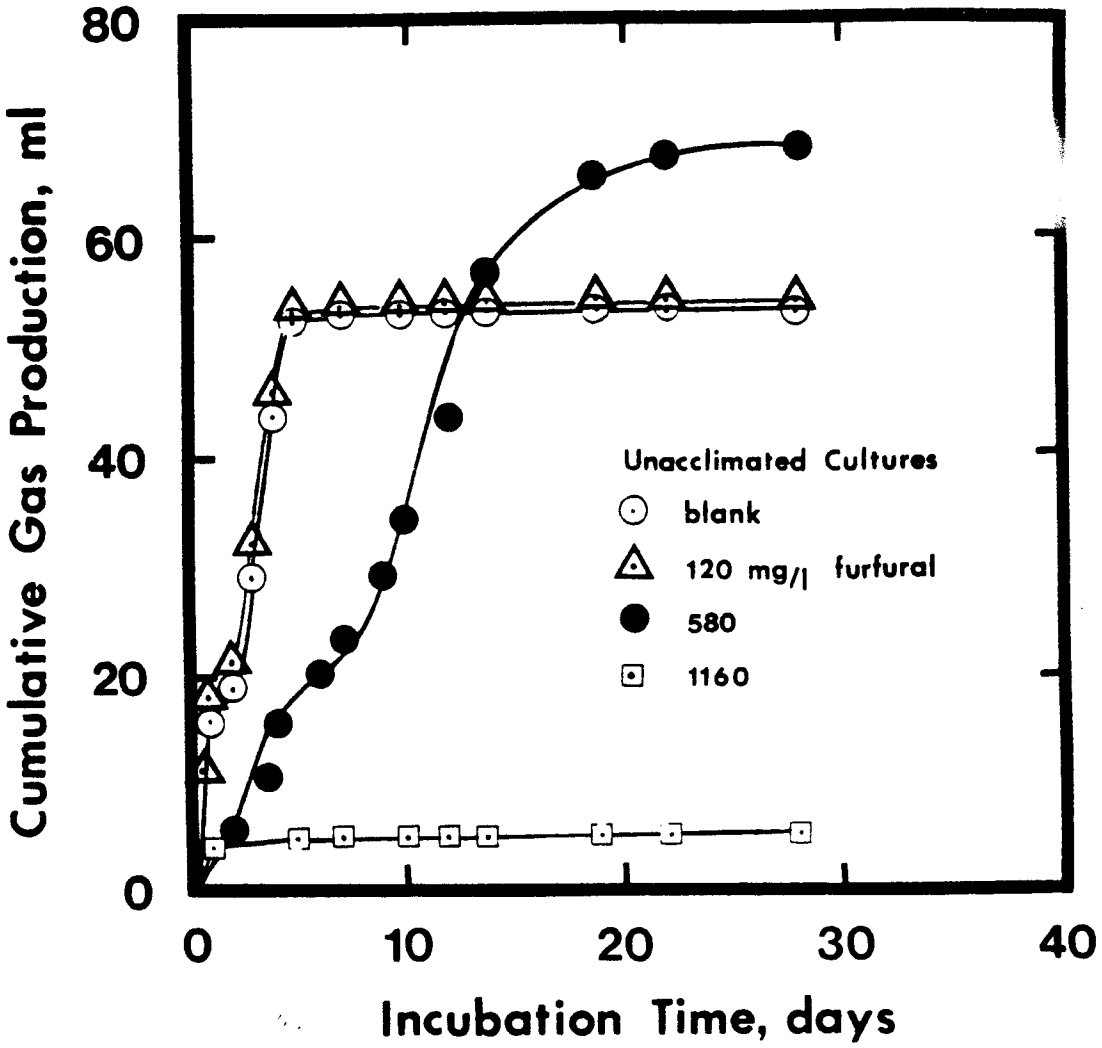


Figure 8. Gas production in ATA's with unacclimated seed and various initial furfural concentrations.

small compared to that from the spike, so it is not clear whether the furfural was fermented in this test.

In a test with 580 mg/l furfural, ultimate utilization of furfural and conversion to methane was clearly indicated. Total gas production in this test after 30 days was consistent with substantially complete conversion of furfural to methane and carbon dioxide. However, the rate of methanogenesis was reduced by about a factor of 3 compared to the blank. The fact that initial gas production was slower in the system with furfural indicates that the furfural was actively interfering with degradation of the spike. There is no indicaton whether the methanol/acetate spike was utilized faster than or prior to the furfural.

When exposed to 1160 mg/l furfural, the unacclimated culture stopped gas production after a short period (< 5 days) and none of the gas produced was methane. Gas production did not resume during the remainder of the 28 day test period.

These tests can be compared with tests in which furfural was added to acclimated cultures. Recall that in this context an acclimated culture is one that has received a feed solution containing an average of approximately 310 mg/l furfural for 8 months. When organisms from this culture were used as seed in an ATA containing 1160 mg/l the gas production was enhanced compared to blanks throughout the test period, suggesting that the furfural did not inhibit fermentation of the spike and that furthermore, the furfural itself was readily fermented (Fig. 9). When acclimated organisms were exposed to 2320 mg/l fufural, the response was rapid until 50-60 ml of gas was produced (9 days), and then was considerably slower for the remainder of the test. Since the blanks produced 54 ml gas it is reasonable to suspect that the non-furfural spike was degraded rapidly, and the furfural more slowly. This

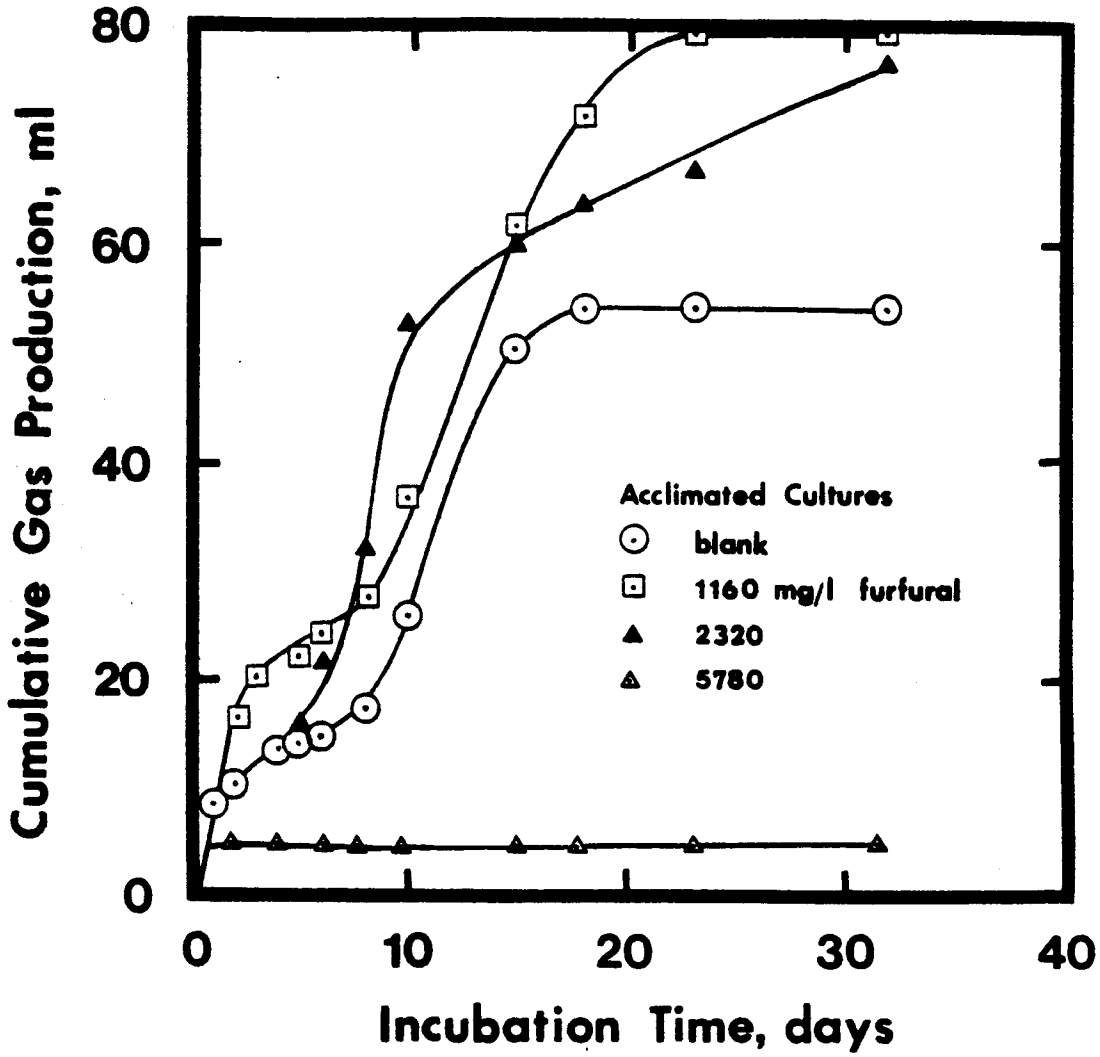


Figure 9. Gas production in ATA's with acclimated seed and various initial furfural concentrations.

could result, for instance, if the organisms involved in the initial steps of furfural utilization were inhibited by the high furfural concentration more so than were the methanol or acetate fermenters.

That high furfural concentrations can inhibit methanogens was demonstrated by the 1160 mg/l test with unacclimated organisms and confirmed by the 5780 mg/l test with acclimated seed. In the latter case, no gas was produced after the first day of the assay.

Degradation of furfural in some of these solutions was verified by gas chromatography. Less than 25 mg/l furfural remained in solution in the unacclimated ATA's at the completion of the 28 day test for bottles fed acetate, methanol and 580 mg/l furfural. Acclimated ATA's spiked with 2320 mg/l furfural also contained less than 25 mg/l furfural after 32 days, corresponding to 99% furfural removal. These values for furfural removal are significantly greater than the 85% removal that can be accounted for by methane production in the ATA's. Furfural removal which does not lead to methane production may result from partial degradation and accumulation of fermentation intermediates, volatilization, or sorption.

Degradability of furfural was also verified by performing biological methane potential (BMP) assays in which furfural was the only source of carbon. Unacclimated organisms produced no methane when fed 2800 mg/l furfural in a BMP assay. However, acclimated cultures started producing gas immediately upon inoculation in 690 mg/l and 2320 mg/l furfural solutions (Fig. 10). Gas production continued in these tests until approximately 100% and 70% of the COD was converted to methane in the 690 mg/l and 2320 mg/l tests, respectively. Since the energetics of furfural utilization are not well known and the solution pH was not monitored, the estimate of total gas expected per mg of furfural utilized is uncertain in this case. Nevertheless, the conclusions

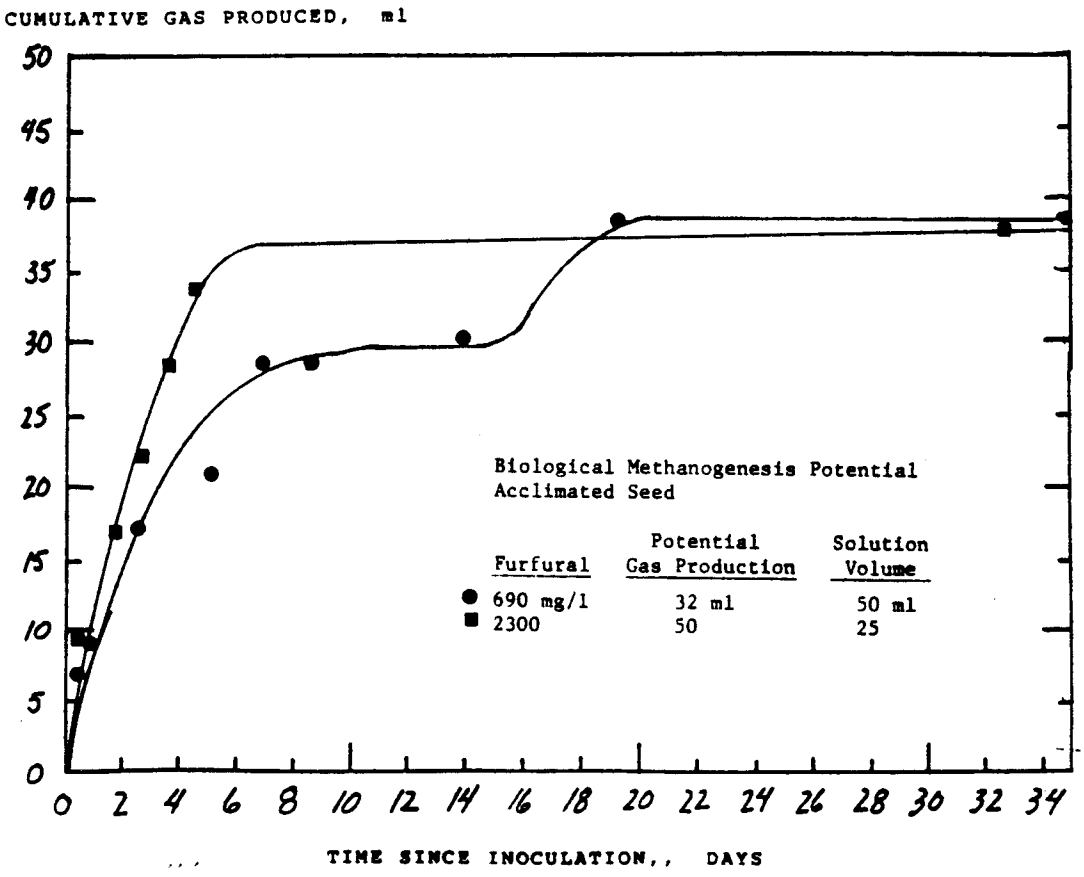


Figure 10. Total gas production in a BMP assay of furfural. The maximum expected gas production is computed assuming 100% conversion of COD to methane, and 87% methane in the gas phase.

that acclimated organisms can utilize 2320 mg/l furfural as their only carbon source for energy and growth and that a significant fraction of the furfural carbon is ultimately catabolized with production of methane are unambiguous.

The responses of the unacclimated and acclimated cultures to furfural in ATA's were very similar qualitatively. In each case, a low toxicant concentration appeared to be readily metabolized, while a higher concentration caused a reduction in metabolic rate, but ultimately led to degradation of the test compound. A still higher concentration of toxicant caused total cessation of methanogenic activity, at least for the duration of the tests. It may be that with further incubation gas production would have begun in these high concentration systems. No tests were conducted as part of this study to determine whether the methanogens were killed or simply temporarily inactivated by the high furfural concentrations.

Guaiacol

The concentration of guaiacol in condensates is generally below 100 mg/l.[13] Gas chromatography indicated that condensates used as feed for the "acclimated" reactor contained less than 25 mg/l guaiacol. Anaerobic toxicity assays were performed for 10 to 5600 mg/l guaiacol using cultures both acclimated and unacclimated to SEC, with results qualitatively similar to those for furfural.

When guaiacol ATA's were run with unacclimated organisms, a concentration of 560 mg/l did not inhibit gas production (Fig. 11). It is possible that some of the guaiacol was fermented to methane in this test. In the 1100 mg/l ATA with unacclimated inocula, gas production slowed down after 4 days incubation relative to cultures with less guaiacol; however it continued after gas production had ceased in the other tests, and by the end of the 32 day test

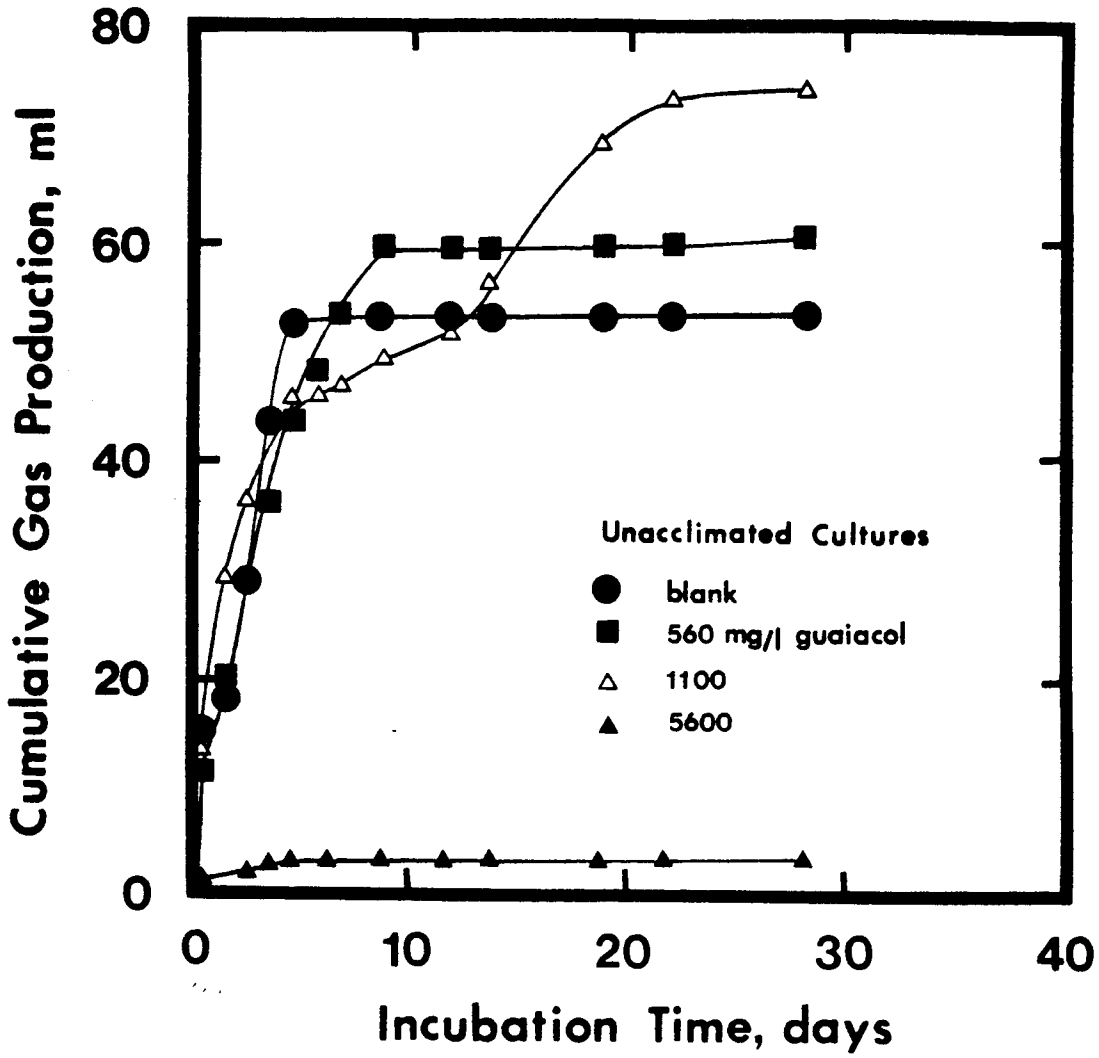


Figure 11. Gas production in ATA's with unacclimated seed and various initial guaiacol concentrations.

period it was clear that some of the guaiacol had been fermented. A 5600 mg/l guaiacol ATA with unacclimated seed produced no methane at all during the 32 day test, indicating that both guaiacol-metabolizing and methane-producing bacteria were killed or at least severely inhibited by this guaiacol concentration.

Since the guaiacol concentration in the feed to the acclimated reactor was small (< 25 mg/l), one would not expect these cultures to behave very differently from unacclimated cultures when exposed to guaiacol concentrations of > 500 mg/l. This was in fact the case (Fig. 12). As in the ATA's with unacclimated organisms, 560 mg/l guaiacol did not retard or inhibit gas production at all, and the final volume of gas produced was slightly greater than in the blanks. Similarly, 1100 mg/l guaiacol caused a reduction in the rate of gas generation after a few days, but after 30 days the gas produced in the 1100 mg/l bottles exceeded that in the blanks, and gas was being produced in the assays after gas production had ceased in the blanks. Gas production in an ATA with 2200 mg/l guaiacol was significantly inhibited for about 10 to 15 days, then proceeded at a rate comparable to that in the blanks and the less concentrated ATA's for a time. After about 20 days, gas production ceased for the remainder of the test period at a value of total gas produced less than that in the blanks or other ATA's. It is clear from this ATA (and from the 5600 mg/l ATA with unacclimated seed) that high guaiacol concentrations can inhibit acetate-utilizing methanogens. Under some circumstances the bacteria can acclimate to such an environment and resume methanogenesis within a few days. The fact that gas production stopped abruptly while a significant amount of COD remained in the system in the 2200 mg/l ATA suggests that some factor other than guaiacol concentration caused the toxicity. One possibility is that a toxic intermediate was formed from guaiacol degradation. Although

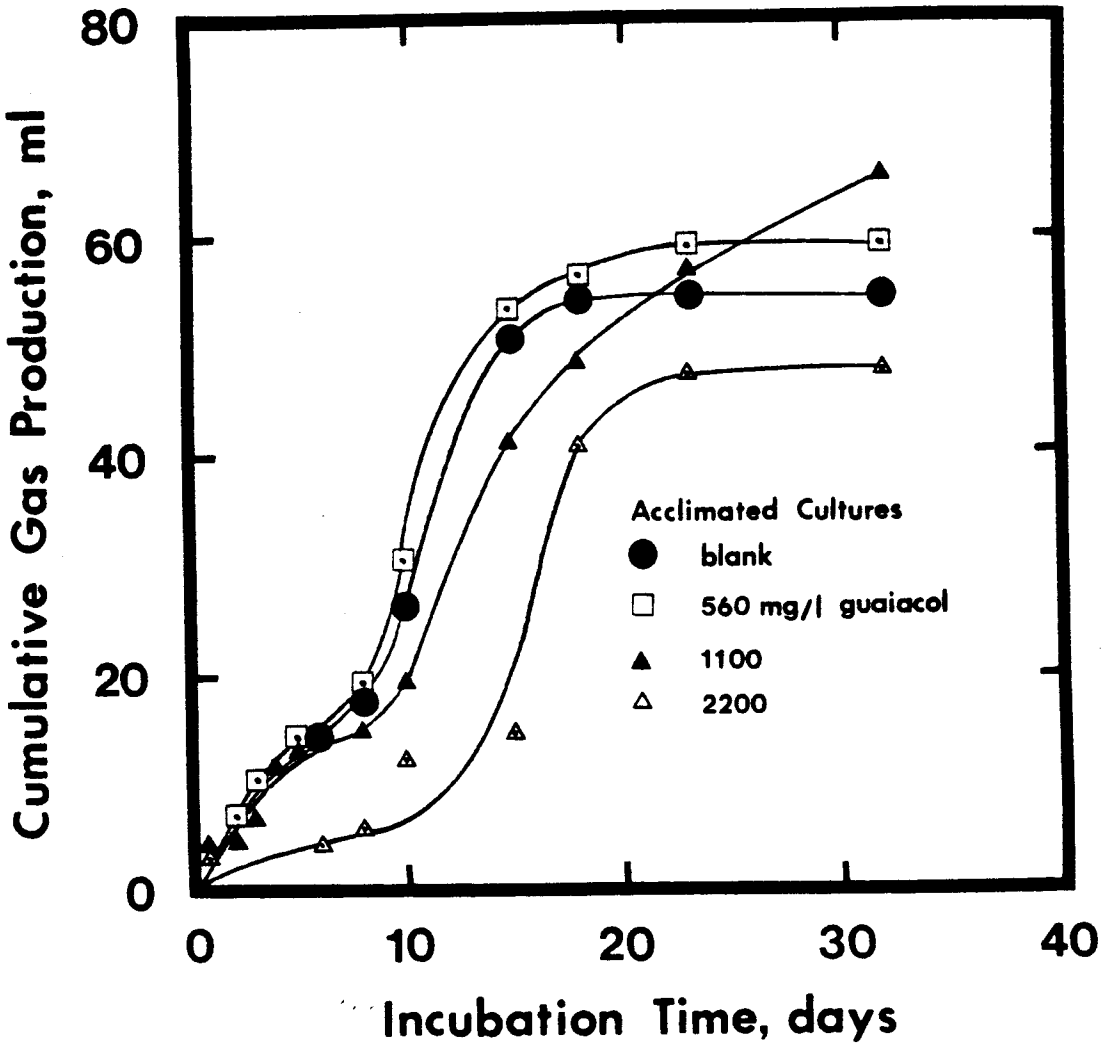


Figure 12. Gas production in ATA's with acclimated seed and various initial guaiacol concentrations.

this possibility was not confirmed, it is supported by the results of a BMP assay with 2200 mg/l guaiacol (Fig. 13). In this case, gas was produced slowly at first, then more rapidly until about 20 days after inoculation. Then gas production ceased, as it had in the ATA. The fact that less than 2% of the added guaiacol remained in solution at this time, while only about 30% had been converted to methane, is at least consistent with the possibility that much of the initial guaiacol had been converted to another compound.

Other Individual Toxicants and Industrial Sulfite Evaporator Condensate

Four other trace constituents of sulfite evaporator condensate were assayed in ATA's: p-cymene, eugenol, limonene, and difurfuryl disulfide (Figs. 14 to 17). For p-cymene and eugenol, the results were similar whether acclimated or unacclimated inocula were used. It is likely that the concentrations of these compounds in SEC are so low that organisms in the reactor receiving SEC did not acclimate to them.

In ATA's in which acclimated organisms were exposed to eugenol (Fig. 14) there was rapid utilization of a low concentration (100 mg/l) of toxicant, partial inhibition of fermentation at a higher concentration (500 mg/l), and complete inhibition at the highest concentration studied (1000 mg/l).

Assays involving p-cymene (Fig. 15) are of particular interest since p-cymene is a hydrocarbon and presumably non-degradable by anaerobic bacteria. One hundred mg/l p-cymene had no effect on methanogenic activity. Gas production in the 1000 mg/l p-cymene ATA did not begin until about 14 days after inoculation, but then proceeded rapidly. Although the ultimate gas production in this test was greater than in the blank, the increment can be accounted for entirely by extra methanol which was added to assure p-cymene solubility in the stock solution. Thus these results provide an example of acclimation to a

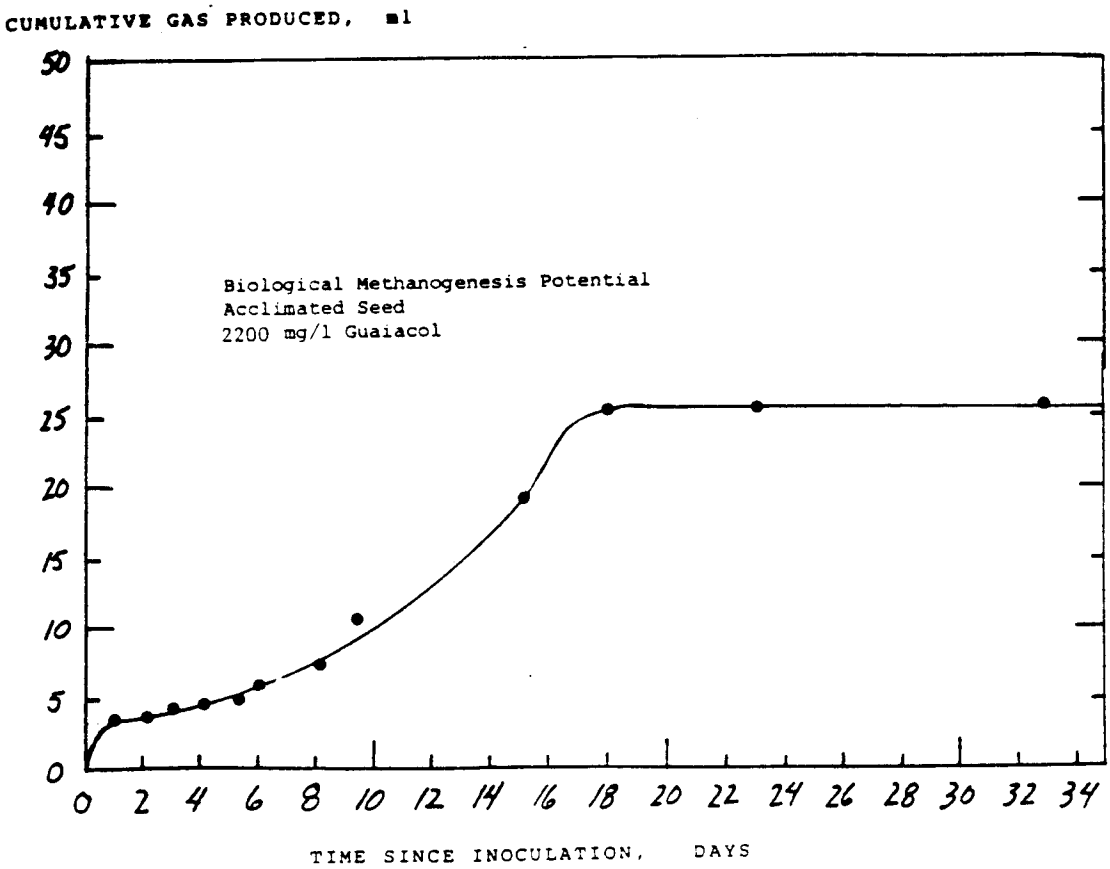


Figure 13. Total gas production in a BMP assay of guaiacol. Up to 16 ml of gas could have been produced from methanol in which the guaiacol was dissolved before being added to the assay solution.

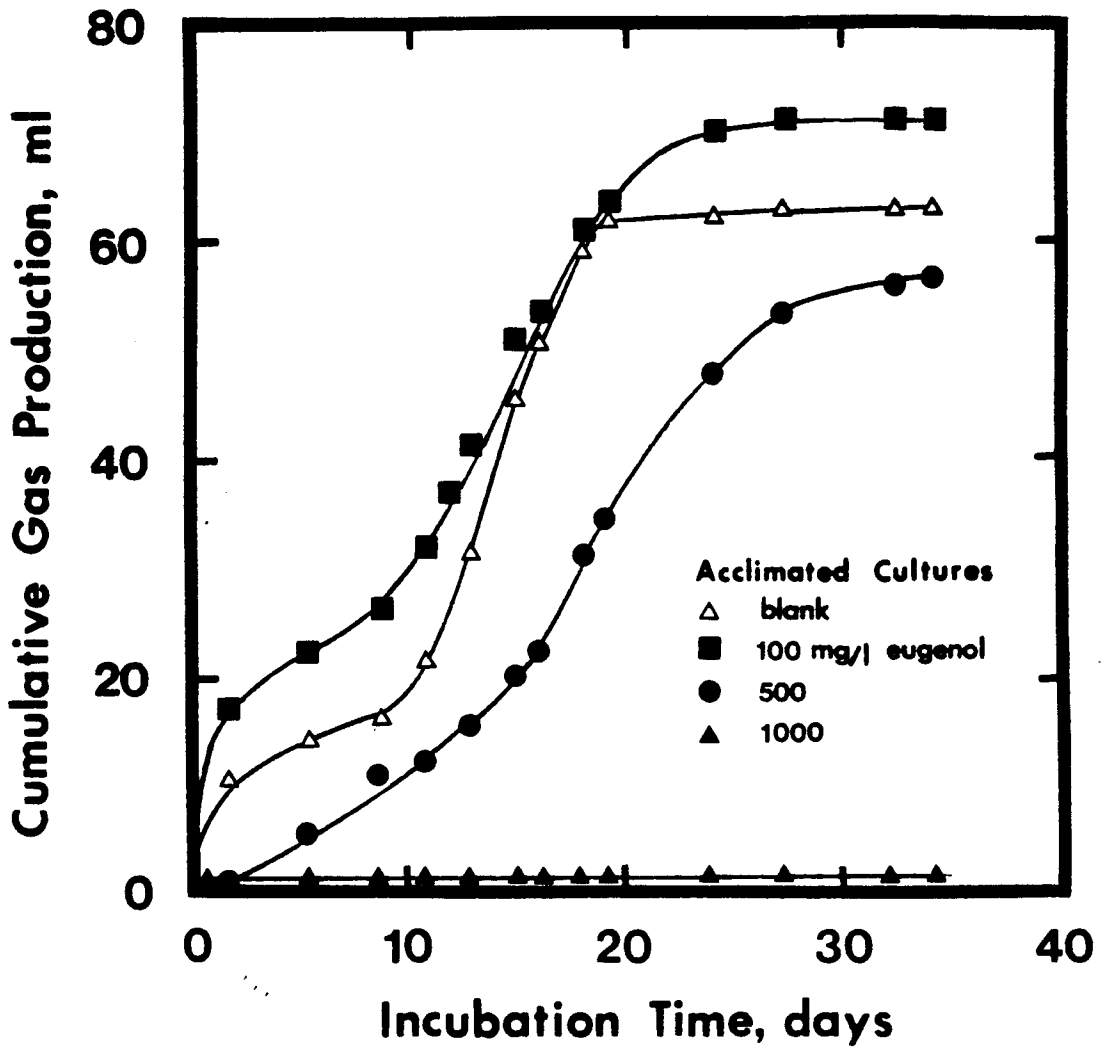


Figure 14. Gas production in ATA's with acclimated seed and various initial eugenol concentrations.

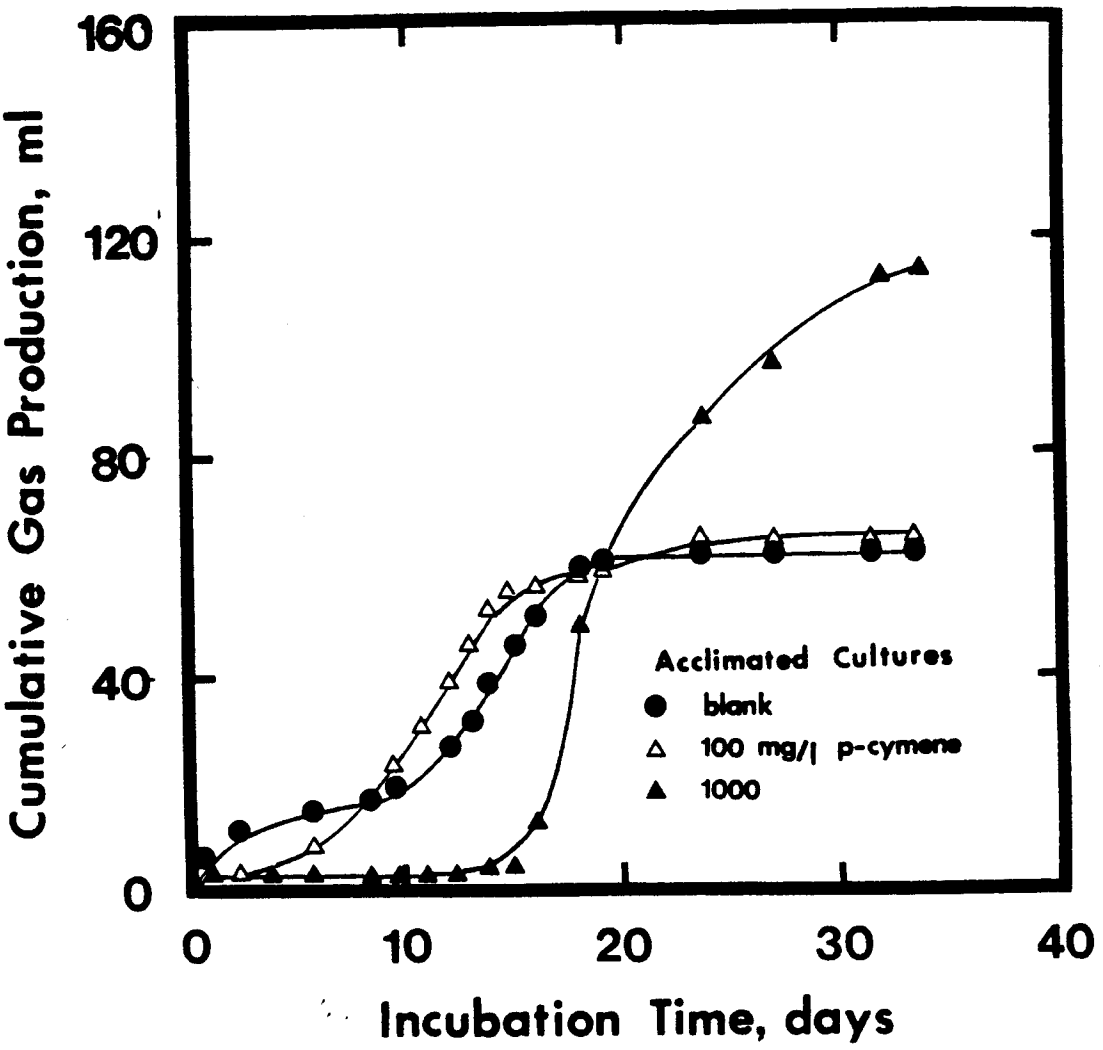


Figure 15. Gas production in ATA's with acclimated seed and various initial p-cymene concentrations. These ATA's contain more methanol than those in the other figures since p-cymene was dissolved in methanol before being added to solution.

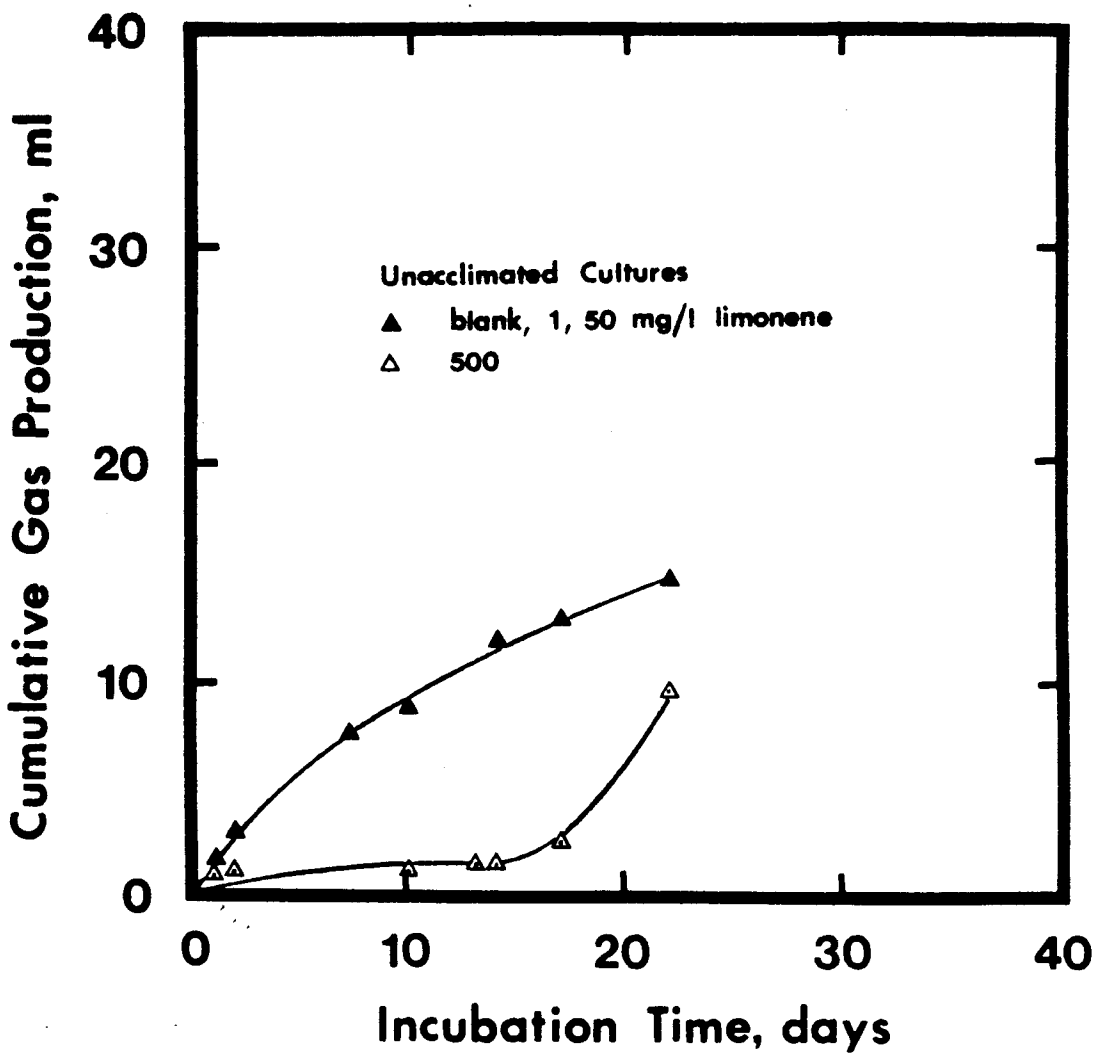


Figure 16. Gas production in ATA's with unacclimated seed and various initial limonene concentrations.

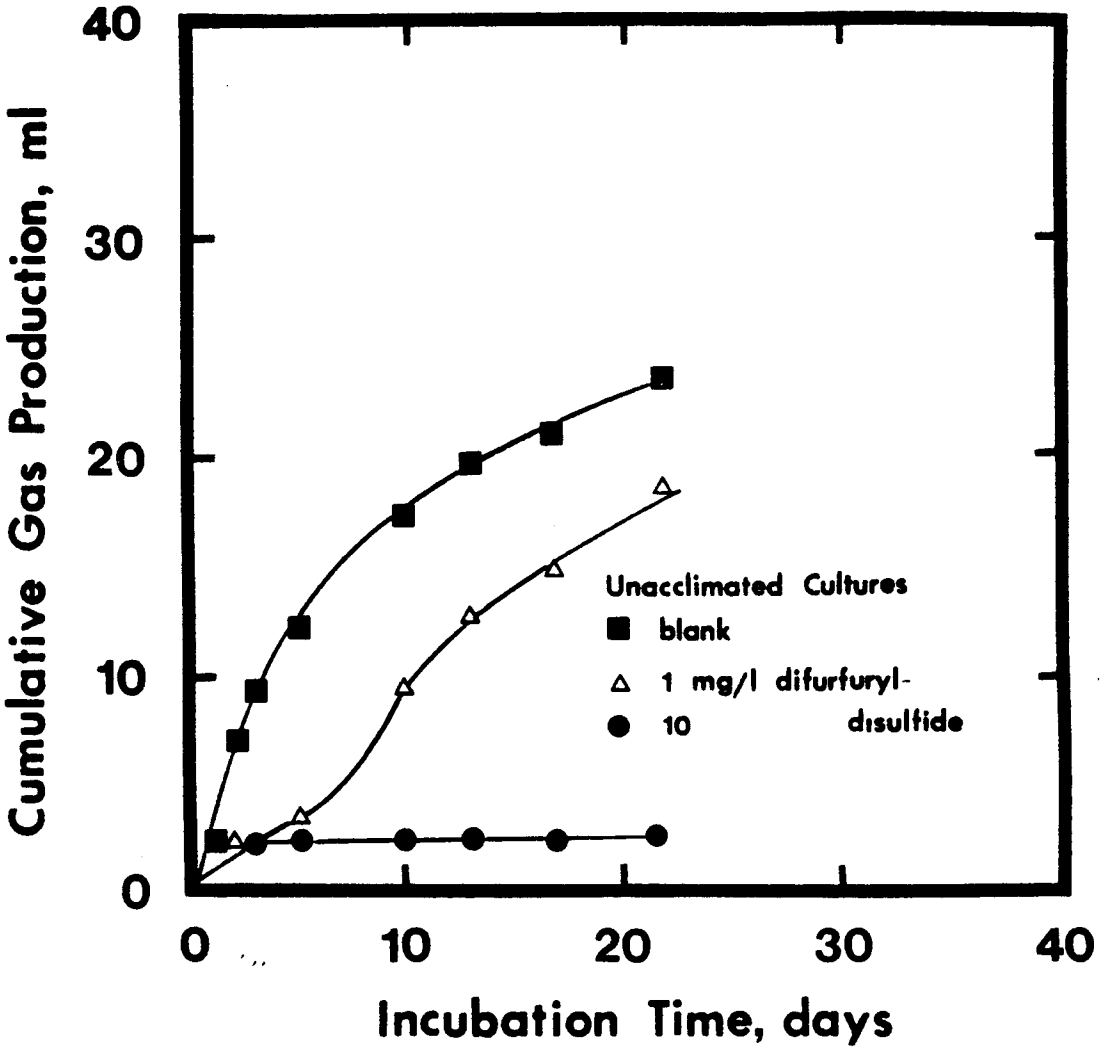


Figure 17. Gas production in ATA's with unacclimated seed and various initial difurfuryl disulfide concentrations.

compound in the absence of its degradation. That is, in other tests where acclimation occurred, it is possible that the lag period represented the time necessary for a group of organisms to partially degrade the toxicant, with fermentation of the spike beginning once the toxicant had been degraded. In the p-cymene ATA's, degradation of the hydrocarbon is extremely unlikely, so detoxification must have occurred some other way, such as complexation or sorption. The speed with which gas production proceeded when the lag period ended is also noteworthy. It appears the methane-forming bacteria switched from nearly zero activity to an activity comparable to toxicant-free systems with essentially no transition period. This may suggest a different mechanism of toxicity, from cases where the methane production rate is significantly different in the presence of toxicant than in its absence.

Assays to determine the toxicity of limonene and difurfuryl disulfide were conducted using unacclimated inocula only. These tests were run several months before the others reported, using a less concentrated inoculum and a different mix of easily degraded substrates as the spike. The gas production rates in these tests were much less than those conducted later. Nevertheless, comparison of methanogenesis in the test bottles with blanks run at the same time yields meaningful results. Limonene had no effect at 50 mg/l and caused a lag of 17 days before any methanogenesis occurred when present at 500 mg/l (Fig. 16). Difurfuryl disulfide was the most toxic compound assayed (Fig. 17). It inhibited methanogenesis somewhat when added at 1 mg/l and completely inhibited it for at least 22 days when added at 10 mg/l.

Finally, the response of unacclimated bacteria was determined when exposed to SEC, a mixture of all the toxicants studied individually (Fig. 18). With increasing SEC dose, there was a progressive decrease in the initial rate of methanogenesis, and, at higher doses, a lag period. In all cases it was

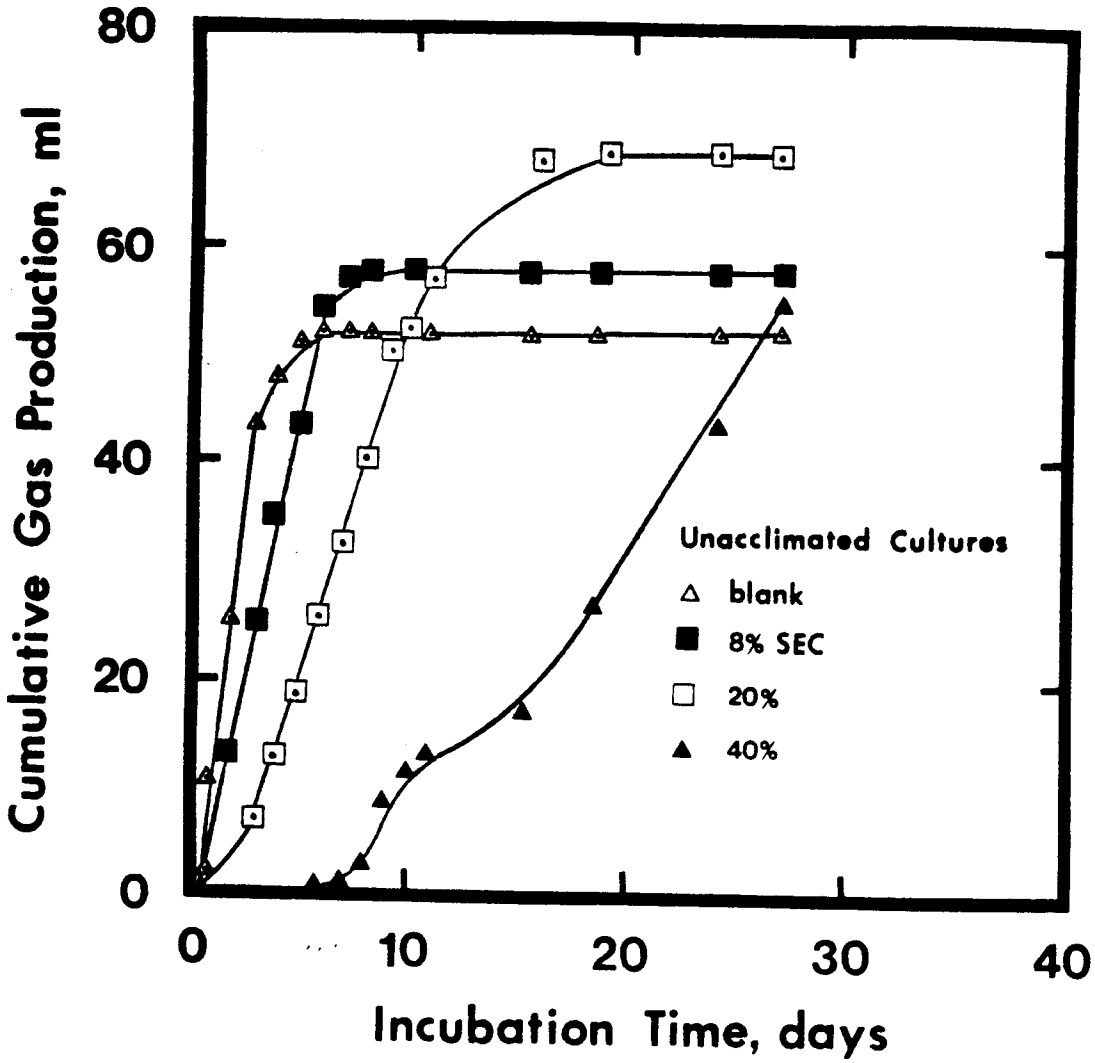


Figure 18. Gas production in ATA's with unacclimated seed and various dilutions of industrial sulfite evaporator condensate.

apparent that the organics in SEC were being degraded as well as those in the spike.

SUMMARY AND CONCLUSIONS

The response of acclimated and unacclimated methanogenic bacteria to several potentially toxic compounds was assayed. Although the range of concentrations studied was not exhaustive in each case, the overall response was, in aggregate, characterized by three ranges: 1) a no-effect range of concentrations; 2) a range of inhibition characterized by a lag period and/or decreased rate of metabolism, but leading ultimately to acclimation and renewed metabolic activity, sometimes including metabolism of the test compound; and 3) a range of complete cessation of metabolic activity.

Seed organisms taken from a reactor which had been used to treat industrial sulfite evaporator condensate were less severely inhibited by furfural than were organisms which had been exposed to a synthetic condensate. Furfural and guaiacol were at least partially degraded by the anaerobic bacteria in both the presence and absence of other carbon sources. The organisms acclimated to p-cymene after a lag period even though it is extremely unlikely that the p-cymene was degraded. The exact mechanism of toxicity and/or acclimation has not been established in any of these cases.

These tests are useful both as a screening procedure for acute and chronic toxicity and degradability, and to make a preliminary assessment of which steps in the fermentation process are affected by a given toxicant. Among other things, they suggest that if an anaerobic reactor is likely to be exposed to occasional pulses of toxic compounds, it may be advantageous in some cases to intentionally and continuously add some of those compounds to the reactor so the organisms become acclimated to them.

REFERENCES

1. Benjamin, M.M., Ferguson, J.F., Buggins, M.E. (1982) "Treatment of Sulfite Evaporator Condensate with an Anaerobic Reactor," (in press) TAPPI.

2. Buggins, M.E. (1981) "Treatment of Sulfite Evaporator Condensate with a Submerged Media Anerobic Reactor," Master's Thesis, Univ. of Washington, Seattle, WA.

3. Chou, W.L., Speece, R.E., Siddiqi, R.H., and McKeon, K. (1978) "The Effect of Petrochemical Structure on Methane Fermentation Toxicity," Progress in Water Technology, Vol. 10, No. 5/6, pp. 545-558.

4. Eis, B.J. (1982) "Limiting Factors in the Anaerobic Treatment of Sulfite Evaporator Condensate," Master's Thesis, Univ. of Washington, Seattle, WA.

5. Hungate, R.E. (1969) "A Roll Tube Method for Cultivation of Strict Anaerobes," Methods in Microbiology, Vol. 3B, pp. 117-132.

6. McCarty, P.L. (1972) "Energetics and Bacterial Growth," Organic Compounds in Aquatic Environments, Marcel Dekker, Inc., pp. 495-528.

7. Miller, T.L. and Wolin, M.J. (1974) "A Serum Bottle Modification of the Hungate Technique for Cultivating Obligate Anaerobes," Applied Micro., Vol. 27, pp. 985-987.

8. Nottingham, P.M. and Hungate, R.E. (1969) "Methanogenic Fermentation of Benzoate," J.Bact., Vol. 98, pp. 1170-1172.

9. Owen, W.F., et al. (1979) "Bioassay for Monitoring Biochemical Methane Potential and Anaerobe Toxicity," Water Research, Vol. 13, pp. 485-492.

10. Parkin, G.F., and Speece, R.E. (1982) "Attached vs. Suspended Growth Anaerobic Reactors; Response to Toxic Substances," Presented at the IAWPR Specialty Seminar on Anaerobic Treatment of Wastewater in Fixed Film Reactors, Copenhagen, June, 1982.

11. Ruus, L. (1964) "A Study of Waste Waters from the Forest Products Industry. 4. Composition of Biochemical Oxygen Demand of Condensate from Spent Sulfite Liquor Evaporation." Svensk Paperstidn, Vol. 67, ro. 6, March 31, pp. 221-225.

12. Thorn, P.A. (1976) "Magnefite Odor Compounds," Master's Thesis, University of Washington, Seattle, WA.

13. Yang, J., Parkin, G.F., and Speece, R.E. (1979) "Recovery of Anaerobic Digestion After Exposure to Toxicants," Final Report to U.S. Department of Energy, Contract No. EC-77-S-02-4391.

14. Yang, J., Speece, R.E., Parkin, G.F., Gossett, J., and Kocher, W. (1980) "The Response of Methane Fermentation to Cyanide and Chloroform," Progress in Water Technology, Vol. 12, pp. 977-989.

CHAPTER 3

THE FATE AND EFFECT OF BISULFITE IN ANAEROBIC TREATMENT[1,2]

Brian J. Eis
John F. Ferguson
Mark M. Benjamin

ABSTRACT

Sulfur (S) in anaerobic treatment has been studied with respect to inhibitory and toxic effects on methane formers, transformation, and odor production. In low detention-time anaerobic treatment, sulfur transformations are incomplete and strongly competitive with methane production. The waste tested contained a few hundred mg/L of dissolved sulfur dioxide (SO_2) and organic sulfur and a few thousand mg/L of organic compounds, primarily acetic acid, methanol, and furfural at a pH of 2 to 3. Dissolved SO_2 and acetic acid require partial neutralization in order to maintain the reactor pH in a range suitable for methanogenic bacteria. The principal sulfur reactions in the process include bacterial reduction, volatilization, and precipitation. Bacterial sulfur reduction is associated with conversions of COD from that exerted by organic compounds to that exerted by compounds of sulfur. It also results in decreased methane production and increased effluent COD concentrations. Sulfur reduction also produces alkalinity, and reduces the neutralization requirements. Both oxidized and reduced sulfur may be toxic. however, acclimation to high concentrations of SO_2 and sulfide was found. Volatilization can remove minor amounts of H_2S.

1. Presented at the 54th annual conference of the Water Pollution Control Federation, October 1981, Detroit, Michigan.

2. Published JWPCF, 55, 1355-65 (1983).

INTRODUCTION

Industrial wastes, particularly those produced at elevated temperatures and containing high concentrations of dissolved organic compounds, are good candidates for anaerobic treatment.

Evaporator condensates, produced during the concentration of spent pulping liquors in the pulp and paper industry, can be anaerobically pretreated to decrease the organic loading on the downstream aerobic system. This decreases aeration requirements that represent the major cost of treatment. The methane (CH_4) produced from the treatment of these warm wastes is not needed for reactor heating and is available for use in the mill to offset purchased energy costs.

The anaerobic treatment of sulfite evaporator condensate (SEC), generated by acid sulfite and bisulfite pulping processes, has been shown to be feasible from economic and process standpoints. Organic loadings of 16 kg COD/m^3 reactor volume/day were reported by Benjamin, Ferguson, and Buggins,[2] utilizing a submerged media anaerobic reactor (SMAR) with effluent recycle and neutralization of the waste with sodium hydroxide NaOH and sodium bicarbonate $NaHCO_3$.

While experimental work has demonstrated significant COD removals at volumetric loadings up to 24 kg COD/m^3-d, consistently lower COD removals maybe obtained from an industrial waste than from a synthetic condensate containing acetic acid and methanol (Fig. 19). To explain these differences, a study of the role of sulfur in the process is needed.

Sulfur compounds may present problems other than their effects on microorganisms. Reduced sulfur compounds often cause strong odors and contribute

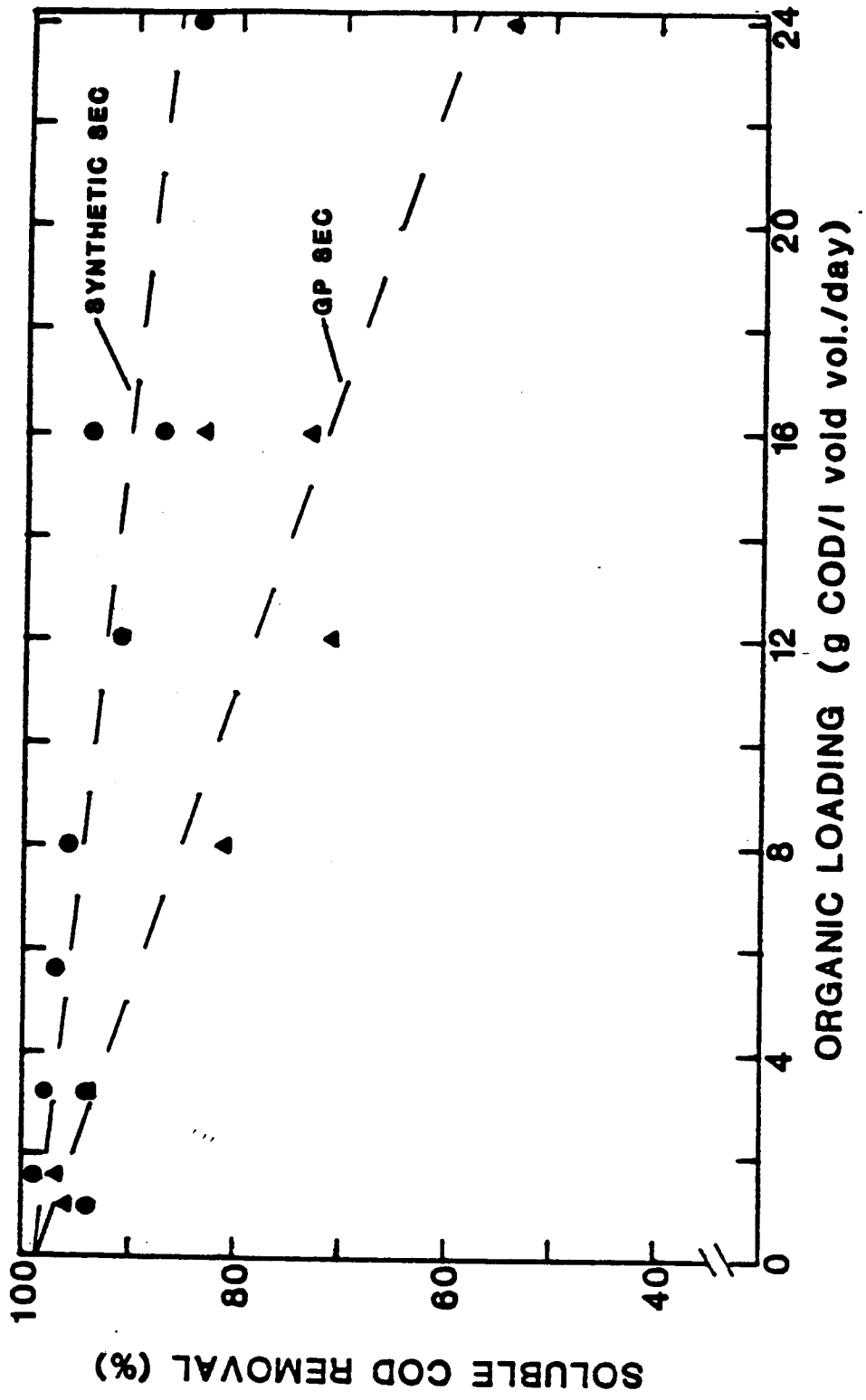


Figure 19. Effect of volumetric organic loading on COD removal for a synthetic waste (acetate and methanol) and for condensate from the Georgia Pacific mill at Bellingham, WA[1,9]

to the oxygen demand in the effluent. Sulfur compounds may affect performance of anaerobic reactors directly by inhibiting or killing methane-forming bacteria, or indirectly by competition between methane-formers and sulfur reducers for organic carbon. The complexity of the situation is increased because chemical and biologically mediated transformations among sulfur compounds are likely. The work reported here includes batch and continuous flow studies of the effects of sulfite (SO_3^{2-}) on performance of an anaerobic reactor, measurement of sulfur forms in reactor influent and liquid and gaseous effluents, and an effort to model the effects of sulfur on the acid-base chemistry in the reactor.

Sulfite Evaporator Condensate

The composition of SEC varies with the specifics of operation at every mill and with the type of wood being pulped. Ruus[18] has reported a range of biochemical oxygen demand BOD_5 concentrations from 2.6 to 8.2 g/L for eight different SEC's with acetic acid ranging from 1.6 to 8.2 g/L, methanol from 0.2 to 1.2 g/L, furfural from 0.2 to 1.0 g/L, and smaller concentrations of formaldehyde, formic acid, acetaldehyde, and methylglyoxal. Ethanol will be present if the spent pulping liquor is fermented before evaporative concentration. In 12 condensate batches from the Georgia Pacific mill, acetic acid, methanol, and furfural accounted for an average of 86% of the measured COD.

Sulfur is present in many forms in both spent pulping liquor and SEC. Sulfur enters the process by dissolution of SO_2 during preparation of the cooking liquor. The pH of the cooking liquor is controlled by the amount of base added and the partial pressure of SO_2. In the acid sulfite process, large partial pressures of SO_2 are maintained, and the pH is between 1.2 and

1.5. In the bisulfite process the pH is higher (3.0-5.0), and the partial pressure of SO_2 is much less.

Aqueous SO_2 reacts from H_2SO_3 which can dissociate into bisulfite (HSO_3^-) or sulfite (SO_3^{2-}). During the cooking process, bisulfite ions react with lignins in the wood to form lignosulfonates. These sulfonation reactions along with hydrolysis reactions solubilize the lignins, and remove them from the cellulose fiber. As a result, much of the sulfur in the spent liquor is in the form of lignosulfonates.

During sulfite cooking, many side reactions that involve bisulfite can occur. These reactions are undesirable because they may convert bisulfite to an unrecoverable form or produce thiosulfate, which catalyzes the oxidation of bisulfite to sulfate. Steps are taken during the cook to limit these reactions.[19]

The concentration of sulfur dioxide in spent liquor is low because most of it enters into reactions during the cook. Except for lignosulfonates, sulfur is mainly present as "loosely bound SO_2" (probably α-hydroxysulfonates).[17] During evaporative concentration of spent pulping liquor, SO_2 is driven off and redissolves in the condensate with the other volatile constituents. In the condensate some SO_2 can combine with volatile organics to form other compounds and form loosely bound SO_2. Other nonvolatile sulfur components, such as the lignosulfonates, sulfate, and thiosulfate, get into the condensate by carry-over of liquor droplets during the evaporation process. The major forms of sulfur that can be analytically distinguished in SEC are free SO_2, loosely bound SO_2 (mostly α-hydroxysulfonates), and sulfonates (including lignosulfonates and other organic sulfur). The concentrations of

these compounds varied considerably among batches of SEC used in this study (Table 6).

The pH of SEC is generally low because of high concentrations of acetic acid and SO_2. Ruus[18] found pH values from 1.8 to 2.6. Since acetic acid is not dissociated in this range, pH is mainly determined by SO_2. However, the total acidity of the waste is mainly from acetic acid. Mineral acidity of Georgia Pacific condensate is 10 to 30 meq/L, total acidity approaches 100 meq/L.

The composition of SEC limits the types of organisms which can use it as a substrate for growth under anaerobic conditions. Acetic acid, methanol and furfural are the carbon/energy sources available in SEC in significant concentrations. The metabolic pathways used to obtain energy from these compounds are limited by the electron acceptors available in the system. In anaerobic environments, a major selective factor is the absence of molecular oxygen as an electron acceptor.

Sulfur-reducing bacteria use sulfate as an electron acceptor. Hydrogen sulfide is the end product of sulfur reduction. However, reduction to elemental sulfur or organic sulfur compounds is also possible.[20] Sulfite appears as an intermediate in the pathway and it is presumed that organisms that can use sulfate can also use sulfite. Therefore, sulfite maybe a more energetically favorable oxidant than sulfate because it may enter the pathway without the initial expenditure of microbial Adenosine triphosphate (ATP). SEC contains large amounts of sulfite but only small amounts of sulfate.

Recent studies have shown that organic sulfur compounds can also serve as electron acceptors for some species of sulfur-reducing organisms. Jurgensen and Patton[11] reported that a species of Desulfovibrio was capable of desulfona-

Table 6: Ranges of Concentrations of Major Sulfur Forms in GP SEC. (σ = standard deviation.)

Form	No. of Samples	Concentrations (mg/L as S) Range	Mean $\pm$ σ
Free SO_2	16	20-850	230 $\pm$ 300
Loosely bound SO_2	16	0-750	290 $\pm$ 250
Total SO_2	16	200-1100	520 $\pm$ 300
Sulfonate Sulfur	7	0-400	110 $\pm$ 160

ting lignosulfonates in spent sulfate liquor, resulting in production of hydrogen sulfide and precipitation of the lignins.

Carbon dioxide can also be used as an electron acceptor by methane producing bacteria. All methanogenic bacteria that have been isolated are capable of coupling hydrogen oxidation in CO_2 reduction to produce energy.[24] Molecular hydrogen is produced during fermentations of some complex organic compounds, and bacteria that mediate these reactions form symbiotic relationships with methanogens in anaerobic ecosystems.

In addition to inorganic electron acceptors, biochemical pathways that use organic molecules as electron acceptors are available to anaerobic organisms with the proper enzymes. The reactions can be thought of as oxidation-reduction reactions involving only one organic molecule; one portion of the molecule is reduced and the other portion is oxidized. Both acetate and methanol are direct precursors of methane. The methyl groups of these molecules are reduced directly to methane, as Pine[16] and Jeris and McCarty[10] showed through use of radioactive labeling techniques. Methanosarcina barkeri has been grown in pure culture with methanol as the sole carbon and energy source. No methanogenic species have yet been cultured on acetate as the sole energy and carbon source,[24] although enrichment cultures have been maintained for years in many labs with acetate as the only organic carbon source.

Probable energy-yielding reactions with acetate, methanol, and furfural and sulfite are summarized in Table 7. Yield coefficients have been calculated using the energetics model proposed by McCarty[14] and are also shown in the Table. The microorganisms can be grouped on the basis of which reactions they mediate -- acid-formers, methane-formers, and sulfur-reducers.

The acid-formers and methane-formers are the two major groups of organisms responsible for the conceptual phases of anaerobic treatment. The acid phase is relatively unimportant in SEC because one or two carbon compounds constitute the bulk of the organic content. Furfural fermentation as shown in Table 7 is only a postulated reaction, and furfural degradation may proceed to other intermediates. As mentioned previously, acid fermentations are closely coupled to methane fermentations. The relationship is more complex than a simple sequential set of reactions and is based on interspecies hydrogen transfer.[8] Other than furfural, substrates that can be used by acid-forming bacteria are usually present in very low concentrations in SEC.

Neither acid fermentation nor methane-producing fermentations result in a net oxidation of carbonaceous COD. In these reactions, COD removal from the aqueous suspension is dependent on the removal of methane to the gas phase. The methane-forming reactions are therefore the critical reactions that determine how efficiently the system will remove COD.

The anaerobic oxidation of acetate by sulfur reducers is well established.[21] The use of methanol as a substrate, while energetically more favorable, has not been documented in the literature.

Reduction of SO_2 to sulfide is an undesirable reaction because it is competititve with methane production for oxidizable organic matter. For every mole of sulfite, reduced 0.75 mole of potential methane is lost. The net result is that the organic COD in SEC is converted to inorganic COD in the form of H_2S, which is much more soluble than methane. Thus, more COD remains soluble in the effluent than if it was converted to methane -- that is sulfur reduction decreases COD removal.

Table 7. Potential energy yielding biologically mediated reactions in SEC. Yields are calculated from free energy changes using the model proposed by McCarty[14].

		Y g cells/ g energy source	Y g cells/ g COD
	Acid Fermentations		
(1)	$\frac{1}{20} C_5H_4O_2 + \frac{1}{5} H_2O \rightarrow \frac{1}{10} CH_3COO^- + \frac{1}{20} CO_2 + \frac{1}{10} H_2 + \frac{1}{10} H^+$	0.10	0.06
	Methane Fermentations		
(2)	$\frac{1}{8} CH_3COO^- + \frac{1}{8} H_2O \rightarrow \frac{1}{8} CH_4 + \frac{1}{8} HCO_3^-$	0.034	0.032
(3)	$\frac{1}{6} CH_3OH \rightarrow \frac{1}{8} CH_4 + \frac{1}{24} CO_2 + \frac{1}{12} H_2O$	0.22	0.15
(4)	$\frac{1}{8} CO_2 + \frac{1}{2} H_2 \rightarrow \frac{1}{8} CH_4 + \frac{1}{4} H_2O$	0.05	0.07
	Sulfur Reduction		
(5)	$\frac{1}{8} CH_3COO^- + \frac{1}{6} SO_3^= + \frac{1}{4} H^+ \rightarrow \frac{1}{12} H_2S + \frac{1}{12} HS^- + \frac{1}{8} HCO_3^- + \frac{1}{8} HCO_3^- + \frac{1}{8} H_2O$	0.12	0.11

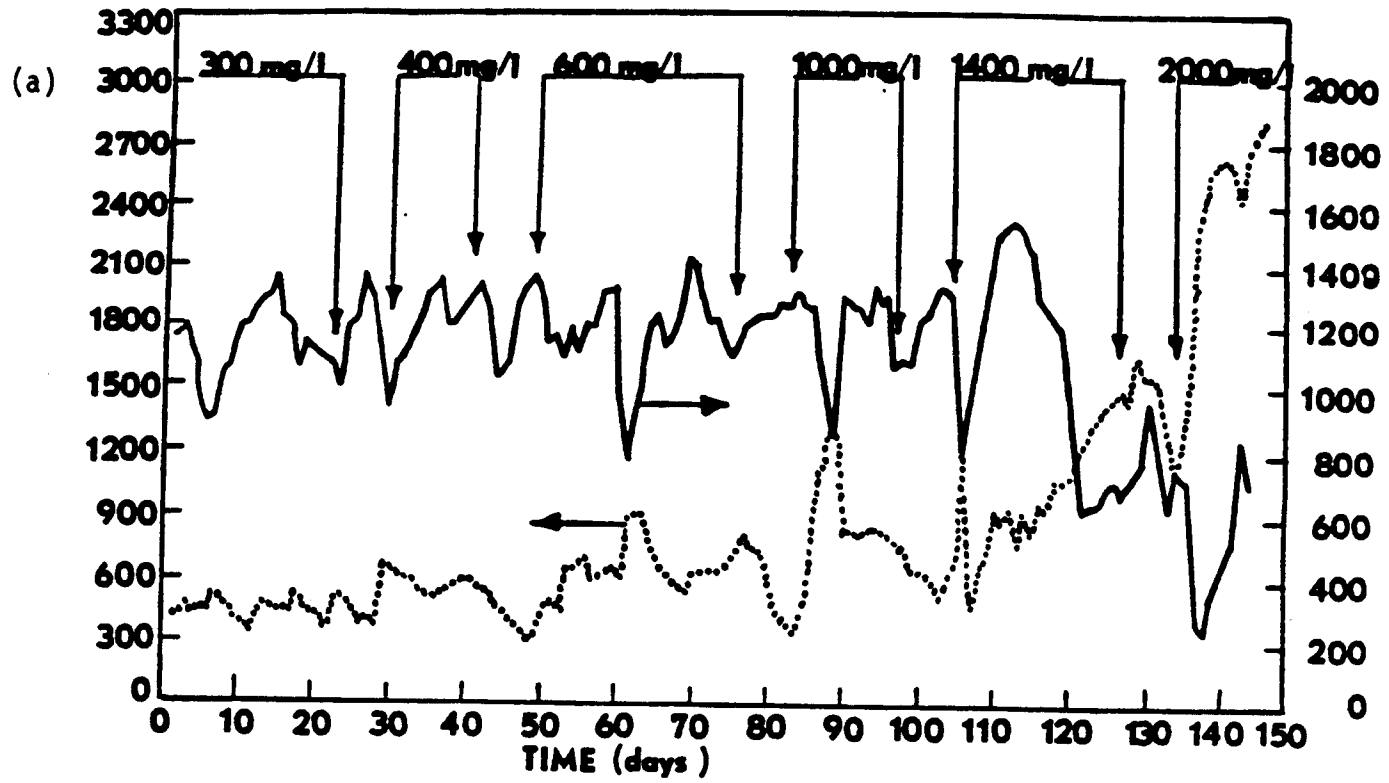
The energetics of the two pathways (methane production versus sulfur reduction) favor sulfur reduction as shown by the theoretical yields presented in Table 7. If other factors are equal, sulfur-reducers should be able to outcompete methanogens for available substrate, and methane production would only occur after most of the sulfur had been reduced. This seems to be the case in both marine[13] and freshwater[22] sediments.

Toxicity and odor problems are other reasons why sulfur reduction is undesirable and might limit the application of anaerobic treatment to sulfur containing wastes. Inorganic sulfur compounds have been reported to be toxic to methane forming bacteria. Lawrence et al.[12] reported that soluble sulfide concentrations above 200 mg/L are extremely toxic. Steady-state additions of sulfite and sulfide to SMAR's were tested by Yang et al.[23]. Their results, presented in Figure 20, show that sulfite or sulfide in the feed can be tolerated at concentrations as high as 1000 mg/L for sulfite and 400 mg/L for sulfide if acclimation is allowed to occur. Concentrations higher than these resulted in somewhat poorer performance but not complete cessation of gas production.

EXPERIMENTAL STUDIES

Batch anaerobic bottle tests and continuous-flow reactors were used to study the effects of sulfur compounds in methane production and of sulfur transformations on anaerobic systems.

Condensate from the Georgia Pacific mill was used in two continuous flow reactors and a synthetic condensate containing 3000 mg/L acetic acid and 1000 mg/L methanol (COD 4700 mg/L) was used in two other reactors. The reactors



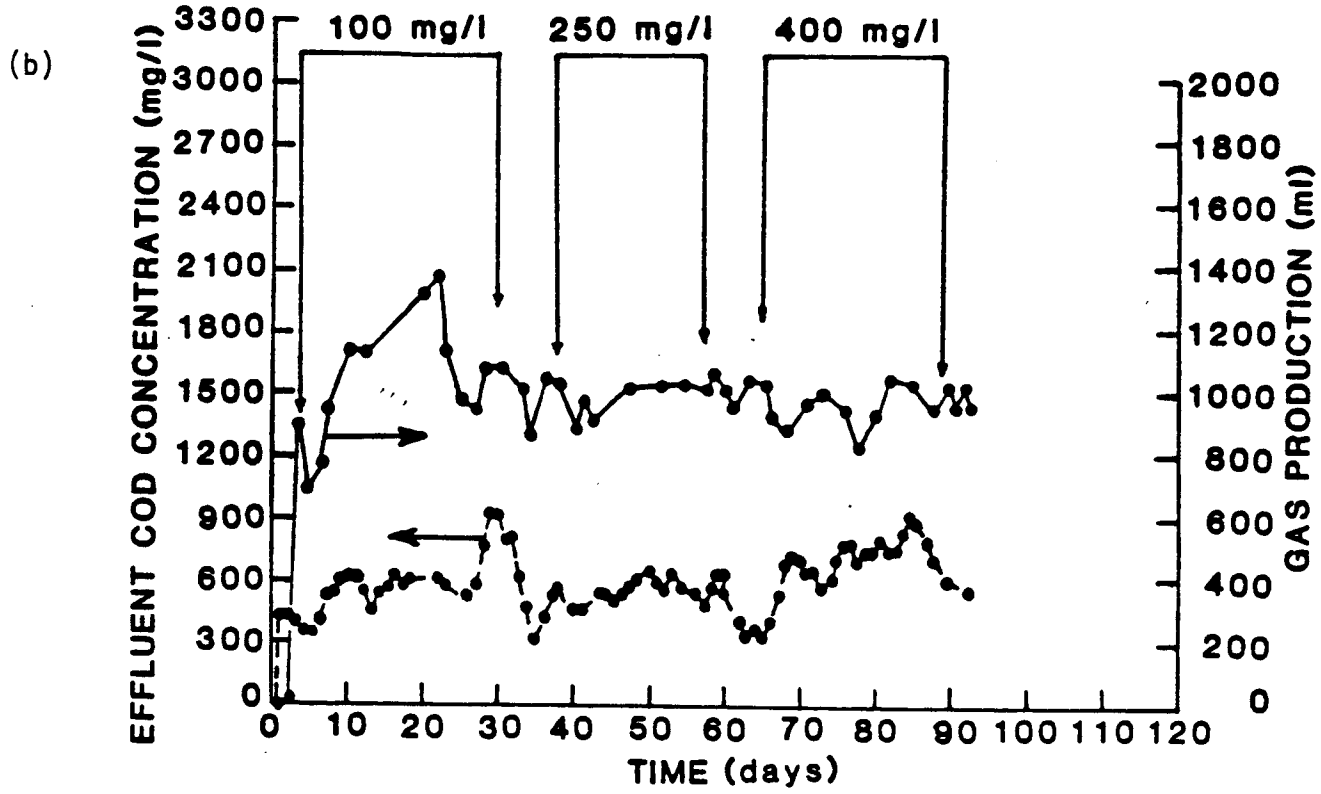


Figure 20. Response of anaerobic filters to continuous additions of sulfur compounds; a) sulfite b) sulfide[9].

were 19-L columns (1.2 m high, 15 cm in diameter) packed with plastic rings. Reactor temperature was maintained between 30 and 35° C. Ammonia-nitrogen, phosphate, and a mixture of trace nutrients were added to both wastes. Sodium carbonate (or other sodium bases) was added to neutralize the feed so that reactor pH values remained between 6.8 and 7.6. Thirty to 65 meq/L of base was used at various times during the study. The recycle ratio was 4 to 10 times the influent flow rate in nearly all the trials. During studies reported in this paper, volumetric loadings ranged from 12 to 24 kg COD/m^3-day. The experimental procedures and operating results for organic removal have been reported elsewhere.[2,4,5]

Batch bioassays were conducted according to procedures described by Owen et al.[15] and developed by Benjamin et al.[3] Both biological methane potential (BMP) and anaerobic toxicity assays (ATA) were performed, in which gas production with time was used as the principal indicator of microbial activity.

Aqueous Sulfur Species

Several sulfur forms were analyzed at laboratories at the Georgia Pacific mill. Total sulfur, sulfonate (organic) sulfur, and non-sulfonate sulfur were measured using the methods of Foley and Johnson.[7] Free and loosely-bound SO_2 were measured by iodometric titration with and without formaldehyde.[9] Sulfide was measured by a sulfide ion electrode. Freshly collected condensate and influent and effluent samples were analyzed on several occasions. Other samples of reactor influent and effluent were frozen and transported to Bellingham, where they were thawed and analyzed.

In addition to the analyses performed by Georgia Pacific, sulfite and sulfide determinations were performed at the University of Washington by iodomet-

ric titration under acid conditions.[5] The methods used are a modification of those presented in "Standard Methods", Sec. 427 and 428.[1] Sulfide is measured as "zinc precipitable sulfur" and sulfite is measured as "non-zinc precipitable sulfur".

The partial pressure of hydrogen sulfide in the gas phase was measured by passing a known volume of reactor gas through a gas trap which contained 200 ml of 1 N NaOH. The sulfide concentration of the liquid in the trap was then measured by the method described above, and the partial pressure of H_2S was calculated.

RESULTS

Sulfur Toxicity

Batch bioassays can be used to assess toxicity and degradability of certain wastes or compounds by specific cultures of organisms. Anaerobic toxicity assays (ATA), which measure the effects of a toxicant on methane production from acetate, and biological methane potential assays (BMP), which assess the biodegradability of a test compound, were both used.

To assay the effect of sulfite on acetate utilization, an ATA series was set up in which the concentrations of sulfite were varied from 0 to 10,000 mg/L as S. Four replicate bottles were used for each concentration. Organisms obtained from a reactor that had treated Georgia Pacific SEC for several months were used as the inoculum, and acetate was the only carbon source. The amount of gas production expected, based on the COD of the acetate spike and assuming 85% methane in the gas, was about 70 ml. Cumulative gas production

vs. incubation time for the sets of bottles which produced gas are shown in Figure 21. No gas was produced in the bottles containing 5,000 and 10,000 mg/L sulfite sulfur.

The rate and amount of gas production were reduced for all levels of sulfite addition above the control. For the samples treated with 100 and 500 mg/L, the decrease in total gas production was roughly equivalent to the decrease in methane production expected if the sulfite present was stoichiometrically reduced to sulfide. The levels of gas production expected in this case are indicated in Figure 21.

For the samples treated with 1000 mg/L SO_3^{2-} addition, significant inhibition is indicated by the 3 week lag before gas production started. After this acclimation period, gas production started at a rate lower than that in the other bottles. In the 5,000 and 10,000 mg/L cases, sulfur is present in excess of the stoichiometric amount needed to consume all the acetate. The fact that no gas (not even CO_2) is produced indicates strong inhibition of all the microorganisms in these bottles because of high sulfite levels.

Sufficient concentrations of sulfite are capable of reducing the rate of methane production or of causing a lag time during which no gas production takes place, and may inhibit gas production indefinitely. The reduction in ultimate gas production indicates that methane production is correspondingly decreased, a fact which strongly implies that sulfite is biologically reduced.

A set of biological methane potential (BMP) assays was prepared to confirm the effects of sulfite on the degradation of organics in SEC. A batch of condensate with a high SO_2 concentration (total SO_2 approximately 1 g/L as S) was treated with lime to precipitate calcium sulfite. In addition, assays

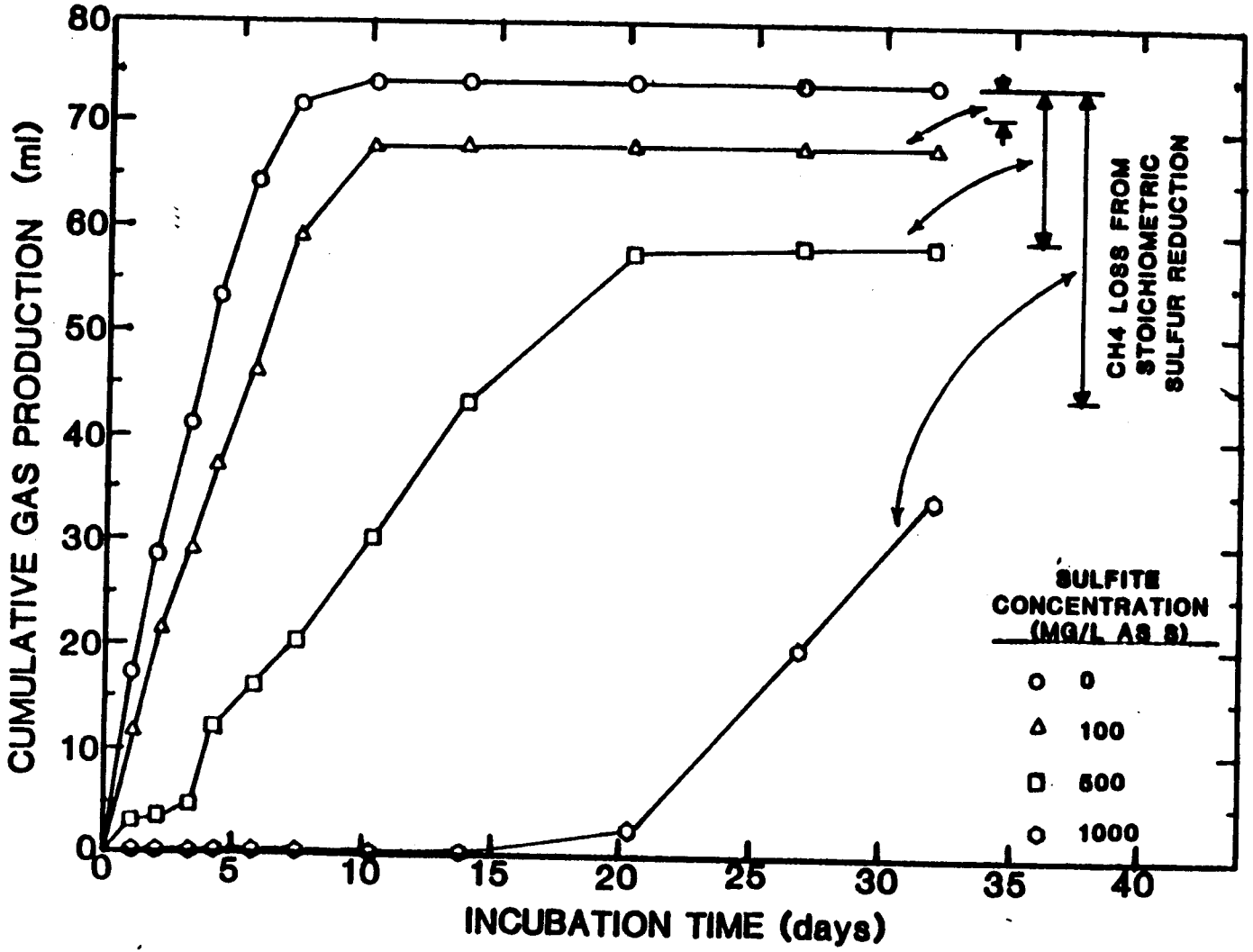


Figure 21. Anaerobic toxicity assays for sulfite. Acclimated cultures were used as the inoculum, acetate spike, 35°C incubation temperature. Expected gas production based on the COD of the spike and 85% methane in the gas = 72 mL.

were conducted using condensate to which 500 or 1000 mg/L sulfite (as S) had been added. The sulfite concentrations in the assay then were about 1.5 and 2 g/L. Additions of SO_2 were about 1 g/L for the condensate, and a much lower concentration in the lime-precipitated sample. As in the ATA's, organisms from a reactor that had been treating industrial condensate were the inoculum. The results (Fig. 22) are similar to those of the ATA's. The initial rate of gas production decreases as the sulfite concentration increases, as does the amount of gas ultimately produced.

To further test sulfite toxicity, sulfite was continuously added to a reactor that had received synthetic feed for several months. The sulfite level was increased in steps with acclimation periods of a few days, and steady-state periods with 400 and 800 mg/L influent SO_3-S were established. The response of the reactor is shown graphically in Fig. 23. The effluent soluble COD increased slightly as sulfite feed levels were increased, presumably as a result of production and dissolution of H_2S. Total gas production increased slightly, presumably because of a reduction in the reactor pH and consequent evolution of CO_2. When the effluent was air stripped to remove H_2S from the aqueous phase, soluble COD was comparable to that prior to sulfite addition. Thus, sulfite is not appreciably toxic at these concentrations in continuously fed reactors. At the experimental loadings there was no significant effect on conversion of organics to methane.

The data indicate that toxicity of sulfite is minimal if proper acclimation is allowed to occur. This was the case in both batch and continuous cultures. No long-term toxic effects were evident, although the initial rate of methane production in batch assays decreases as the sulfur content increases. The decreased rate with increasing sulfur concentration can affect COD removal

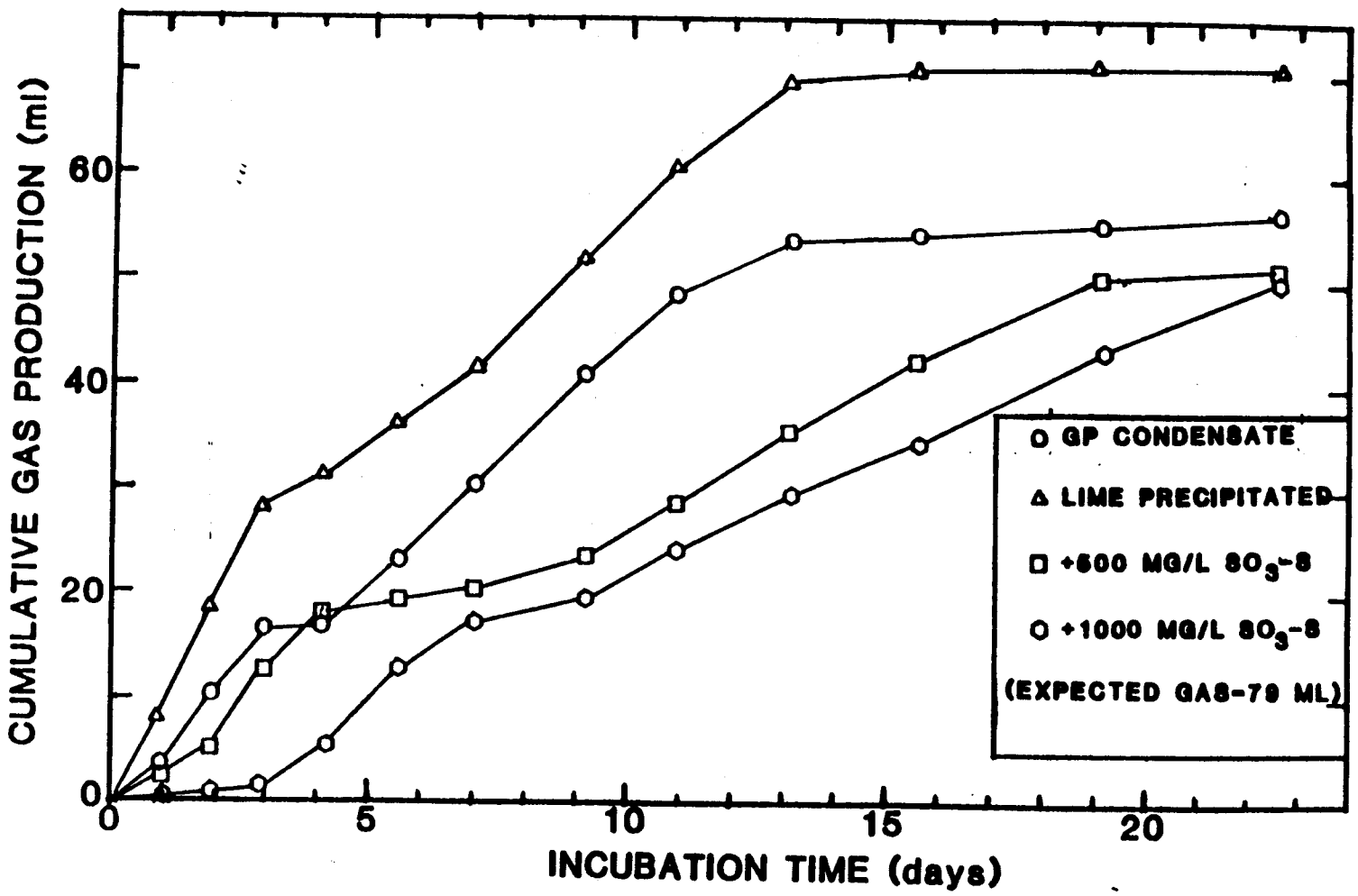


Figure 22. Biological methane potential assay of Georgia Pacific SEC with acclimated cultures. For the lime precipitated sample the pH was raised to 12 and precipitate was settled; the supernatant was neutralized to pH 7 for the bioassays. Sulfite additions were in the form Na_2SO_3.

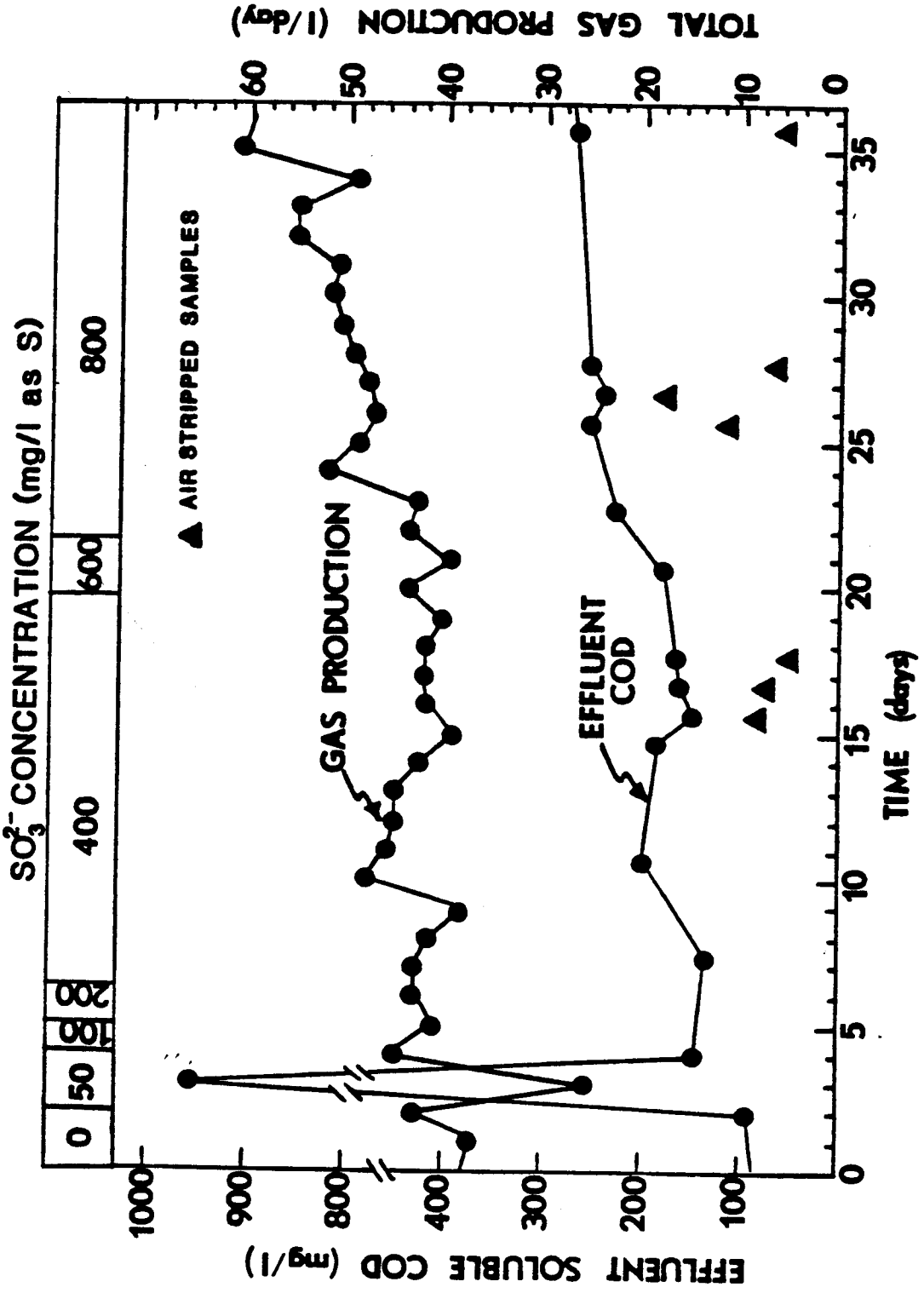


Figure 23. Response to continuous addition of sulfite. Sulfur was added as Na_2SO_3. The reactor was fed an acetate-methanol synthetic waste at a loading of 6 g COD/l.d.

at very high organic loadings or when the concentration of sulfite is increased suddenly. Gas production in ATA bottles was reduced by an amount that indicates that acetate was used by sulfur reducers. In continuous culture experiments the addition of sulfite had a slight effect on COD removal. A stoichiometric decrease in methane production must have occurred, but was masked by the concomitant increase in CO_2 evolution.

Sulfur Transformations

On several occasions samples from reactors treating evaporator condensate were analyzed for the major forms of sulfur. The same analyses were performed on the synthetic waste amended with sulfite. The reactors were operated at volumetric loadings between 12 and 24 kg COD/m^3-day, at mesophilic temperatures, and at hydraulic detention times of 5 to 9 hours. The reactor treating evaporator condensate had been operating for more than 1 year on that waste. The reactor with synthetic waste had been acclimated to sulfite (as shown in Fig. 23) for a total period of 1 month. The industrial condensate (Table 6) was very variable.

The variability in composition, combined with analytical uncertainties in measuring all the sulfur forms and the small number of samples analyzed, make interpretation of the sulfur data shown in Table 8 difficult. The Table shows the results of individual analyses performed on six occasions. Inconsistencies exist in the data, nevertheless, much useful information can be obtained.

Total sulfur losses from the aqueous phase seem to be moderate, from less than 100 mg/L to 300 mg/L. The possible mechanisms for sulfur loss are volatilization of H_2S, mercaptans or other volatile forms to the gas phase; precipitation of FeS; formation of elemental sulfur (S°) and incorporation

Table 8. Results of sulfur analyses.

Feed	Date	Sample	Sulfur Forms (mg/L as S) Total Sulfur	Sulfonate Sulfur	NonSulfonate Sulfur	"Free" SO_2	"Loosely Bound" SO_2	Sulfite	Free[1] Sulfide	Total[2] Sulfide
Synthetic plus 400 mg/L SO_2-S	7/7/81	Influent	402	3	400	290	0	160	0	(30)
		Effluent	338	5	290	20	10	10	20	40
Synthetic plus 800 mg/L SO_2-S	7/29/81	Influent	210	45	190	40	100	750	0	0
		Effluent	70	50	60	25	70	10	60	150
Evaporator Condensate (Total SO_2 350 mg/L as S)	5/13/81	Influent	220	20	210	---	---	---	---	---
		Effluent	240	30	130	---	---	---	---	---
Evaporator Condensate (Total SO_2 200 mg/L as S)	5/25/81	Influent	60	4	60	---	---	---	---	---
		Effluent	110	20	80	---	---	---	---	---
Evaporator Condensate (Total SO_2 1000mg/L as S)	6/3/81	Influent	540	30	500	200	120	---	0	---
		Effluent	320	130	240	120	50	---	170	---
Evaporator Condensate (Total SO_2 1100 mg/L as S)	6/4/81	Influent	860	290	580	850	190	---	0	---
		Effluent	590	180	430	130	240	---	150	---
Evaporator Condensate (Total SO_2 400 mg/L as S)	7/7/81	Influent	75	3	70	25	47	10	0	(20)
		Effluent	70	20	70	20	20	10	30	60

Table 8 - Cont.

Feed	Date	Sample	Sulfur Forms (mg/L as S) Total Sulfur	Sulfonate Sulfur	NonSulfonate Sulfur	"Free" SO_2	"Loosely Bound" SO_2	Sulfite	Free[1] Sulfide	Total[2] Sulfide
Evaporator Condensate (Total SO_2 550 mg/L[3] as S)	7/29/82	Influent	900	390	550	850	0	30	0	(20)
		Effluent	710	140	580	45	33	10	60	110

1.) Free sulfide measured by sulfide electrode at high pH.

2.) Total sulfide measured by difference in iodometric titration before and after zinc precipitation.

3.) Total SO_2 was measured at time of collection of condensate.

into biomass. The last three processes cause sulfur to accumulate in the reactor.

Precipitation of FeS and biological uptake are unimportant in the overall sulfur balance. The maximum amount of FeS formation can be calculated from a mass balance on iron. Fe addition during the study was only 4 mg/L. This amount of iron could precipitate about 2 mg/L of sulfide. The amount of biological uptake can be estimated from the yield coefficient; assuming a 7% yield, 5 g/L influent COD, 90% COD removal and 1% S by weight in the biomass, about 3 mg/L could be removed. At most approximately 5 mg/L is lost through FeS precipitation and biological uptake.

The importance of other mechanisms was not conclusively investigated. Losses of gaseous H_2S were measured and are unlikely to account for the total sulfur loss. Odors from the reactors were strong and not entirely characteristic of H_2S. It is likely that some quantities of other volatile sulfur compounds were formed and released. Attempts at identification and measurement were not successful. Elemental sulfur may have been formed, but analysis was not attempted during the period when sulfur balances were being performed. A spot test attempted several months later did not indicate sulfur in the solids in the reactor. Therefore, the mechanism of sulfur loss is not known. It should be investigated further, because two possible mechanisms, volatilization and sulfur formation, have significant implications for gas handling and/or solids wasting.

Reduction of SO_2 to sulfide is very important in these reactors because of its effect on methane production and COD removal. Up to 160 mg/L of sulfide was measured in the effluent. Sulfide concentrations in the gas phase

ranged from 0.4 to 1.3% H_2S or about 5 to 40 mg/L of feed. These calculations indicate that up to 20% of the sulfur that is reduced ends up in the gas phase.

Effluent sulfite was measured by the Georgia Pacific (GP) lab in Bellingham and at the University of Washington (UW). The UW values are consistently lower than the sum of free and loosely bound SO_2 measured at GP. This may be partially because of the failure of the UW method to detect loosely bound SO_2. The range of total SO_2 in the effluent measured by GP was 30 to 370 mg/L as S, which corresponds to 30 to 800 mg/L of SO_2-S removal through the reactors. In most cases, sulfide production does not account for all of this removal, which indicates that other reactions, such as the production of S° are taking place.

The fraction of SO_2 which is reduced to sulfide, calculated from the above data, varies widely. The range is from 10 to 60% which corresponds to about 30 to 200 mg of sulfide produced per liter of feed.

The sulfide concentration, 30 to 200 mg/L P(H_2S) 0.4 to 1.3%, was below concentrations reported as toxic to acclimated cultures.

COD Removal

The experimental observations of sulfur transformations and their effects can be generalized and extended to two major considerations of anaerobic treatment of acidic condensates: COD removal, and acid-base reactions in the reactor. COD removal has been estimated for a waste with and without 400 mg/L sulfite sulfur. The conditions for the calculation without sulfur are:

1) SEC containing 3 g/L acetic acid and 1 g/L methanol (total organic COD = 4700 mg/L),

2) 90% of the organics are converted to CO_2, methane, and biological solids,

3) Yield coefficients shown in Table 7, and

4) Methane is assumed to be insoluble.

Based on these conditions, the COD is partitioned in the effluent as shown in Fig. 24; 81% is converted to gaseous methane, 10% becomes residual soluble COD and 9% is incorporated into cells.

With 400 mg/L SO_2 as S in the influent (Fig. 24), the additional assumptions are:

1) 20% of the SO_2 is reduced, which results in 80 mg/L sulfide production, and

2) The H_2S produced is partitioned; 20% to the gas phase and 80% to the aqeuous phase.

Four hundred mg/L sulfite increases the influent COD by 4%, from 4700 to 4900 mg/L. Because sulfite is only partially reduced to sulfide, both forms contribute significantly to the effluent soluble COD. The net effect is a 50% increase in the soluble COD in the effluent. There is also a decrease in methane production from 81% to 75% of the influent organic COD. This represents a loss of approximately 8% in energy recovery as methane. Higher levels of SO_2 or greater conversion to sulfide would have a larger impact on COD removal and methane production.

Neutralization

The neutralization of acidic wastes is a major cost of anaerobic treatment and also results in significant mineralization of the water. Neutralization of SEC, including the effects of different bases, effluent recycle, and CO_2 stripping from the recycle stream, has been discussed,[6] based on a mathematical model which incorporates stoichiometric biological transformation and

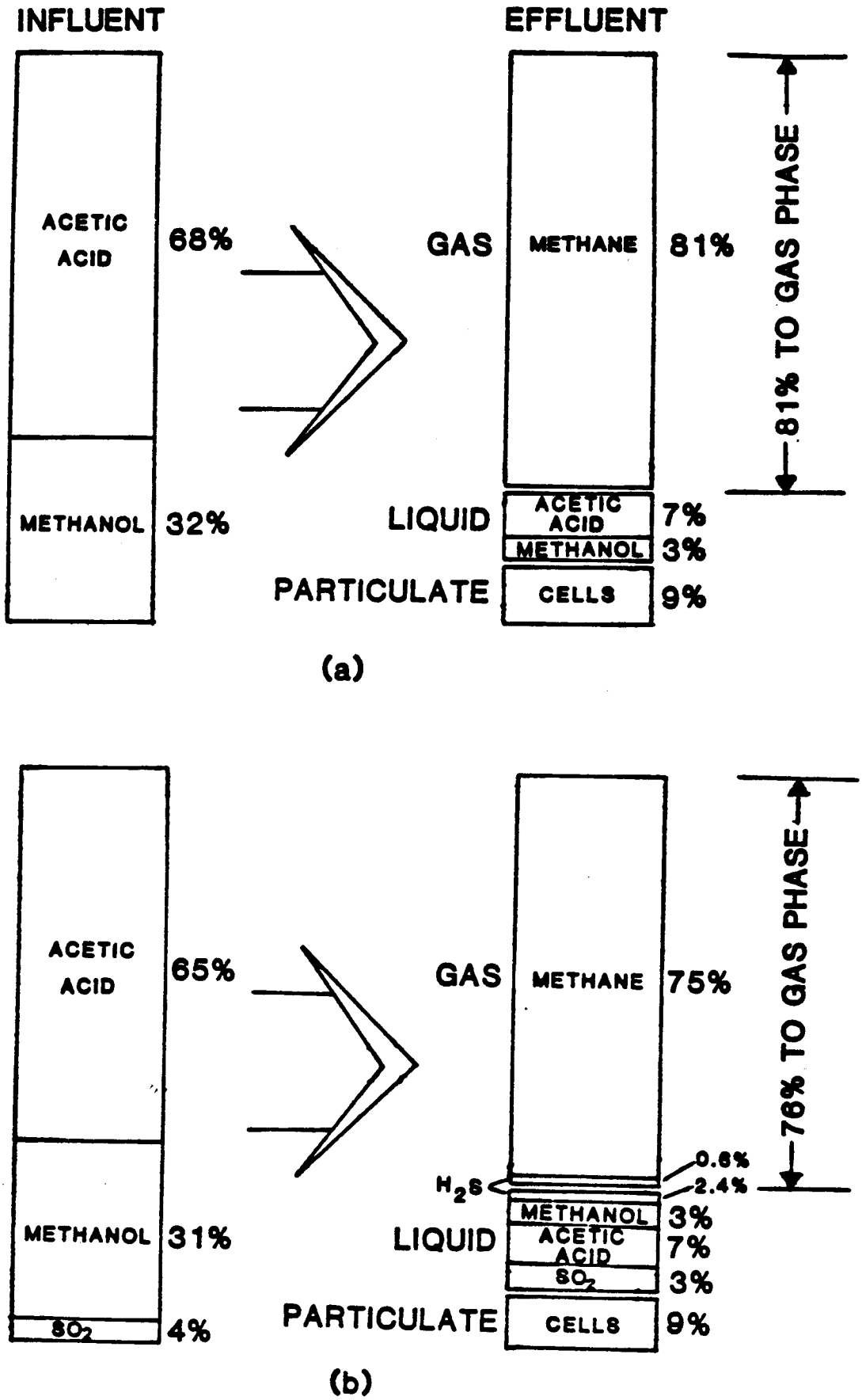


Figure 24. Effect of SO_2 on COD balance; a) no SO_2; b) 400 mg/l SO_2 as S, 20% reduction of SO_2. Fifty mM acetic acid and 31.3 mM methanol, 90% organic removal assumed for both cases.

acid-base and gas-liquid equilibria.[5] The specific role of sulfite and sulfide in neutralization are considered in the following discussion.

The model involves calculation of the concentrations of 7 chemical components (acetic acid, methanol, sulfur dioxide, carbon dioxide, hydrogen sulfide, methane, and hydronium ion, H^+) as a function of the influent concentrations and degree of biological transformation. Concentration of other chemical species in the aqueous phase, such as OH^- and HS^-, can then be computed from the known concentrations and appropriate equilibrium constants. Model calculations also yield the total volume of gas produced and the partial pressure of each volatile substrate, assuming a total pressure of 1 atm. The biological transformations considered are:

$$CH_3COO^- + H_2O \longrightarrow HCO_3^- + CH_4 \qquad 1$$

$$CH_3OH \longrightarrow 1/4\ CO_2 + 3/4\ CH_4 + 1/2\ H_2O \qquad 2$$

$$CH_3COO^- + 4/3\ HSO_3^- \longrightarrow 4/3\ HS^- + HCO_3^- + CO_2 \qquad 3$$

It is convenient to assume that the sulfur reducers use only acetate as a carbon source. Conversion of reactants to products is assumed to follow stoichiometries shown. Values for the fraction of methanol, acetate and sulfite converted to products are set independently.

The problem can be posed mathematically by writing mass balances for 6 components and for exchangeable protons (a proton condition). These expressions for the combined gas and liquid phases are shown in Table 9, which includes only species of significance in the pH range from 5 to 8. The sum of the partial pressures of CH_4, CO_2 and H_2S are set at 1 atm total pressure. The mass balances, equilibrium expressions for weak acids and bases, and the expressions for the total pressure of the gas phase form a system of equations which can be simplified and solved simultaneously. A trial and error solution

Table 9. Summary of equations for mass balances and chemical equilibrium in anaerobic treatment of sulfite evaporator condensate.

Mass Balances

$ST4 = (HSO_3^-) + (SO_3^=)$

$ST2 = (H_2S) + (HS^-) + (PH2S)\ (KR)\ (VGR)$

$CT = (H_XCO_3^*) + (HCO_3^-) + (PCO2)\ (KR)\ (VGR)$

$AT = (HAc) + (Ac^-)$

$MT = (CH_4) + (PCH_4)\ (KR)\ (VGR)$

$PDR = (HAc) + (HCO_3^-) + 2\ (CO_3^=) + (HS^-)$

Partial Pressures

$PT = PCH4 + PCO2$

Equilibrium Expressions

$$KW = (OH^-)\ (H^+)$$

$$K1 = \frac{(CO_3^-)\ (H^+)}{(H_2CO_3^*)}$$

$$K2 = \frac{(CO_3^=)\ (H^+)}{(HCO_3^-)}$$

$$K3 = \frac{(HSO_3^-)\ (H^+)}{(H_2SO_3^*)}$$

$$K4 = \frac{(SO_3^-)\ (H^+)}{(HSO_3^-)}$$

$$K5 = \frac{(HS^-)\ (H^+)}{(H_2S)}$$

$$K6 = \frac{(S^=)\ (H^+)}{(HS^-)}$$

$$KAC = \frac{(H^+)\ (HAc)}{(Ac^-)}$$

Henry's Law Expressions

$$KSO_2 = \frac{(H_2SO_3^*)}{PSO_2}$$

$$KH2S = \frac{(H_2S)}{PH2S}$$

$$KCO2 = \frac{(H_2CO_3^*)}{PCO2}$$

$$KCH4 = \frac{(CH_4)}{PCH4}$$

scheme is used, because the equations are not linear and cannot be solved explicitly.

Model calculations are made for a waste containing 50 mM/L acetic acid and 30 mM/L methanol, neutralized to varying degrees with Na_2CO_3 and assuming 100% biological conversion of the organics. When SO_2 is added to the waste there are pronounced effects on the pH and neutralization requirements. In Figure 25, the model predictions for reactor pH as a function of influent SO_2 concentration are shown for 20% sulfur reduction, which is a reasonable value based on the experimental measurements. The pH is heavily dependent on influent sulfur concentration for the conditions shown. For example, if 50 meq/L base is used to neutralize SEC, and the sulfur influent concentration is 400 mg/L, the reactor pH would be about 6.8. If the influent SO_2 concentration doubled, the reactor pH would drop to 6.5, causing pH stress if extra base was not added. SO_2 fluctuation of this magnitude is commonly observed in evaporator condensates. Therefore, careful pH control and influent neutralization is needed to avoid reactor upsets from fluctuations in SO_2 concentrations.

The relationship between sulfur reduction and pH is shown more clearly in Fig. 26. Here the base required to maintain the reactor pH at 6.8 is plotted as a function of influent SO_2 concentration for several levels of sulfur reduction. Increasing sulfur reduction decreases the slopes of the lines in Fig. 26 because H_2S is a weaker acid than SO_2. Assuming 20% sulfur reduction, the base requirement would increase from 47 meq/L to 62 meq/L as SO_2 concentration increases from 400 to 800 mg/L (12.5 mM to 25 mM). This is a 30% increase in base required to maintain the reactor pH at 6.8. Because it has been shown that SO_2 toxicity is minimal in this range as long as

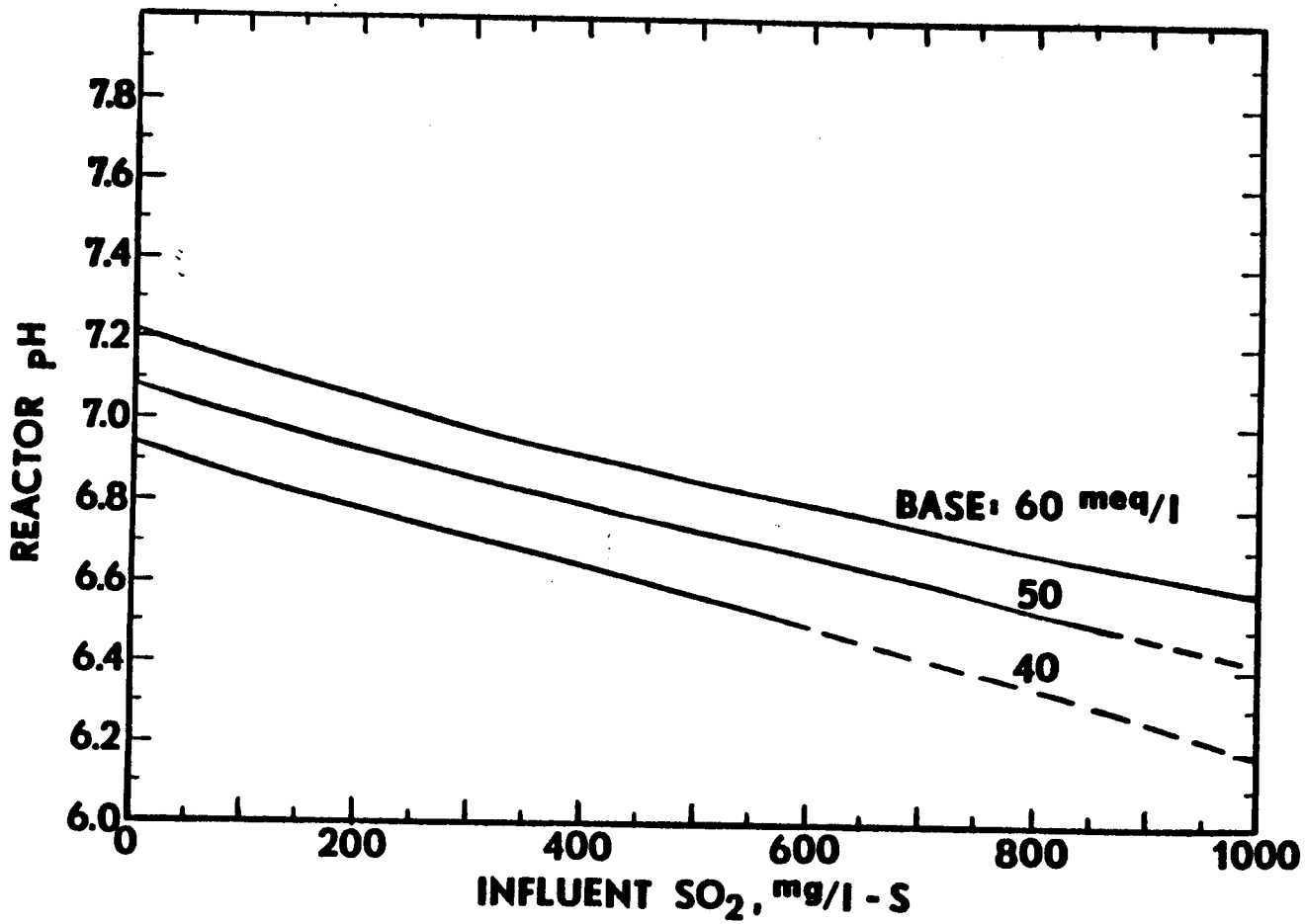


Figure 25. Effect of influent SO_2 concentration on reactor pH. Twenty % of the influent SO_2 is reduced to sulfide. Na_2CO_3 is the assumed base.

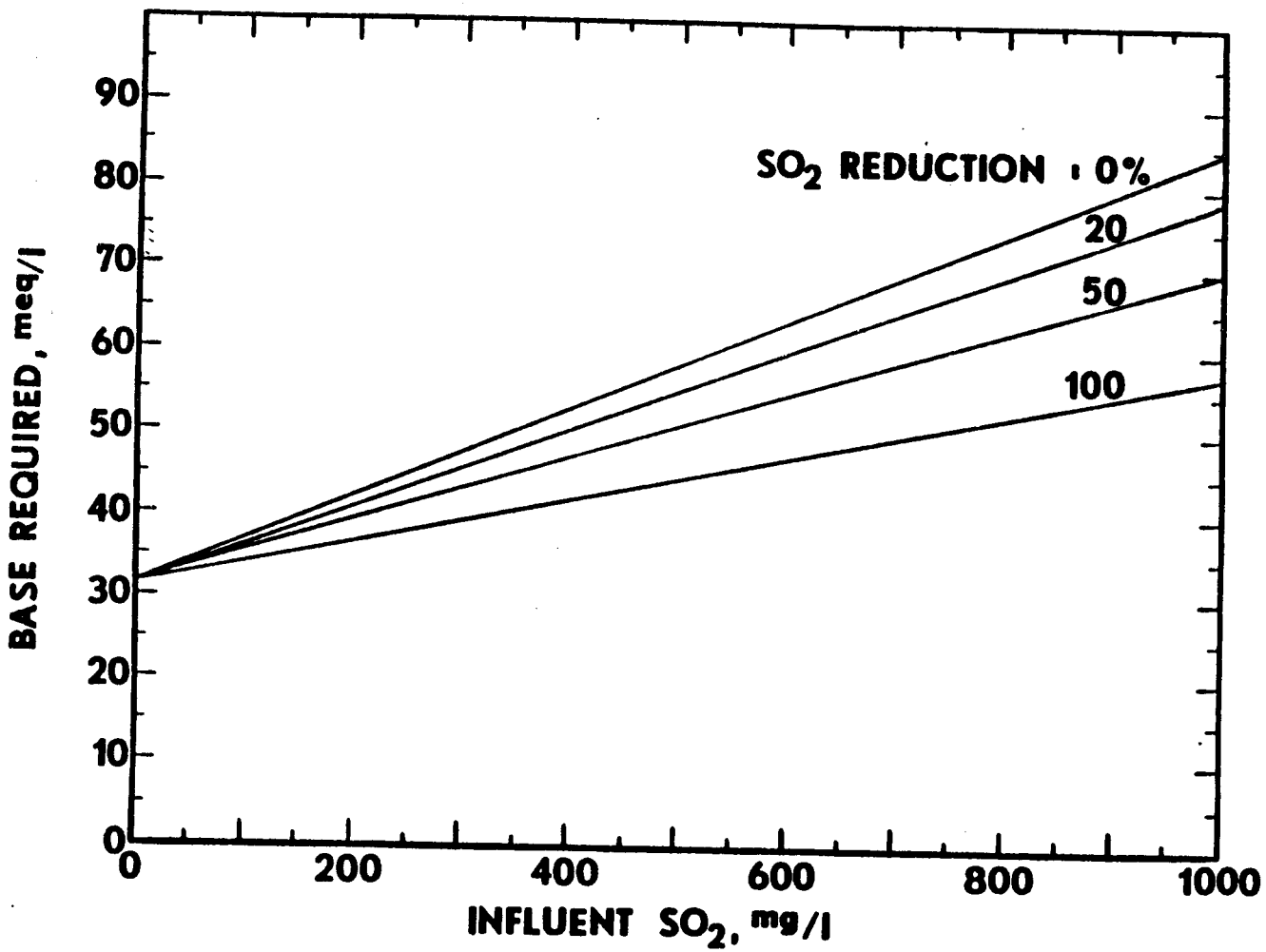


Figure 26. Base (Na_2CO_3) required to maintain a pH of 6.8 in the reactor as a function of the influent SO_2 concentration. Twenty % SO_2 reduction is assumed.

acclimation is allowed to occur, the increased requirement for neutralization may be the major effect of increasing SO_2. For the case of no sulfur reduction the slope of the line in Fig. 26 is 1.7 meq of Na_2CO_3 per mml of sulfur. If a pH of 7.4 were selected, the slope would be closer to 2, since much of the HSO_3^- would have to be titrated (pKa_2 = 7.2). The slope of the line for 100% sulfur reduction is about 0.8 meq Na_2CO_3 per mml. If NaOH were used, the corresponding value would be about 0.7 meq per mml of SO_2 converted to sulfide.

The effect of sulfur on methane production is indicated in Fig. 27, which shows methane evolved to the gas phase as a function of influent SO_2 concentration for several levels of sulfur reduction. The slopes of the lines are derived from the stoichiometric relationship of 0.75 moles of methane lost for every mole of sulfur reduced. For the average conditions experienced in this study (400 mg/L S, 20% reduction), the decrease in methane is from 1.86 to 1.81 L per liter of liquid, or about a 3% decrease. At higher levels of sulfur and sulfur reduction, the effect is greater.

Another problem associated with sulfur reduction in the reactor is production of odorous and potentially dangerous H_2S gas. In Fig. 28, the H_2S percentage in the gas phase is plotted as a function of the influent sulfur for reactor pH of 6.8. For the case of 400 mg/L sulfur and 20% reduction, a 1% concentration of H_2S in the gas phase is predicted. At more extreme conditions, the H_2S percentage increases rapidly. These levels of H_2S could present serious problems if gas leaks occur; they are another reason to minimize the influent sulfur concentration.

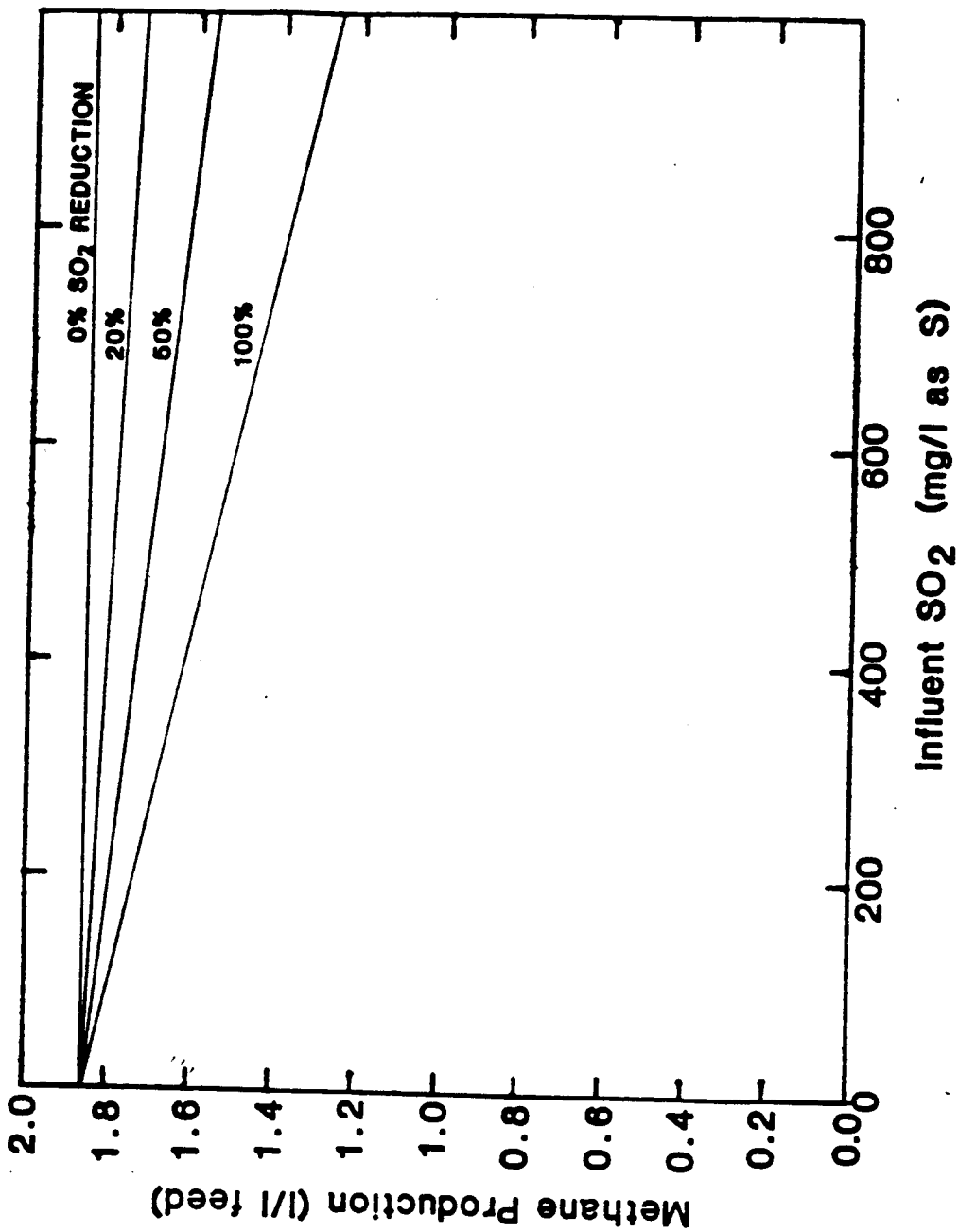


Figure 27. Effect of sulfur reduction on methane production. Na_2CO_3 is the assumed base. Reduction refers to the percentage conversion of SO_2 to H_2S.

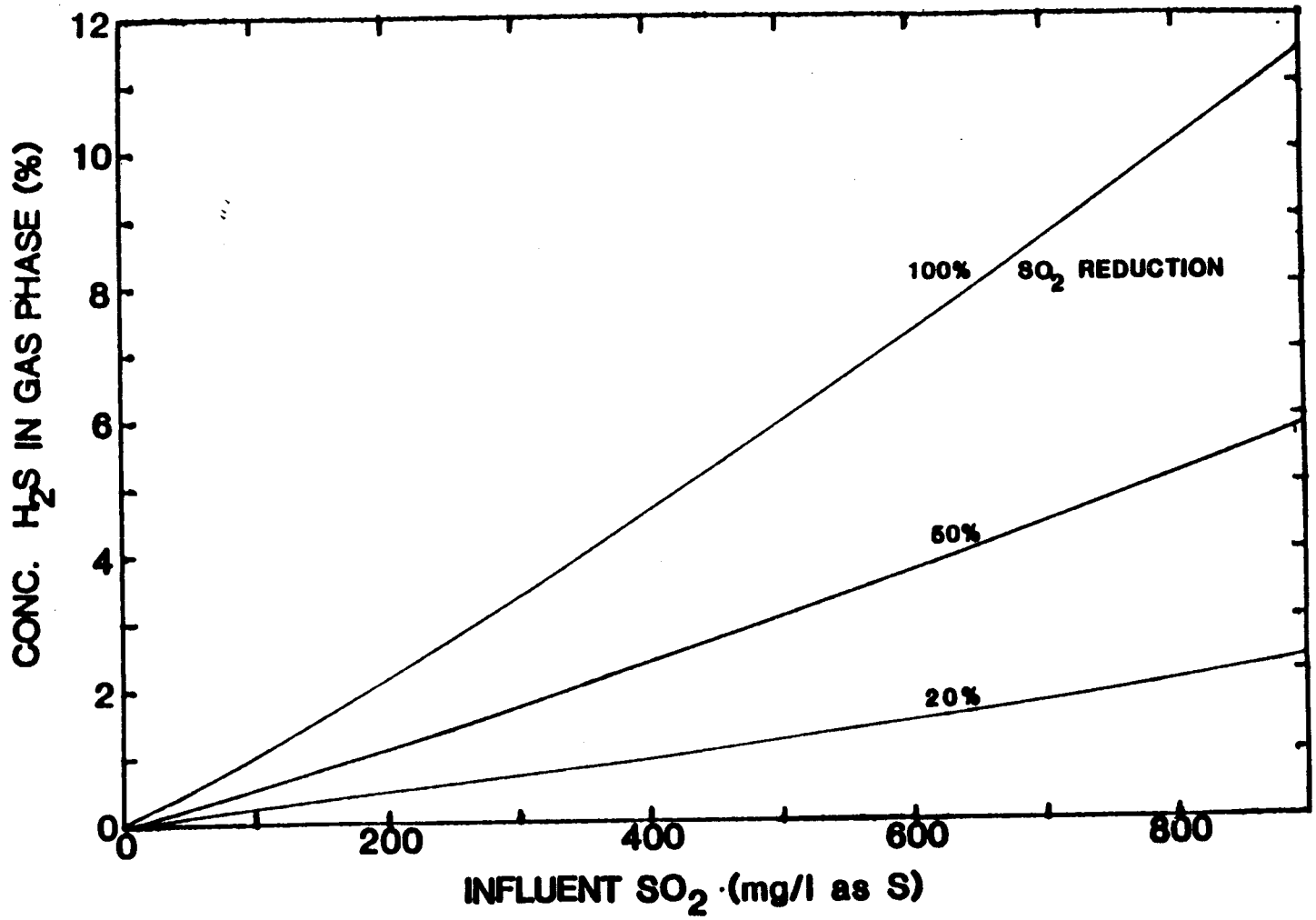


Figure 28. Evolution of H_2S to the gas phase. Fifty meq/l Na_2CO_3 is the base. Reduction refers to the percentage conversion of SO_2 to sulfide.

CONCLUSIONS

Sulfur, mainly in the form of SO_2, in evaporator condensate from sulfite pulping processes has been shown to be partially reduced to H_2S and partially removed in an anaerobic process operated at volumetric loading rates greater than 10 kg COD/m^3-d. Toxicity of sulfite and sulfide is low when acclimation is allowed to occur, and stable operation is possible at relatively high influent sulfite concentrations. In both batch and continuous flow experiments, short periods of decreased methanogenesis were followed by a resumption of methane production and easy acclimation to increasing concentration of sulfur. In batch tests, there was a noticeable decrease in the rate of methane production at high sulfite concentrations.

A major impact of sulfur on the capabilities of the reactors to remove COD is the production of H_2S, a relatively soluble, oxygen demanding compound. The production of H_2S instead of CH_4 resulted in a significant decrease in soluble COD removal efficiency for the experimental reactors. There is the potential for much greater impacts at higher sulfur concentrations or higher sulfur-reducing activity.

Sulfur reduction in the reactors is not stoichiometrically complete. Sulfide production accounts for about 10 to 60% of the influent SO_2. This is surprising since sulfur reduction using acetate as the carbon source is more energetically favorable than methane production from acetate.

A model of the process using chemical equilibrium principles is useful for studying the interactions between the influent COD and sulfur concentrations, the amount of base added to neutralize the waste, and the chemical environment in the reactors.

Based on the model results, the major impact of SO_2 on reactor performance is an increased requirement for base to maintain pH in the reactor in the optimal range for methanogenesis. Sulfur reduction lessens the severity of this impact.

The practical result of the study is an assessment of the costs and effects of SO_2 in an acidic waste. There are no benefits, but the adverse effects were found to be manageable. Specifically, toxicity to or severe inhibition of methane-formers was not found. In fact, conversion of organics to methane was found to be nearly complete, even though a small fraction of the possible sulfur reduction was occurring. SO_2 in the waste carries high neutralization costs, higher effluent COD concentrations and a smaller decrease in methane production.

ACKNOWLEDGEMENTS

This paper was presented at the Annual Conference of the Water Pollution Control Federation in Detroit in October 1981. The contributions of Mark Buggins and Sandra Woods, graduate research assistants, Joseph McCarthy, co-principal investigator and professor of Chemical Engineering, and Ed Dahlgren, Georgia Pacific Corporation, Bellingham, Washington, are gratefully acknowledged.

The study was supported by a matching grant (Project No. 145-01-11N-39943-3068) from the Office of Water Research and Technology, U.S. Department of Interior, Washington, D.C. through the Washington Research Center as authorized by the Water Research and Development Act, 1978.

REFERENCES

1. American Public Health Association, Standard Methods for the Examination of Water and Wastewater, Washington, D.C. (1980).

2. Benjamin, M.M., J.F. Ferguson, and M.E. Buggins. Treatment of sulfate evaporator condensate with an anaerobic reactor, TAPPI, 65, 96, 1982.

3. Benjamin, M.M., S.L. Woods, and J.F. Ferguson. Toxicity and Biodegradability of Pulp Mill Waste Constituents Exposed to Anaerobic Bacteria, presented at the International Association for Water Pollution Research, Specialized Seminar on Anaerobic Treatment, Copenhagen, Denmark, June 1982.

4. Buggins, M.E. Treatment of Sulfite Evaporator Condensate with a Submerged Media Anaerobic Reactor, Master's Thesis, University of Washington, Seattle, WA, 1981.

5. Eis, B.J. Limiting Factors in the Anaerobic Treatment of Sulfite Evaporator Condensate. Master's Thesis, University of Washington, Seattle, WA, 1982.

6. Ferguson, J.F., B.J. Eis, and M.M. Benjamin. Neutralization in Anaerobic treatment of an Acidic Waste, presented at the International Association for Water Pollution Research, Specialized Seminar on Anaerobic Treatment, Copenhagen, Denmark, June 1982.

7. Foley, F.R., and Johnson, L.H., Direct Determination of Sulfonate and Non-sulfonate Sulfur in Spent Sulfite Liquor, Analytical Chemistry 32, 850-52, 1960.

8. Gaudy, Jr., A.F. and E.T. Gaudy. Microbiology for Environmental Scientists and Engineers, McGraw-Hill Book Company, New York (1980).

9. Georgia Pacific Corporation, Personal communications, Bellingham, WAA 1982.

10. Jeris, J.S. and P.L. McCarty. The Biochemistry of Methane Formation Using C^{14} Tracers, Journal of the Water Pollution Control Federation, 37, 178 (1965).

11. Jurgensen, M.F. and J.T. Patton. Bioremoval of Lignosulphonates from Sulphite Pulp Mill Effluents, Process Biochemistry, Vol. 14, No. 1, p. 2, 1979.

12. Lawrence, A.W., P.L. McCarty, and F.J.A. Guerin. The Effects of Sulfide on Anaerobic Treatment, Proceedings of the 19th Industrial Waste Conference, Purdue University, p. 343, 1964.

13. Martens, C.S. and R.A. Berner. Interstital Water Chemistry of Anoxic Long Island Sediments. 1. Dissolved Gases, Limnology and Oceanography, 22, 10, 1977.

14. McCarty, P.L. Energetics and Bacterial Growth, in Organic Compounds in Aquatic Environments, edited by Faust and Hunter, Marcel-Dekker Inc., New York, 495 (1971).

15. Owen, W.F., D.C. Stuckey, J.B. Healy, Jr., and L.Y. Young. Bioassay for Monitoring Biochemical Methane Potential and Anaerobic Toxicity, Water Research, Vol. 13, p. 485 (1979).

16. Pine, J.J. The Methane Fermentations, in Anaerobic Biological Treatment Processes, R.F. Gould (Ed.), American Chemical Society, Advances in Chemistry Series, No. 105.

17. Rexfelt, J. and O. Samuelson. The Compositiion of Condensates from the Evaporation of Sulfite Spent Liquor, Svensk Papperstidnig, 73, 689 (1970).

18. Ruus, L. A Study of Waste Waters from the Forest Products Industry. 4. Composition and Biological Demand of Condensate from Spent Sulfite Liquor Evaporation, Svensk Papperstidnig, 67, 221 (1964).

19. Rydholm, S. Pulping Processes, Interscience Publishers, New York (1965).

20. Trudinger, P.A. Assimilatory and Dissimilatory Metabolism of Inorganic Sulfur Compounds by Microorganisms, Advances in Microbial Physiology, Vol. 3, p. 111, 1969.

21. Widdel, F. and N. Pfennig. A New Anaerobic Sporing, Acetate-Oxidizing, Sulfate-Reducing Bacterium: Desulfotomaculum (emend.) Acetoxidans, Archives of Microbiology, 112, 119, 1977.

22. Winfrey, M.R. and J.G. Zeikus. Effect of Sulfate on Carbon and Electron Flow During Microbial Methanogenesis in Fresh Water Sediments, Applied Environmental Microbiology, 33, 275, 1977.

23. Yang, J., G.F. Parkin, R.E. Speece. Recovery of Anaerobic Digestion After Exposure to Toxicants, Final Report to the U.S. Department of Energy, December 1979.

24. Zeikus, J.G. The Biology of Methanogenic Bacteria, Bacteriological Reviews, 41, 514 (1977).

CHAPTER 4

NEUTRALIZATION IN ANAEROBIC TREATMENT OF AN ACIDIC WASTE[1, 2]

John F. Ferguson
Brian J. Eis
Mark M. Benjamin

ABSTRACT

Anaerobic treatment requires maintenance of a stable pH near the neutral range. In evaluating treatment of an acidic waste from chemical pulping, neutralization costs were identified as an important factor. Conceptual and mathematical models of the anaerobic process were formulated incorporating bacterial transformations and chemical equilibria. Simulations were used to compare the effects of several sodium bases, to assess the role of SO_2 and H_2S in controlling the neutralization requirements, and to evaluate effluent recycle as a tool for increasing influent pH. Gas stripping to reduce CO_2 in the recycle was also evaluated. This modeling approach can be applied to other industrial wastes that may be treated anaerobically and can be an important tool in assessing feasibility of treatment of acidic wastes.

1. Presented at the IAWPR Specialized Seminar,"Anaerobic Treatment of Wastewater in Fixed Film Reactors" Copenhagen, Denmark June 1982

2. Accepted for publication in Water Research

INTRODUCTION

The maintenance of stable pH values near the neutral range is necessary for successful anaerobic treatment. Buffering with the carbonic acid/bicarconate system is both desirable, since it has high buffer intensity at pH values from 5.5 to 7, and unavoidable, since massive quantities of CO_2 are produced in anaerobic biodegradation. McCarty[6] has summarized the relation between ranges of alkalinities, CO_2 partial pressures, and pH values acceptable for anaerobic treatment (Fig. 29). The entire range of P_{CO2} and pH values encompasses alkalinities from about 20 meq/L to 100 meq/L. Clark and Speece[1] have shown that with acclimation the pH range may extend from 6 to 8, indicating that lower alkalinities may be acceptable.

The waste composition and biological transformations often combine to yield solutions with pH and alkalinity in the desired ranges. However, if adjustment of alkalinity and pH is necessary, the large amounts of chemicals required can be costly. Chemical costs may approach the value of the digester gas produced. Neutralization problems may arise when a waste is either excessively acid or alkaline or contains constituents that when anaerobically treated result in excess production of alkalinity. Acidic wastes include ones with mineral acids, insufficient organic nitrogen, or organic acids. Alkaline wastes contain excess mineral bases or organic nitrogen, which results in alkalinity production proportional to ammonia release.

The waste used as a case study in this paper is a condensate produced from the evaporative concentration of spent pulping liquors from the acid bisulfite process. Evaporation of water in a multiple effect evaporator is accompanied by volatilization of acetic acid, methanol and sulfur dioxide. Other volatile compounds, droplet carryover, and washdown from evaporators and

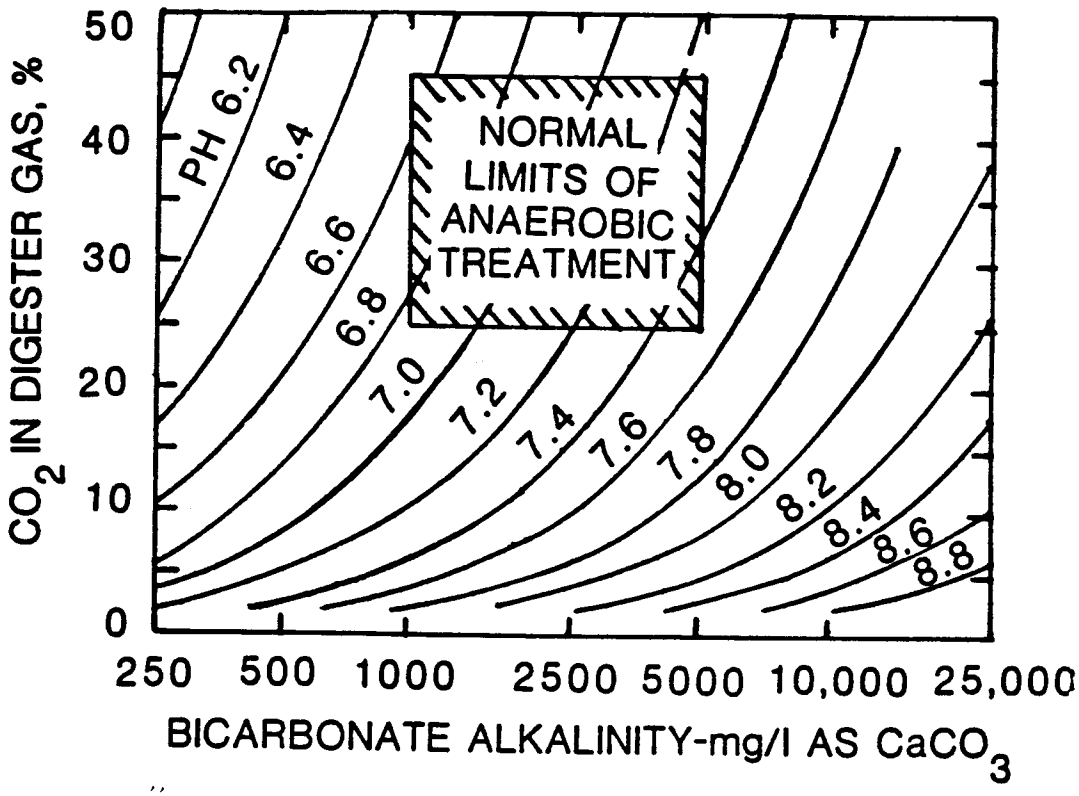


Figure 29. Anaerobic process alkalinity as a function of CO_2 partial pressure and pH.[5]

condensors contribute minor constituents. Sulfite evaporator condensate (SEC) is quite variable from mill to mill and with time in a single mill. Typical concentrations of these major constituents are 50 mM/L acetic acid, 30 mM/L methanol and 12 mM/L sulfur dioxide (sulfurous acid). Speciation of the acids as a function of pH is represented in Fig. 30. The pH of the condensate is about 2.1, which can be derived from the diagram as the pH of a pure acetic acid, and sulfurous acid solution for the given concentrations (where $[H^+] = [CH_3COO^-] + [HSO_3^-]$).

Such an acidic waste must be at least partially neutralized in order to maintain pH values suitable for anaerobic bacterial metabolism. The amount of neutralization will depend on acidity of the raw waste, the mixing regime of the reactor, and the biological conversions, which tend to form weaker acids from stronger ones. In the most extreme case, the titration curve (Fig. 30b) shows that H^+, $H_2SO_3^*$, CH_3COOH and some HSO_3^- must be titrated to raise the pH of the waste. If such a waste were treated in a completely plug-flow reactor, 60 to 70 meq/L of base would be required to raise the influent pH to between 6 and 7. The cost of this chemical addition, if accomplished with NaOH, Na_2CO_3 or $Ca(OH)_2$, is approximately \$0.60, 0.30 or 0.10 per m^3 of waste treated, respectively. In comparison for the Pacific Northwest the gross value of the methane produced is about \$0.20 per m^3 of waste treated. The aeration savings (energy for blowers) due to removal of the acetate and methanol is \$0.15-0.20/m^3 of waste if aerobic treatment is used following anaerobic treatment.

The cost of neutralization is very significant, but due to the biological conversions and to backmixing (or effluent recycle) the need for base can be reduced. In the following discussion, the effects on neutralization requirements of biological conversion, partitioning of acidic gases to a gas phase,

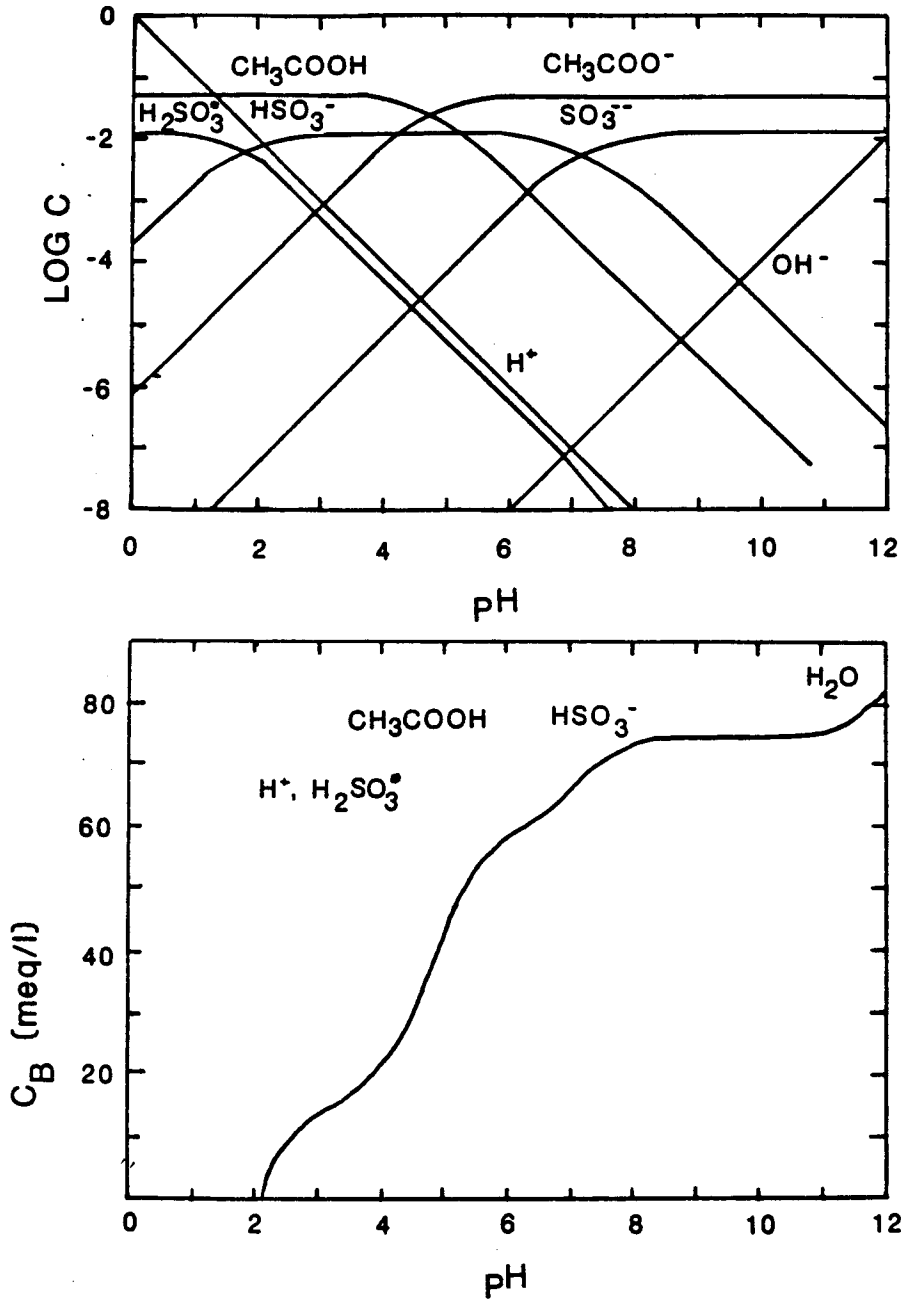


Figure 30. Acetic acid - sulfur dioxide system. a. Special concentration versus pH for 50 mM/L acetate (pK_1 = 4.75) and 12 mM/L H_2SO_3* (pK_1 = 1.8, pK_2 = 7.3). b. Titration curve for strong base addition to 50 mM/L carbonic acid and 12 mM/L sulfurous acid.

and recycle and reactor mixing regime are systematically presented. Full chemical neutralization may be considered as one extreme with complete mix and complete biological conversion as the other. Intermediate cases are analyzed, including use of effluent recycle to dilute and partially neutralize the influent, and effluent recycle with CO_2 stripping.

Anaerobic treatment of acetic acid and SO_2 results in formation of weaker acids which increase the solution alkalinity and pH. These changes can be estimated assuming stoichiometric conversion of acetic acid to CO_2 and CH_4, and of SO_2 to H_2S. A log C vs. pH diagram for a solution with 50 mM $H_2CO_3^*$ and 12 mM $H_2S(aq)$ is shown in Fig. 31. The equilibrium pH of this solution is about 3.8, derived as the pH where $[H^+] = [HS^-] + [HCO_3^-]$. The computed titration curve for this system is shown in Fig. 31b. About 20 meq/L base is needed to reach pH 6 and 55 meq/L to reach 7. These values are considerably less than needed to reach the neutral pH range before any bioconversions occur (Fig. 30b). The biological transformations, in effect, reduce the need for neutralization.

The possible reduction is not, however, as straightforward as shown in the titration curve analysis because sulfite reduction and acetate fermentation are not totally independent processes; organisms forming methane and those forming sulfide compete for the same carbon substrate. Sulfide production results in more CO_2 and less methane formation. Thus, both knowledge of reaction stoichiometry and experimental measurements of the extent of competition are needed to compute the final solution composition. In addition, the dissolved gases partition between solution and vapor phases, further complicating the computation of the equilibrium pH. For CO_2, the partitioning considerably reduces the solution total carbonate and reduces the amount of base needed to maintain an acceptable pH. The titration curves for

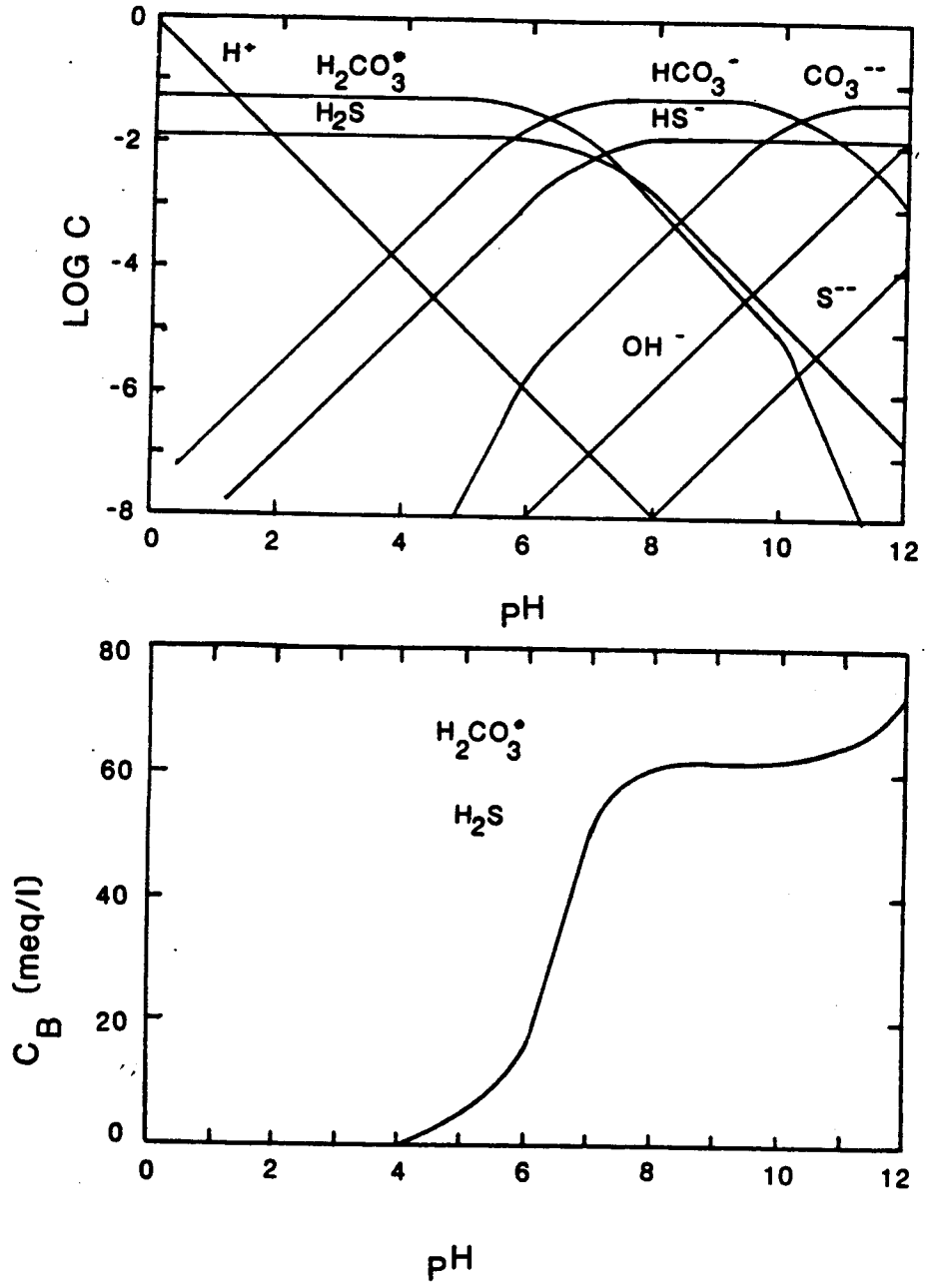


Figure 31. Carbonate-sulfide system. a. Species concentration versus pH for 50 mM/L carbonate (pK_1 = 14.0). b. Titration curve for strong base addition to 50 mM/L carbonic acid and 12 mM/L hydrogen sulfide (aqueous).

raw waste and treated waste constituents set approximate limits on the neutralization requirement. In the worst case, complete neutralization of the raw waste may be needed. However, advantage may be taken of the biological transformation to reduce the neutralization requirement by recycling a portion of the effluent to increase the pH of the influent. Also, carbon dioxide may be stripped from the effluent to increase the pH in the recycle stream and the mixed reactor influent.

In the paper, these factors are systematically discussed and modeled. Possible biological transformations for acetate, methanol and sulfite are presented. Partitioning of gases to the vapor phase is described in an acid-base and gas-liquid equilibrium model coupled to the biological conversions taking place in the anaerobic reactor. The predictions for a complete mixed reactor are compared to data for pH, gas production, and gas composition. Most high rate anaerobic reactors are quite well-mixed by fluid flow and rising gas bubbles. However, most fixed film reactors are not completely mixed. To account for this the reactor is modeled with an influent zone, where the pH must be suitable for anaerobic growth followed by a well-mixed zone where the biological reactions occur. The role of the effluent recycle, with and without CO_2 stripping of the recycled fluid, is evaluated for its potential to reduce chemical addition requirements. Finally, the specific role of sulfite reduction on the base requirements is summarized.

ANAEROBIC TREATMENT OF ACETIC ACID AND SO_2

Acetic acid is the preferred substrate for Methanosarcina barkeri and probably other species. The metabolic reaction splits acetic acid into equimolar amounts of methane and carbon dioxide and produces useful biological

energy for bacterial growth. However, the energy yield is low, so no more than 5% of the acetate is converted to bacterial cells. The carbon dioxide produced dissolves, is hydrated in solution, and may dissociate one or two protons. By convention $CO_2(aq)$ and H_2CO_3 are combined as $H_2CO_3^*$.

$$CO_2(aq) + H_2O = H_2CO_3^* \quad \log K_{Henry} = -1.5 \tag{1}$$

Sulfur dioxide dissolves and undergoes an analogous series of reactions. It is both more soluble and more acidic than CO_2.

$$SO_2(g) + H_2O = H_2SO_3^* \quad \log K_{Henry} = 0.08 \tag{2}$$

Oxidized sulfur (sulfate or sulfite) can serve as a terminal electron acceptor in the anaerobic bacterial oxidation of simple organic compounds by bacteria such as Desulfovibrio desulfuricans. For many years, only a very few organics were known to be substrates coupled to sulfate reduction, most notably lactate. In recent years, many short chain alcohols and acids, including methanol and acetic acid, have been found to be substrates for this process.

Bacterial sulfur reduction is well understood in its general characteristics. Sulfate requires one mole of adenosine triphosphate (ATP) to produce adenosine phosphosulfate (APS), the active compound that facilitates reduction to sulfite. Sulfite can enter the reduction pathway without the initial expenditure of a mole of ATP. Hence sulfite reduction is energetically favorable compared to sulfate reduction. Sulfite reduction can apparently be carried out by most, if not all, bacteria capable of sulfate reduction. The normal product of these pathways is hydrogen sulfide. Balanced reactions for the energy yielding reactions for sulfate and sulfite reduction with acetate and

for acetate splitting are presented in Table 10 with computed values for growth yield coefficients and alkalinity changes (McCarty, 1972). Predicted yield values for sulfite are significantly higher than for sulfate. Similar reactions for methanol rather than acetate result in slightly higher yield coefficients.

Since the yield coefficients are higher for sulfur-reducers than for methane-formers, they should out-compete methane-formers for acetate, and this is apparently the case in marine sediments.[4] Acetate fermentation should not begin until all available sulfite has been reduced to sulfide. Such a result is very undesirable in anaerobic treatment for several reasons: sulfide in the effluent requires further treatment; hydrogen sulfide in the gas phase is poisonous, corrosive and odorous; H_2S is oxidized to SO_2 on combustion; and sulfide production stoichiometrically reduces methane production.

In studies with two anaerobic reactors, one that operated for several months and one for more than a year at high sulfite loadings, measurements of sulfite and sulfide in influent, effluent and gas indicated that sulfide production ranged from 50 to 200 mg/L.[3] Only about 20% of the potential sulfide production actually takes place. The actual sulfide production is limited to a fraction of the sulfite present. In this related study, experimental measurements and calculated results are presented in which sulfite concentration and extent of conversion are varied. In this paper, the average measured value of 20% conversion is used to represent the competition between sulfite-reducers and methane-formers.

Biological transformation, acid-base and gas-liquid equilibria

In the following sections a model for anaerobic treatment of SEC is formulated. The model can readily be generalized to other wastes provided that the

Table 10. Anaerobic energy yielding reactions for methane production and sulfide production.

Reaction	Yield g cells / g substrate	Equivalents of Alkalinity* Produced Per Mole of Substrate
(1) $CH_3COO^- + H_2O \longrightarrow CH_4 + HCO_3^-$	0.034	1
(2) $CH_3COO^- + SO_4^{2-} \longrightarrow HS^- + 2HCO_3^-$	0.059	3
(3) $CH_3COO^- + 4/3\ HSO_3^- \longrightarrow$ $4/3\ HS^- + HCO_3^- + H_2CO_3$	0.12	7/3
(4) $CH_3OH \longrightarrow 3/4\ CH_4 + 1/4\ H_2CO_3 + 1/4\ H_2O$	0.22	0

* Alkalinity $\equiv (HCO_3^-) + 2(CO_3^{2-}) + (HS^-) + (OH^-) - (H^+)$

waste composition, i.e., the concentrations of acids and bases and constituents that are altered by anaerobic treatment, is known. Alternatively, methane and CO_2 production can be roughly estimated from measurements of COD and total organic carbon. The acid-base characteristics of the waste can be determined from analysis of a titration curve, and specific analyses can be performed for inorganic species that are measured as COD or are acidic. The three steps involved in modeling SEC treatment are:

1. The influent composition and chemical additions are used as terms of inputs for mass balances on 4 weak acids (carbonate-carbon, acetate-carbon, sulfite-sulfur, and sulfide-sulfur), on 2 additional components (methanol and methane), and on alkalinity.
2. Parameters are introduced for the stoichiometric bacterial transformations (reactions 1, 3 and 4 of Table 10) to establish the conversion efficiency to methane and sulfide end products.
3. After the biological transformations are computed and the mass balances adjusted, the system is allowed to equilibrate with a gas phase of one atmosphere pressure, subject to a proton condition that incorporates changes in alkalinity and acidity and allows computation of the solution phase pH.

The resulting set of equations has been simplified and solved by a trial and error algorithm in a computer program that computes the volume and composition of the gas phase, the pH and composition of the reactor effluent, and the partitioning of methane, carbon dioxide and hydrogen sulfide between the gas and the liquid phase. The model has been used to explore the effectiveness of various bases at various concentrations and to assess the

role of sulfite and sulfide in the process. The model formulation is shown schematically in Fig. 32 and is documented by Eis.[3] Equilibrium constants for acid base reactions and Henry Law constants are for 35°C with corrections made using the Davies Equation for a presumed ionic strength of 0.1.

Effects of sodium bases

The effect of neutralizing the influent with sodium hydroxide, sodium carbonate, or sodium bicarbonate on reactor pH and gas composition has been calculated for a waste containing 50 mM/L acetic acid and 30 mM/L methanol (Fig. 33). The amount of base needed (meq/L) to attain a given pH increases in the order NaOH < 8 Na_2CO_3 < $NaHCO_3$. The difference increases as the reactor pH is increased. Based on relative costs in the Pacific Northwest, sodium carbonate is the most economical of the three sodium bases. Lime is much less expensive per equivalent of base, but its use is severely restricted by calcium salt precipitation.

Sodium hydroxide use results in a lower CO_2 content in the reactor gas than the carbonate or bicarbonate bases (Fig. 33b). Methane percentages typically are 70-80% for hydroxide or carbonate neutralization and 60% for bicarbonate neutralization. The ratio of methane produced (at 1 atm., 35 C) to liquid processed is 1.8 l/L for the waste used in the calculation. In the experimental tests, approximately 80 to 90% of the theoretical methane gas was directly measured." Two % is lost in the effluent. The remainder can be accounted for by conversion of some substrate to cells and by gas losses in the collection system.

Carbonate carbon is partitioned more equally between the liquid and gas phases. For neutralization with Na_2CO_3, from 20 to 40 mM of carbon dioxide is transferred to the gas/L of waste treated, constituting more than 30% of the

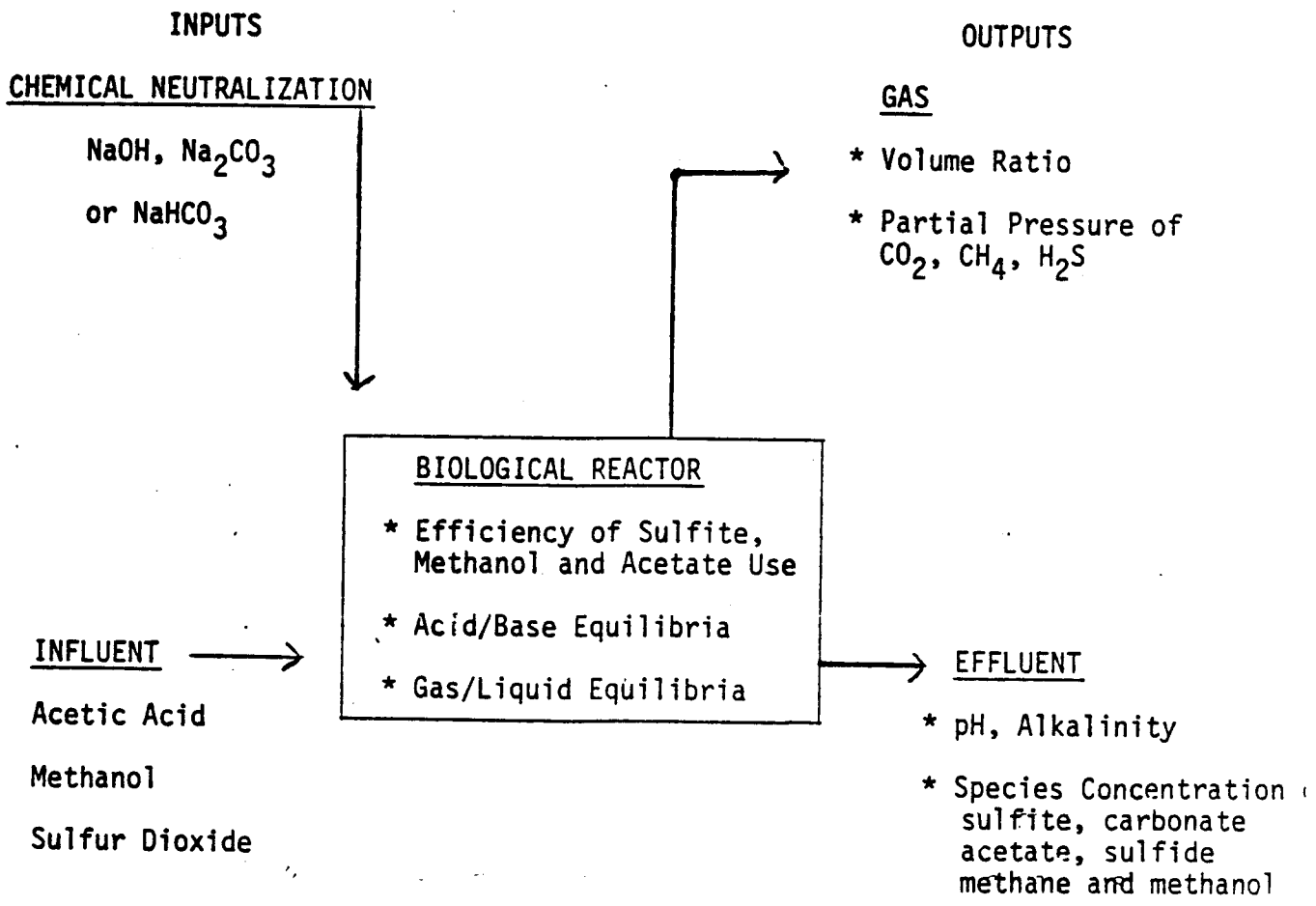


Figure 32. Schematic of the elements of calculations of reactor effluent and gas composition.

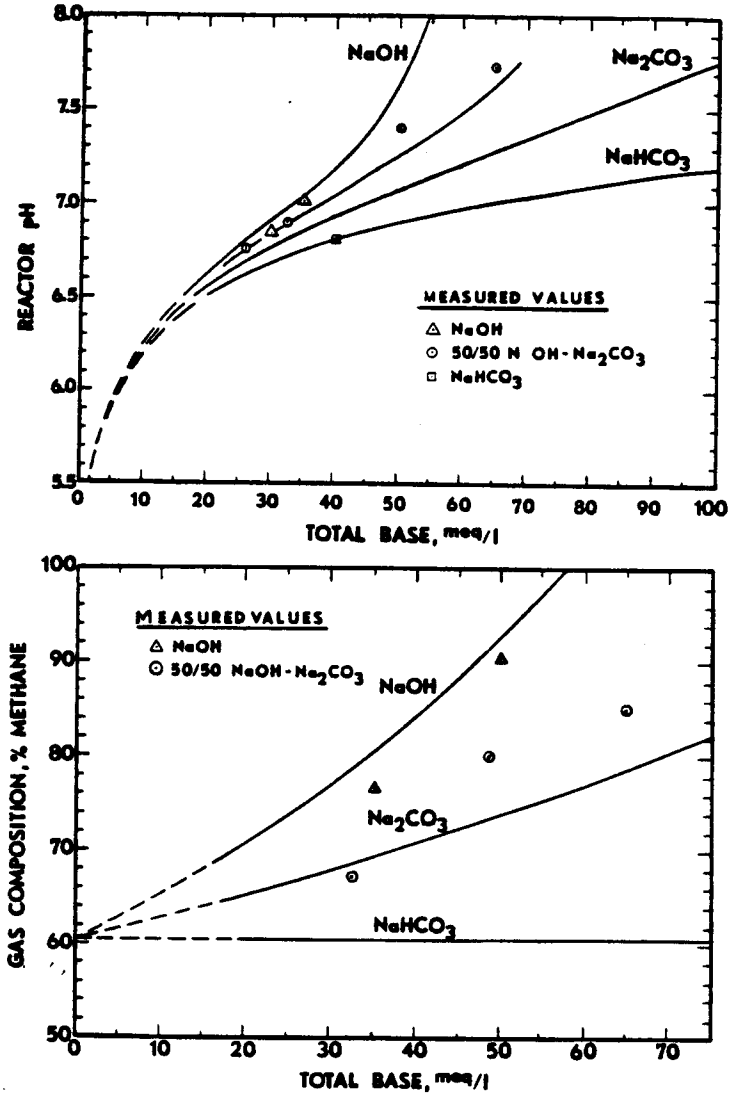


Figure 33. Simulation for acetate-methanol waste. a. Calculated reactor pH values for varying additions of NaOH, Na_2CO_3 and $NaHCO_3$. Waste contains 50 mM/L acetate, 30 mM/L methanol, 100% conversion to methane. Experimental data for NaOH, $MaHCO_3$ and 50% NaOH, 50% Na_2CO_3 neutralization. Reactor loadings were between 5 and 10 g/L per day COD. b. Calculated and measured gas composition.

carbonate carbon (57.5 mM/L CO_2 is produced in methanogenesis of the waste used in the calculations).

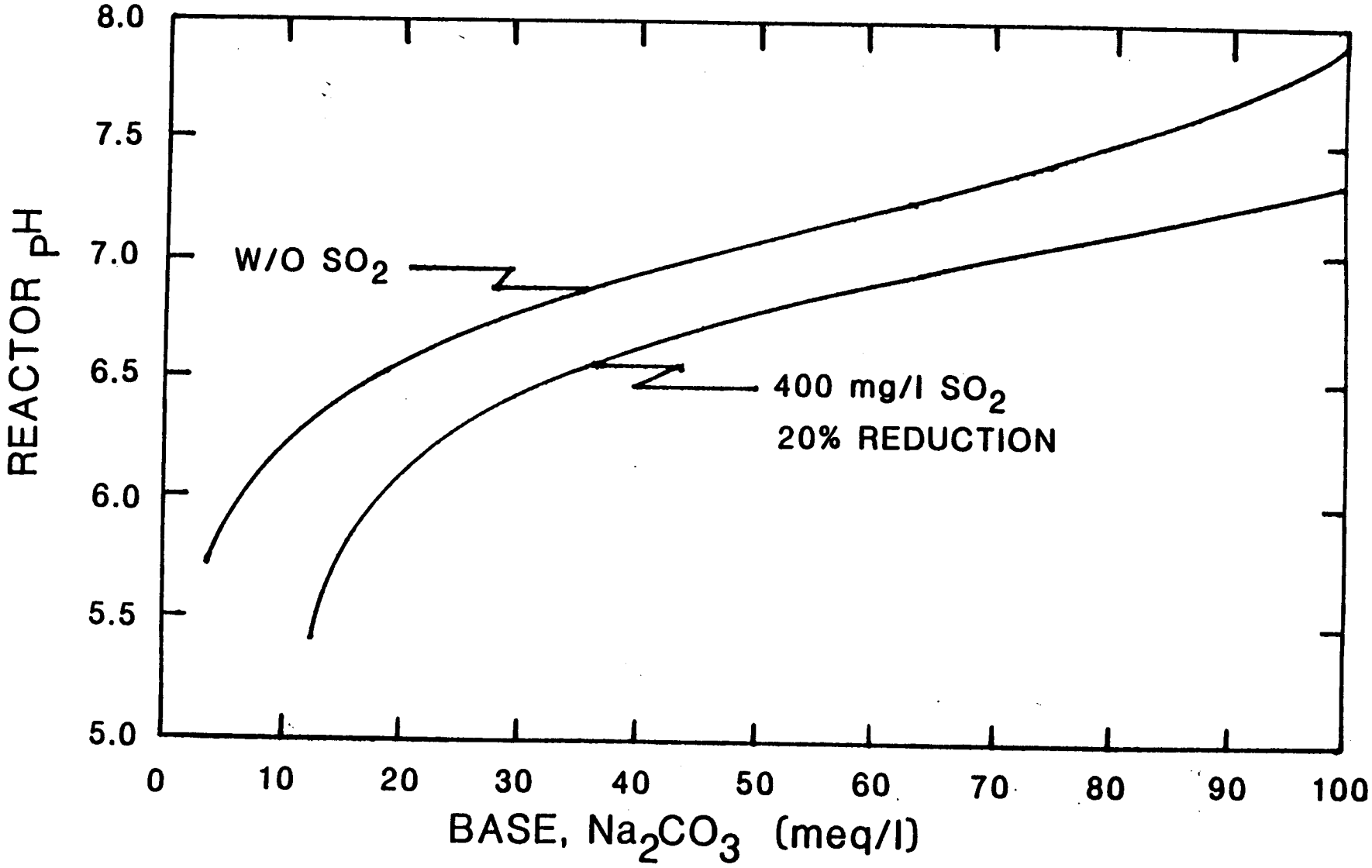
Effluent pH, gas production, and composition of gas and solution computed for the various bases are in good agreement with experimental values for anaerobic submerged media reactors, which operated at loadings of 5 to 10 g COD/L/d with high recycle rates. The tests were carried out with the same acetate and methanol concentrations used in the calculations; however, neutralization was often with a mix of 50% NaOH and 50% Na_2CO_3 which yielded results intermediate between calculated results for the pure bases. COD removal efficiency exceeded 90%. The results justify extending the calculations to consider the effects of sulfite and of recycle on the process.

Effects of SO_2

Sulfur dioxide has only adverse effects on anaerobic treatment. Our studies[3] and others[7] have found that methane-formers can acclimate to high influent SO_2 concentrations so long-term toxicity at steady-state is not likely to be a problem. However, increased neutralization requirements, H_2S production, decreased methane production, and decreased COD removal are disadvantages due to sulfur in anaerobic treatment.

In the absence of sulfide production, sulfur dioxide requires neutralization with between 1 and 1.6 moles of base to reach pH values from 6 to 7.2. With sulfide production, the neutralization requirement changes in a complex way, since sulfide production is accompanied by increased carbon dioxide production, decreased methane production and production of bisulfide alkalinity. The net effects of these changes are shown in Fig. 34 for a typical influent SO_2 concentration (400 mg/L as S, 12.5 mM/L) assuming 20% reduction to sulfide. Concentrations of other constituents are the same as considered

Figure 34. Relation between sodium carbonate neutralization and reactor pH for 50 mM/L acetic acid and 30 mM/L methanol (100% conversion) with and without 12.5 mM/L SO_2 (20% conversion).



earlier. The extra base required to neutralize the acidity produced by sulfite reduction ranges from 12 meq/L to reach pH 6 to 23 meq/L to reach pH 7. For the case calculated, at pH = 7 CH_4 production is reduced about 2 mM/L or about 2% compared to the sulfur-free system. The sulfide is partitioned about one-half to the solution and one-half to the gas phase. The dissolved sulfite and sulfide also contribute significantly to the effluent COD.

For SEC wastes, the adverse effects of SO_2 and H_2S production may be managed by operation of the evaporation process to keep levels below those assumed in the calculations. In other wastes, oxidized sulfur acids may have impacts severe enough to rule out anaerobic treatment.

Effluent recycle

The preceding results are for a well-mixed reactor. However, many anaerobic reactors may have a plug-flow component to their flow regime. Since the biological transformations in the reactor destroy acidity, the downstream fluid in the reactor will have pH values significantly higher than the influent. If minimal neutralization is used and reliance is placed on biological destruction of acetic acid, and/or loss of sulfide and CO_2 to reduce chemical use, then low pH values in the influent zone, where the biological reactions are incomplete, may inhibit methane bacteria. If this happens, gas production will stop, mixing will be drastically reduced, and the low pH zone will propagate through the entire reactor, causing failure.

A suitable pH in the influent zone can be obtained by recycling part of the effluent. This dilutes the raw waste and adds the biologically produced alkalinity to the influent. Most of our experimental studies, including the tests represented in Fig. 33, incorporated recycle ratios (recycle flow:influent flow) between 5 and 20. The recycle flow resulted in a nominal

detention time $V/(Q + Q_r)$ of about 1.5 hours and a face velocity of about 0.6 m/hr.

The role of recyle flow at minimal neutralization was modeled in order to understand how recycle can be used to provide the maximum advantages to the process. The model involved first computing the pH of a mixture of raw waste plus neutralizing chemicals and recycled reactor effluent (Fig. 35). The computations involved mass balances on the weak acid components based on the recycle ratio, an alkalinity balance, and calculation of acid/base equilibria for the solution phase.

For sodium carbonate neutralization of the acetate plus methanol waste without SO_2, the effect of varying recycle ratios is represented in Fig. 36 by a family of curves, indicating that the influent zone pH is severely depressed at low base additions and low recycle. As the recycle ratio reaches 10 or more, the sodium carbonate required to attain a given pH is within a few meq/L of the value computed for a well-mixed reactor. Thus high recycle ratios can be used to keep the influent zone pH high enough so that the chemical dosage is reduced to nearly the values for the bioconverted waste. It is also seen that even modest recycle greatly reduces the base addition from the values computed for neutralization of the raw waste.

The effects of SO_2 on chemical dosage are only slightly reduced by recycle. SO_2 requires 1 to 2 meq alkalinity per mole for neutralization. A fraction of the SO_2'' is converted to sulfide with net production of alkalinity and extra CO_2. The recycle of wastes with SO_2 has the same benefits as noted without SO_2, but no additional ones.

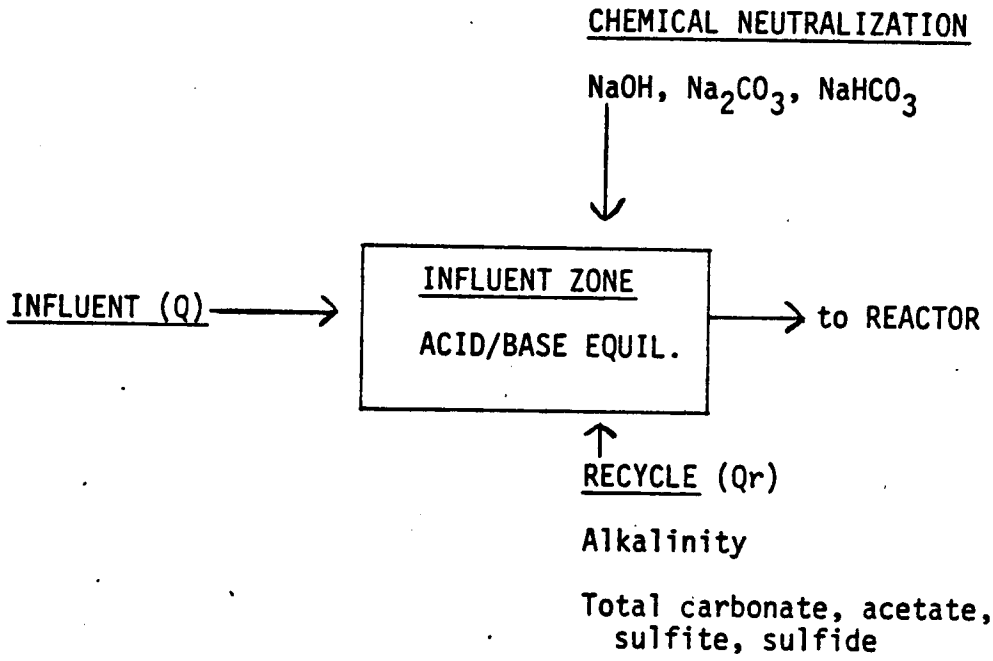


Figure 35. Schematic of the elements of calculation of influent or missing zone pH.

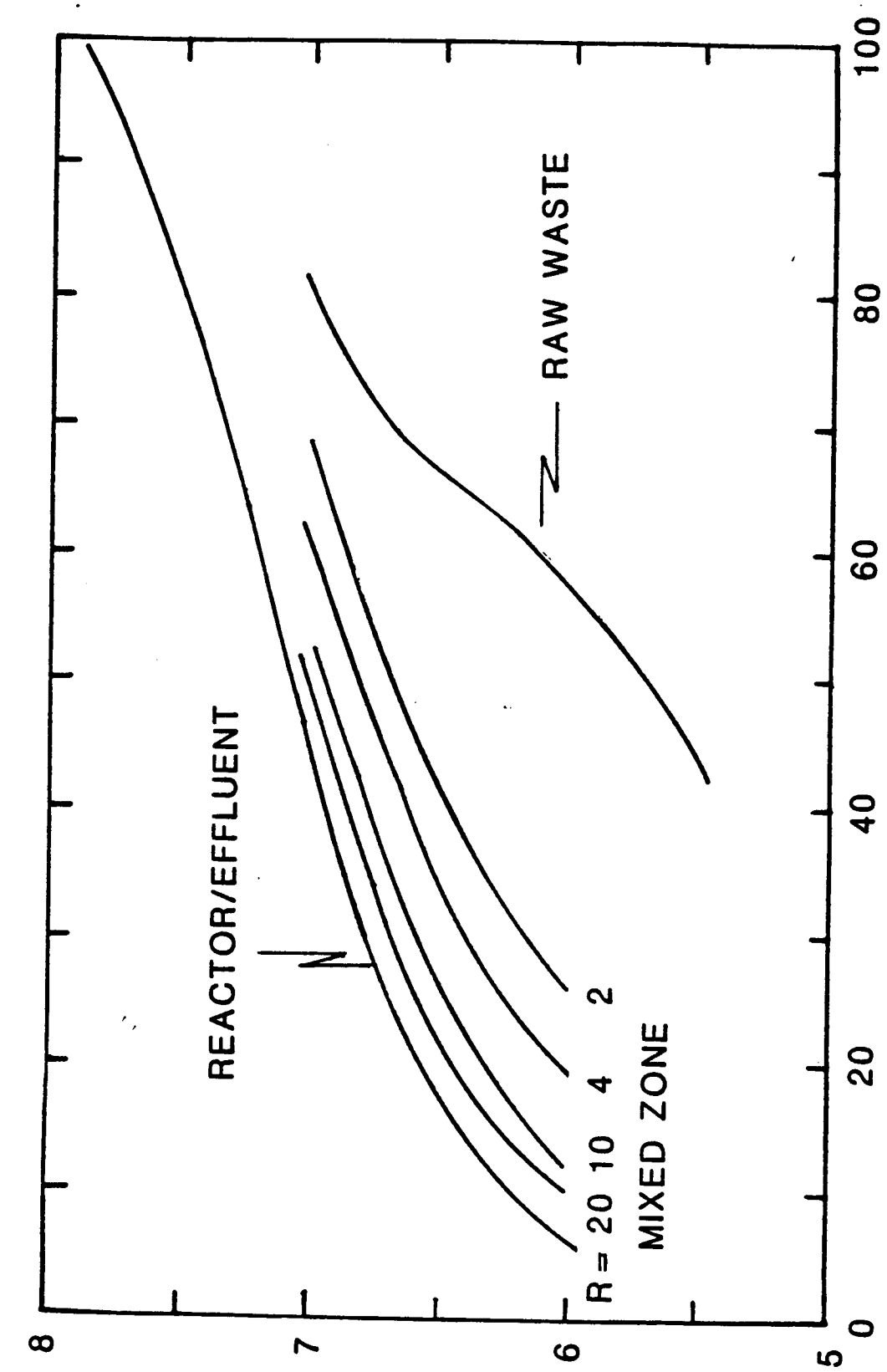


Figure 36. pH values computed for sodium carbonate addition to 50 mM/L acetic acid, 30 mM/L methanol waste, showing neutralization of waste, pH in reactor after bioconversion and gas equilibration, and pH in influent zone with varying recycle ratios.

Recycle with CO_2 Stripping

Since a major source of acidity in the recycle is carbon dioxide, its removal by stripping has been considered as another alternative for reducing chemical neutralization requirements. The flow diagram for the process is indicated in Fig. 37 and includes stripping of CO_2 from the recycle flow prior to mixing with the influent and adding neutralization chemicals. If air stripping is used, both CO_2 and methane are lost in the stripper gas and O_2 will be added to the recycle stream. High recycle flow rates coupled with stripping of the recycle stream cause more dissolved CO_2 and CH_4 to leave in the stripper gas and less to be captured in the reactor gas. In principle, total carbonate in the recycled fluid could be reduced to very low levels by exhaustive stripping with a low CO_2 gas phase or by absorption into a non-aqueous base. Reduction to 0.01 atm P_{CO2} was considered as a practical limit due to high pH values resulting in the stripped effluent.

Carbon dioxide removal was modeled by calculating the composition of reactor effluent after equilibration with a specified low P_{CO2} value. The equilibrium pH of a mixture of the stripped effluent at flow rate Q_r with the influent at flow rate Q was calculated as before. To calculate the amount of CO_2 and CH_4 in the reactor gas, the bioconversion reactions, acid/base and gas/liquid equilibria were computed for the mixed influent ($Q + Q_r$). The composition and volume of the stripped gas phase was determined by mass balances on methane and carbonate carbon.

The results indicate that CO_2 stripping is a feasible way of increasing the mixed influent pH. However at higher recycle ratios, the amount of CO_2 to be stripped becomes excessive, and if CH_4 is concurrently removed, the energy loss is significant. These effects are illustrated by calculations for the acetate plus methanol waste partially neutralized by 30 meq/L Na_2CO_3. The pH

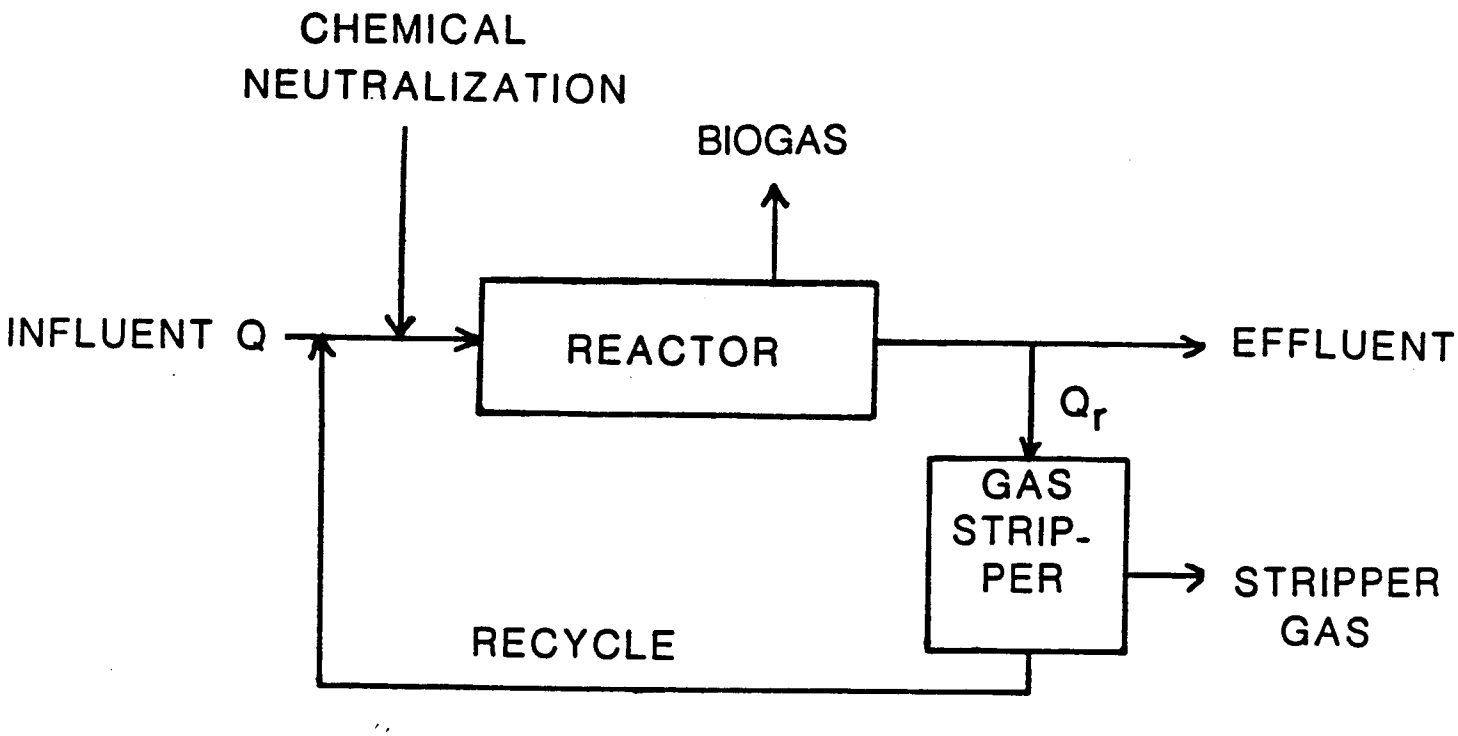


Figure 37. Flow chart for anaerobic treatment incorporating recycle with CO_2 stripping.

of the influent and effluent without recycle would be about 5.5 and 6.75, respectively. Changes in these values when recycle (without CO_2 stripping) is considered have been presented previously in Fig. 36. The effects of stripping the recycle flow are shown for varying P_{CO2} values in Fig. 38. A combination of efficient stripping (low P_{CO2}) and high recycle ratio can increase the pH in the mixing zone to values above 6.5, which is a considerable improvement over the recycle-without-stripping system.

However, the disadvantages of such a process appear to be considerable. Continuing with the same basic case at 0.1 atm CO_2, the partitioning of carbonate and methane has been calculated along with the relative volumes of the gas phases produced (Fig. 39). As recycle increases (recycle ratios greater than 3 are needed to reach pH above 6.5 in the mixing zone), the ratio of stripper gas volume to inflow volume increases to greater than 40. As the stripper gas volume increases, the reactor gas produced decreases from 2.7 to 1.5 l/L of waste treated, reflecting loss of both CO_2 and CH_4. Without recycle, carbonate carbon is split nearly equally between the reactor gas (CO_2) and the effluent (HCO_3^- and $H_2CO_3^*$) (Fig. 39b). At high recycle ratios, 30% or more of carbonate-carbon is removed in the stripper. Methane, similarly, is lost in the stripper (Fig. 39c). As recycle increases more than 10% will be lost to the stripper gas.

Combinations of high recycle ratios and low P_{CO2} values are also not feasible because of O_2 addition, which would create partially aerobic metabolism and further reduce CH_4 production.

The costs and benefits of CO_2 stripping have not been completely defined. However, for air stripping to moderately low P_{CO2} values, there are disadvantages that probably outweigh the benefits of installing the unit process. The implications of sorption processes for CO_2 removal apparently are similar.

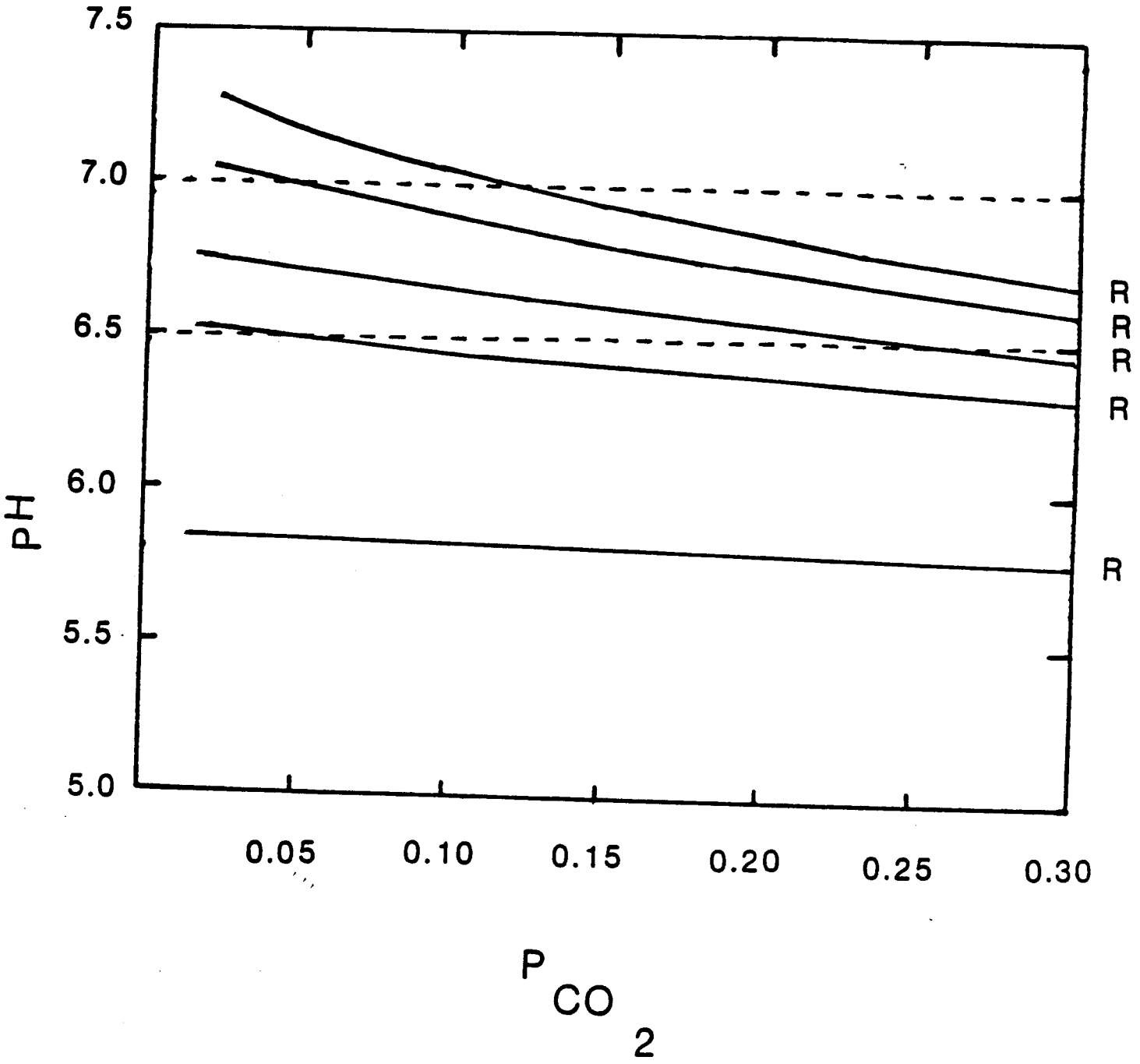


Figure 38. Effects of CO_2 stripping to varying P_{CO2} values on mixing zone pH for varying recycle ratios. 50 mM/L acetate, 30 mM/L methanol. 100% conversion, neutralization with 30 meq/L Na_2CO_3.

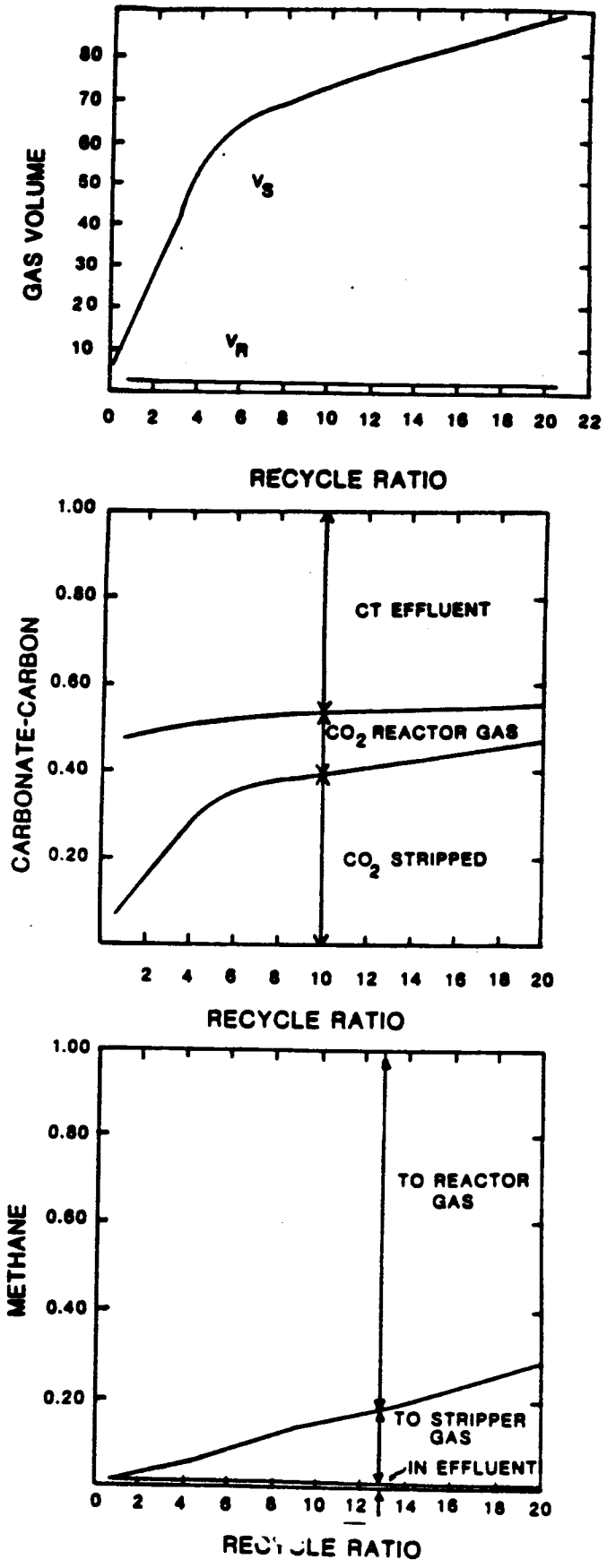


Figure 39. Effects of CO_2 stripping to 0.1 atm for varying recycle ratios. a. Gas volume to liquid volume ratios (l/L) for stripper and reactor. b. Fraction of carbonate-carbon in effluent, striper gas and reactor gas. c. Fraction of methane in effluent, stripper gas and reactor gas.

CONCLUSIONS

Modeling neutralization of anaerobic treatment of an acetic acid, methanol, SO_2 waste has led to several conclusions about effects of sulfur on the process, the role of different bases, and the utility of including recycle and recycle with gas stripping in the system. These observations could not feasibly have been experimentally tested in reactors because of the time and cost of anaerobic treatment studies and because of the sensitivity and slow recovery of anaerobic systems to excursions in pH, the parameter that was being tested. Hence the calculations were necessary for understanding a system of this degree of complexity, and the results are useful in understanding how to minimize the large cost of neutralization, while maintaining an environment suited to anaerobic metabolism.

The upper limit on neutralization requirements, namely neutralization of the untreated, acidic waste, can be computed by a titration curve analysis. Determination of the lower limit, namely the base required to maintain a minimum pH value in all parts of the reactor, is approached in several ways. Calculation of a titration curve from estimated concentrations after biological conversion provides a reference point, but is not sufficient because of indeterminate partitioning of CO_2 and H_2S to a gas phase and because of incomplete mixing in the reactor influent zone. The net effect of losses of these acidic gases is a reduction in the amount of base required.

A model incorporating biological conversion to CH_4, CO_2 and H_2S, additions of bases, and gas/liquid and acid/base equilibria, modified to simulate the effects of effluent recycle and gas stripping of the recycle flow, has allowed the following specific conclusions for treatment of the SEC waste.

1) The required amounts of various sodium bases depend strongly on the pH needed for biological treatment, with hydroxide considerably more effective than carbonate or bicarbonate as the pH increases above 6 to 6.5. However, when the chemical cost is considered, sodium carbonate is the preferred neutralization chemical.

2) Dissolved SO_2 strongly affects the amount of base required to attain neutral pH values. Biological sulfite reduction reduces the neutralization requirement by more than 1 meq/mM sulfide produced because H_2S is a much weaker acid and because it is also less soluble than SO_2. However, the beneficial effects on neutralization costs are outweighed by reduced CH_4 production and problems of handling effluents containing dissolved or gaseous sulfide.

3) High recycle ratios can reduce requirements for neutralization chemicals to an economical level. Recycle ratios above 10 bring the sodium carbonate requirement with in 10 meq/L of the value computed for the completely mixed reactor. These values are 20 to 40 meq/L less than those needed to neutralize the raw wastes. Recycle allows 2/3 to 4/5 of the theoretical possible reduction towards a completely mixed reactor with bioconversion and gas production.

4) The base required decreases very rapidly as the pH decreases below 7. The calculations point to the need to determine experimentally the stability of the process at pH values near the lower bound for methane-formers. Fifty % savings in neutralization costs are possible, for instance, if a process can be operated with an influent zone pH of 6.3 and a reactor/effluent pH of 6.6, compared to values 6.8 and 7.0, respectively.

5) Gas stripping to reduce CO_2 in the recycle stream appears to have merit for reducing base addition and recycle ratios. However, the reductions in base requirements are rather small, while the volumes of gas required for air stripping are large and cause loss of CH_4 to the stripper exhaust gas.

These conclusions have influenced the experimental studies that have been carried out and that are planned. Neutralization is an important consideration in anaerobic treatment. The procedures used for calculation of neutralization requirements for the waste in this study are readily applicable to other chemically characterized wastes. The results of mathematical modeling can be an important guide to feasibility of anaerobic processing.

REFERENCES

1. Clark and Speece

2. Eis, B.J. (1982) "Investigation of Factors Controlling the Operation of an Anaerobic Submerged Media Reactor, Master's Thesis, Univ. of Washington, Seattle, WA.

3. Eis, B.J., Ferguson, J.F. and Benjamin, M.M. (1983) "The Fate and Effects of Bisulfite on Anaerobic Treatment," Journal Water Pollution Control Federation, in press.

4. Martens, C.S. and Berner, R.A. (1977) "Interstitial Water Chemistry of Anoxic Long Island Sound Sediments. 1. Dissolved Gases," Limnology and Oceanography 22, 10-25.

5. McCarty, P.L. (1964) "Anaerobic Waste Treatment Fundamentals, Environmental Requirements and Control," Public Works, October, 1964, 123-126.

6. McCarty, P.L. (1972) "Energetics and Bacterial Growth," Organic Compounds in Aquatic Environments, Marcel Dekker, Inc., pp. 445-528.

7. Yang, J., Parkin, G.F. and Speece, R.E. (1979) "Recovery of Anaerobic Digestion After Exposure to Toxicants.' Final Report, U.S.D.O.E. Contract No. EC-77-S-02-4391, Drexel University, Philadelphia, PA.

CHAPTER 5

EVAPORATOR CONDENSATES: PRELIMINARY ESTIMATES OF CAPITAL AND ANNUAL COSTS FOR ANAEROBIC FERMENTATION TO METHANE[1]

Peter D. Haggerty
Brian Wines
Joseph L. McCarthy

ABSTRACT

Although sulfite and kraft pulp mill evaporator condensates (SEC and KEC) account for only 10 to 15% of the total effluent volume from a pulp mill, they can represent 30 to 50% of the total biochemical oxygen demand because of their relatively high content of volatile organic substances. The processing of both condensates to produce methane by anaerobic fermentation is being studied at our University and some results with SEC have recently been published by Benjamin, Ferguson and Buggins. Based on these and other findings, preliminary estimates of the capital and annual costs associated with the processing of 3790 m^3 (one million gallons) per day have now been developed and are similar for both condensates, i.e., $1,500,000 and $490,000/yr, respectively. The annual cost includes credit for by-product methane production.

1. Published in TAPPI.

INTRODUCTION

Evaporation of the spent liquors from sulfite and kraft pulp mills produces sulfite evaporator condensates (SEC) and kraft evaporator condensates (KEC) in large volumes. These condensates contain volatile organic compounds at concentrations too low to permit economic recovery, and yet the overall oxygen demand of these streams is very substantial. Russ[1] and Blosser[2] have shown illustrative compositions of SEC and KEC from various sources.

Several processes for treating the condensates have been studied: recycling and process reuse,[3] neutralization to make acidic solutes nonvolatile,[6] steam and air-steam stripping to remove volatile components but not acetic acid,[5] and the production of single cell proteins.[3] In our laboratories, the anaerobic fermentation of SEC and KEC to yield methane is under continuing study, and some findings have recently been reported in a paper by Benjamin, Ferguson and Buggins,[1] and in theses by Fors[7], Haggerty[8] and Buggins.[4]

This type of processing promises at least 3 economic advantages relative to aerobic treatments. No air is used, and thus a significant reduction in compression capital and operating costs is achieved. Sludge disposal costs are minimized since the yield of anaerobic sludge amounts to about one-fifth that of aerobic sludge. Thirdly, a gaseous fuel (about 80% CH_4 and 20% CO_2) is produced in significant quantities. Two main disadvantages are associated with anaerobic processing: the operating conditions (temperature, pH, feed composition consistency, etc.) must be closely controlled; a long period of time (perhaps 1 to 2 months) appears to be required for startup compared with a few hours or days with aerobic processing.

Since our results suggested that the process may be useful on an industrial scale for treating both SEC and KEC, it is worthwhile to make the prelminary estimates given below of the full scale capital and annual operating costs associated with each condensate type in order to identify the major costs involved.

Capital and Annual Costs for an Anaerobic Fermentation Plant Processing Sulfite Evaporator Condensates

Costs were estimated mainly by following the procedures recommended by, and using the data provided by Peters and Timmerhaus,[11] Perry and Chilton,[12] and Pikulik and Diaz.[11] Cost estimates are set forth in July 1981 United States dollars, and equipment costs have been scaled up using the indices of Marshall and Swift.[5]

Base Case Assumptions and Process Flow Sheet

For our base case calculations we have assumed: that SEC is available at 35°C, 2 atm. pressure, containing 5000 mg L^{-1} of chemical oxygen demand (COD); that it is to be processed at a rate of 3790 m^3/day (one million gallons per day); that the processing is conducted at about pH 7.0 in three submerged media anaerobic reactors (SMAR's) operating in parallel with a hydraulic retention time of 12.0 hours; that the recycle rate is 8/1; that equipment is constructed of carbon steel with rubber coatings and stainless steel fittings or, Fiber Reinforced Plastic, as needed; and that 80% of the COD in the influent stream is removed by the processing. Laboratory experiments[1] have shown that these conditions are workable, although not necessarily optimum.

The proposed flow scheme is shown in Figure 1. Process streams are identified by the letter S followed by a number, and each major piece of

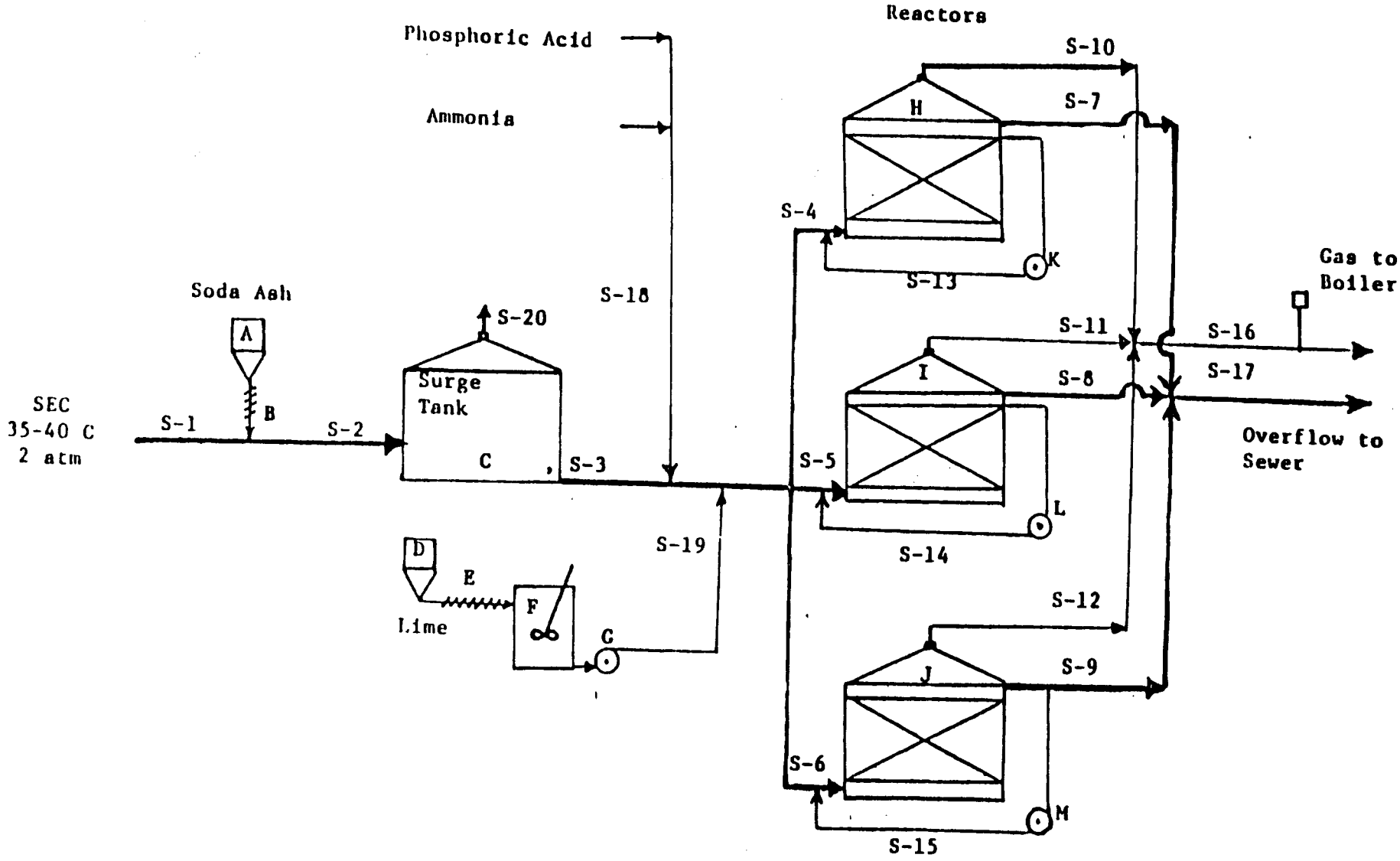


Figure 40. Process Flow Sheet.

equipment by a letter. A very brief description of the processing will now be given.

SEC (S-1) is mixed with soda ash from a 133 m^3 (4300 ft^3) carbon steel silo (A) with a 2.1 m long x 0.23 m dia. screw feeder (B). The SEC-soda ash mixture (S-2) enters a 632 m^3 (167,000 gal). cone roof surge tank (C)[10] where carbon dioxide is vented at a rate of 55 m^3/hr. Nitrogen and phosphoric nutrients as ammonia and phosphoric acid are metered (S-19) into the SEC stream (S-3) from existing mill storage facilities.

In addition to soda ash, a lime solution (S-19) is pumped (G) into the SEC stream (S-3) to help maintain the needed pH 7. Lime is fed by a 6.1 m (20 ft) x 23 cm (9 in) dia. screw conveyor (E) from a 56.6 m^3 (2000 ft^3) carbon steel silo (D) into a 19 m^3 (5000 gal) carbon steel mixing tank (F). Each silo has a holding capacity to provide for a 1 month operation.

Once sufficient soda ash, lime, and nutrients have been added, the SEC stream (S-3) is split and fed (S-4, S-5, S-6) to three reactors H, I, J) operating in parallel. The reactor shells are 632 m^3 (167,000 gal) carbon steel tanks, 8.6 m in diameter, which are rubber coated to resist corrosion, and have cone roofs.[10] The reactor solutions are recycled (S-13, S-14, S-15) using an 8:1 recycle feed ratio by use of three stainless steel recycle pumps (K, L, M), each capable of pumping 7.2 m^3/min (1900 GPM). A fourth recycle pump is kept in reserve. Reactor overflow is drawn off (S-7, S-8, S-9), collected and sewered (S-17). Product biogas is also vented from the reactors (S-10, S-11, S-12), collected and flared, or else piped (S-16) to a boiler plant where it is burned and energy is recovered.

Stream characteristics in terms of a COD balance are shown in Table 11. The COD balance was calculated assuming that 80% of the influent COD was

Table 11. Characteristics of SEC Process Streams

COMPONENT	STREAM NUMBERS AND COMPONENT FLOW RATES[a]						
	1	4,5,6[a]	7,8,9	10,11,12[b]	13,14,15	16	17
Liquid Flow Rate, L day^{-1}	$3.79(10)^6$	$1.26(10)^6$	$1.26(10)^6$	$2.3(10)^6$	$10.1(10)^7$	$6.9(10)^6$	$3.79(10)^6$
COD Flow Rate, kg day^{-1}	18900	6308	1260	4682	10100	14050	3780
Sodium Flow Rate, kg day^{-1}	0	872	872	0	15400	0	5760
Phosphorus Flow Rate, kg day^{-1}	0	3.03	3.03	0	24.2	0	9.09
Nitrogen Flow Rate, kg day^{-1}	0	24.9	24.9	0	199	0	74.7
Methane Flow Rate, m^3 day^{-1} @ STP	0	0	0	1760	0	5270	0

(a) Bacterial accumulation in each reactor = 260 kg day^{-1} (570 lbs day^{-1}), or, for all three reactors, a total of 780 kg day^{-1} (170 lbs day^{-1}).

removed in the reactors, and that 0.08 g of bacteria were retained per g COD removed, as has been reported by Benjamin, Ferguson, and Buggins.[1]

Purchased Equipment Costs

The required pieces of equipment and their 1979 purchase costs[10] are listed in Table 12 along with information concerning capacities and construction materials. The 1979 cost of the needed equipment totals $235,000. By multiplying this 1979 cost by the Marshall and Swift equipment cost index (717/569), and adding 3% for delivery charges, the 1981 purchased and delivered equipment cost is estimated to be $305,000.

Reactor Core Design and Cost

It is proposed that the SMAR's would be constructed as indicated in Fig. 41. Most reactor volume is occupied by a high void-volume packing used to help retain bacteria in the reactor, and supported by a corrosion resistant grill. SEC is distributed below the grill by a sparge system. Product biogas is channeled by use of gas baffles. During operation, bacterial solids are brought upwards from the packed bed either by attachment to gas or entrainment in the bulk flow, and the baffles provide a low-turbulence, nearly gas-free region which allows solids to settle back into the packed bed and not be lost from the reactor.

Many types of packing are available and costs vary widely. For the present illustrative calculations, we have assumed use of 3-1/2 inch polypropylene "Biorings", available from the Glitsch Corporation of Dallas, Texas. The reactors are to be randomly packed and the total volume occupied in all 3 SMAR's would be about 1900 m^3 (47,000 ft^3). "Biorings" are available for

Table 12. Purchased Equipment Costs for SEC Processing

Materials Handling Equipment

Item	Flow Rate	Cost - Jan. 1979 $
#1 Recycle pump	1900 GPM (7.2 m^3/min)	$ 5,000
#1 Recycle Motor	10 hp	700
#2 Recycle Pump	1900 GPA (7.2 m^3/min)	5,000
#2 Recycle Motor	10 hp	700
#3 Recycle Pump	1900 GPM (7.2 M^3/min)	5,000
#3 Recycle Motor	10 hp	700
Extra Recycle Pump	1900 GPM (7.2 M^3/min)	5,000
Extra Recycle Motor	10 hp	700
Lime Solution Pump	3.5 GPM (13 L/min)	1,000
Lime Solution Motor	2 hp	200
Lime Screw Conveyor	3 ton/hr - 10 hp (max.)	3,100
Soda Ash Feeder	1 ton/hr (max.)	2,000
Total Materials Handling Costs		$29,100

Vessels

Vessel	Material	Capacity	Cost Jan 1979 $
Soda Ash Silo	Carbon Steel	4300 ft^3 (133m^3)	$ 3,400*
Lime Silo	Carbon Steel	2000 ft^3 (56.6m^3)	2,000*
Lime Mixing tank	Carbon Steel	5000 gal_5 (18.9m^3)	9,000
Surge tank	Carbon Steel	1.67(10)^{5}gal (632m^3)	35,000
#1 Reactor shell	Rubber lined C-steel	1.67(10)^{5}gal (632m^3)	52,000
#2 Reactor shell	Rubber lined steel	1.67(10)^{5}gal (632m^3)	52,000
#3 Reactor shell	Rubber lined steel	1.67(10)^{5}gal (632m^3)	52,000
	Total Vessel Costs		$205,400
	Total purchased equipment costs		$234,500
	In 1981 $ (M&S Index = 717/569)		$295,500
	Delivered Equipment Cost		$305,000

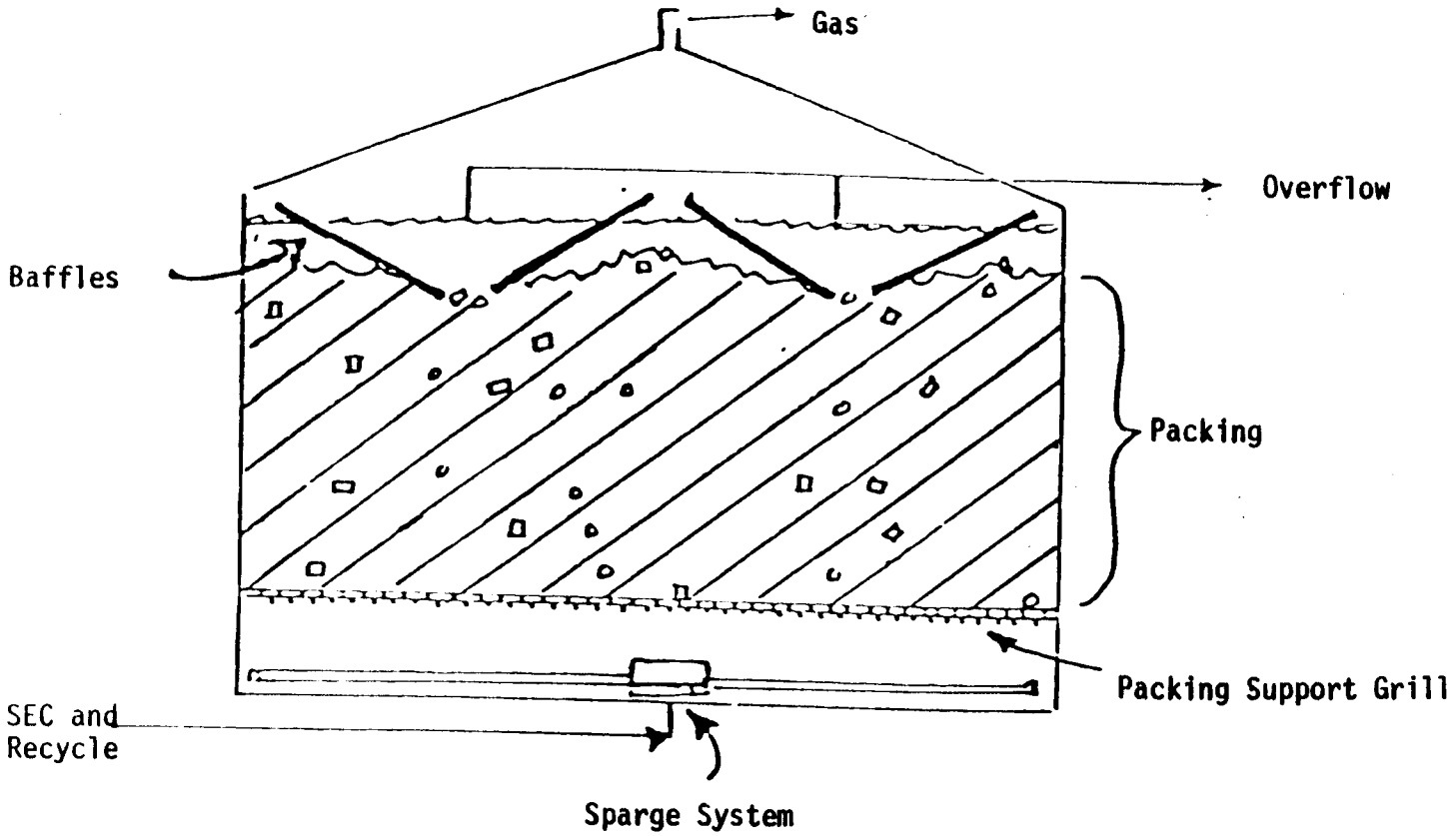


Figure 41. Reactor Cross Section.

about $\$88.30/m^3$. Thus, the purchased cost for the packing would be about $167,000 and the installed cost is estimated to be about $171,000.

The gas baffles, which function to enhance solid, liquid and gas separation, preferably are corrugated fiberglass and cost $18,000 in all, assuming material and labor cost for each reactor at $5,000 and $900, respectively,

For the packing support grills, the 1979 installed cost for stainless steel floor type grating has been estimated[10] to be about $\$86/m^2$ ($\$8,000/ft^2$). Since each reactor is 8.6 m in diameter, or 57 m^2 (616 ft^2) in cross sectional area, the installed grill cost in 1979 dollars is $4,900, and after adjusting for inflation, the total 1981 installed cost is $18,600.

A sparge system is used to distribute the feed and recycle stream uniformly below the reactor bed. By operating the system in reverse periodically, and for short periods of time, excess bacterial solids may be removed if necessary. If sludge is removed semi-annually, about 80 dry tons (73 tons metric) of sludge is wasted from each reactor during each purge. It is proposed that 16 sparge arms of PVC pipe (4" dia., Schedule 80) or about 700 feet in all, be used with material costs of $24/ft., and installation cost of 0.2 hr/ft at $28/hr. On this basis the material and installation costs amount to $16,800 and $3,900, or $20,700 in all.

The direct core construction cost for packing, gas baffles, support grills and sparge system totals $228,000. If a contractor's fee of 5%, and engineering and supervision costs at 7%, are included, the total capital investment for reactor core construction is $255,000.

Direct Plant Costs and Total Capital Investment

Estimates of capital investment entities have been made, following Peters and Timmerhause,[10] by use of ratio factors operating upon the delivered equipment cost. Table 13 shows the application of these factors to the present case. Here the purchased equipment cost of $305,000 is taken as 100%, and percentages of this number are used to obtain estimates of other direct costs, e.g., 47% or $153,000 for installation costs, etc. The items listed in Table 13 are: the purchased and delivered equipment itself; equipment installation which would include construction of foundations, the blasting and painting of tanks and silos, and the mounting of pumps, motors, and feeders; instrumentation and controls for pH and temperature monitoring and recording, controls for alkalinity addition, and liquid and gas flow rates; piping costs which include the cost for the pipeline from the mill, the recycle lines, gas lines, effluent pipelines to the broiler and sewer, the solids purge lines, and auxiliary piping; electrical systems to supply power to pumps, feeders, instruments, lighting and various outlets; buildings needed to house pumps, motors, instruments, controls and sampling equipment; yard improvements to include plant site grading, foundation excavation and roadway extensions; and reactor core construction as described above.

The addition of these eight cost elements gives a total direct cost of $1,079,000. The indirect costs of engineering and supervision, and construction expenses plus the contractor's fee, and contingencies bring the estimated fixed capital investment to $1,497,000. Costs not included are service facilities and purchased land. These are assumed to be already available at a developed mill site. Also, startup expenses are not included although they will be significant and could amount to as much as 20% to 30% c

Table 13. Ratio Factors for Estimating Capital Investment for SEC Processing

Item	% of delivered Equipment Cost	Cost 1981, $	Ratioed % of Total
1. Purchased equipment del.	100	$ 305,000	20.7
2. Installation	47	143,000	9.7
3. Instrumentation & controls	18	55,000	3.7
4. Piping	66	201,000	13.7
5. Electrical	11	34,000	2.3
6. Buildings	18	55,000	3.7
7. Yard improvements	10	31,000	2.1
8. Reactor Core Capital Investment	---	255,000	15.5
TOTAL DIRECT	270	$1,079,000	71.4
Plant Cost			
Indirect Cost			
9. Engineering & supervision	33	101,000	6.9
10. Construction expenses	41	125,000	8.5
TOTAL DIRECT & INDIRECT COST	344	$1,305,000	86.8
11. Contractors fee	21	64,000	4.4
12. Contingency	42	128,000	8.7
FIXED CAPITAL INVESTMENT (not including start-up costs)	407	$1,497,000	100

one year's operating cost: further laboratory and pilot plant investigations must be completed to permit estimation of these costs.

Using the calculation procedures described above, repetitive calculations were done to estimate fixed capital investments required for processing at various hydraulic retention times, and the results are presented in Fig.42. For the base case, a three parallel reactor configuration was chosen because it provides more processing safety and construction effectiveness although at higher cost than a single reactor. Thus costs increase both with the number of reactors and the hydraulic retention time.

Annual Operating Cost

The annual costs of operating the plant are made up of manufacturing costs and general expenses. Manufacturing costs are direct operating costs plus fixed charges, (e.g., depreciation) while general expenses consist of administration, financing, interest, and research and development costs (see Table 14).

The single largest manufacturing cost is incurred for raw materials, i.e. chemicals, and amounts to about 50% of the final annual cost. The chemical costs are incurred mainly to provide the lime and soda ash needed for neutralization. The use rate of lime and soda ash shown in Fig. 43 is the amount needed to provide for 50 milliequivalents of alkalinity per liter of reactor solution, which was the concentration used by Benjamin, Ferguson and Buggins[1] in their bench scale experiments.

However, more recent experiments have suggested that efficient anaerobic fermentation of SEC might be conducted at considerably lower levels of alkalinity, e.g., 20 to 30 milliequivalents per liter. Concentrations in this range may possibly be achieved mainly by the addition of lime. If this proves

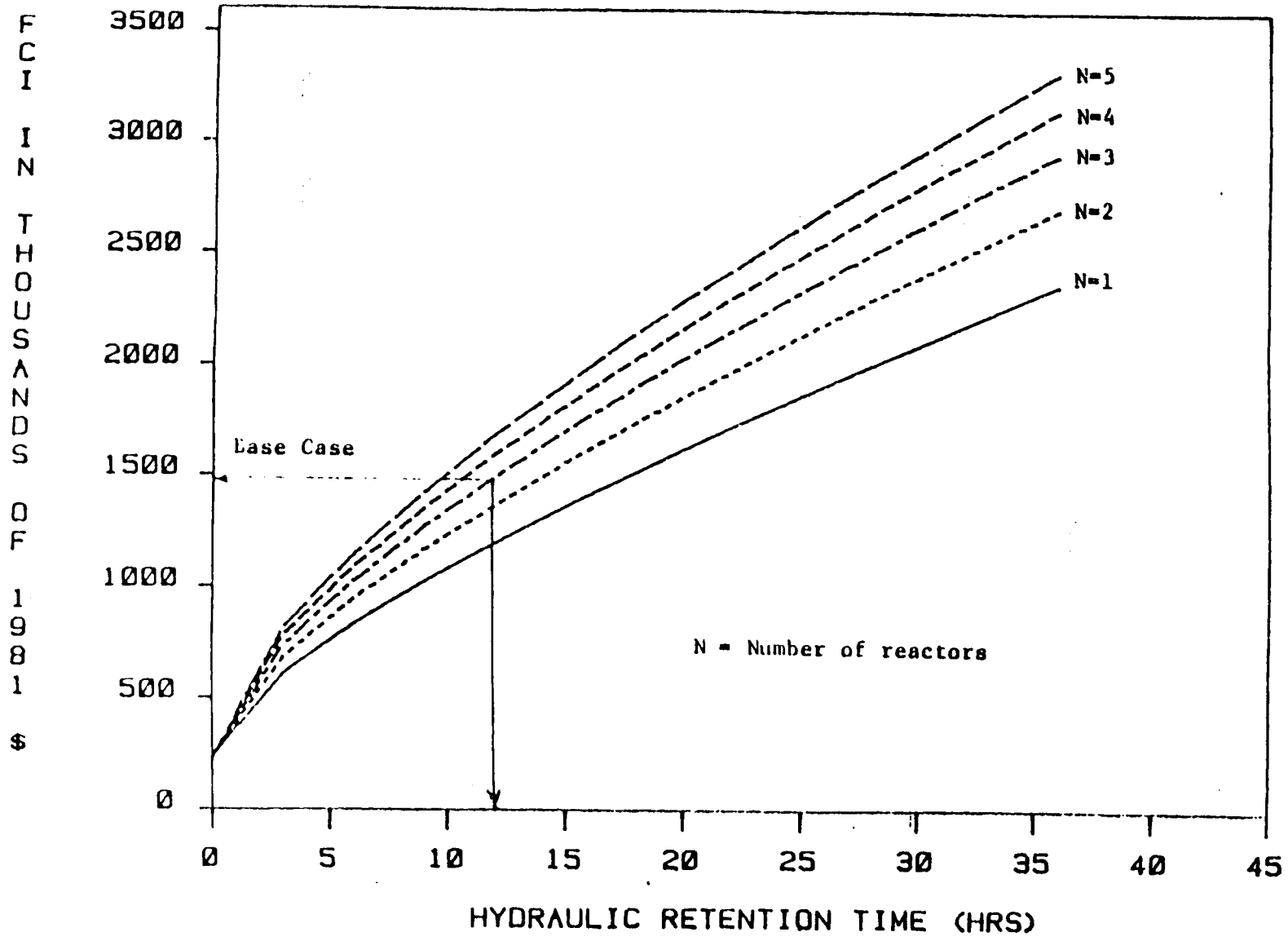


Figure 42. Sensitivity of Fixed Capital Investment for SEC Processing

Table 14 Estimation of Operating Costs

1. Manufacturing Costs = Direct Treatment Costs & Fixed Charges

2. Operating Costs (360 operating days/year):

1. Raw Materials

Raw Materials	Rate of Use	Cost/Ton	Approximate Annual Cost
Lime	1110 ton/year	31	$ 34,000
Soda Ash	2390 ton/year	86	$206,000
Aqueous Ammonia	36 ton/year	175	$ 6,300
Phosphoric Effluent	11.4 ton/year	242	$ 2,800
Lagoon Effluent	----	~0	~ 0
		Total Raw Material Costs =	$249,000

2.	Operating Labor	$ 81,000
3.	Direct Supervisory and Clerical Labor	$ 16,000
4.	Utilities	$ 11,000
5.	Maintenance and Repairs	$ 29,000
6.	Operating Supplies	$ 6,000
7.	Laboratory Charges	$ 40,000
	Total Direct Treatment Costs ~	$432,000

B. Fixed Charges:

1.	Depreciation	$105,000
2.	Insurance	$ 6,000
	Total Fixed Carages =	$111,000
	Total Manufacturing Costs =	$543,000

II. General Expenses

A.	Adminstrative	$ 19,000
B.	R & D	$ 15,000
C.	Financing Interest (at 15%)	$225,000
	Total General Expenses =	$259,000

III. Treatment Cost Before Income = Manufacturing & General Expenses $802,000

IV. Income Product Biogas $309,000

V. Final Operating Cost $493,000

feasible and is found to be workable, depending on the particular level of alkalinity needed, the annual costs for neutralization might prove to be much less than indicated for the base case as shown in Fig. 43. Since the annual neutralization costs might vary from the base case estimate of $240,000 down to as low as $50,000, further investigations of the neutralization steps are being conducted.

Operating labor is another major direct operating cost. It is assumed that one operator working one 8 hour shift daily can easily handle all sampling and monitoring duties, and that the operator is needed 360 days/yr at an effective cost of $28/hr. Thus, the annual operating labor cost is $81,000. The cost of expanded direct supervisory and clerical duties, estimated at 20% of the operating labor cost, is $16,000/yr.

Utility costs have been calculated based upon the electrical power consumed at rated of $3/kWhr, after correcting the horsepower requirements of the pumps and motors for their efficiencies, to be approximately $11,000/yr.

Maintenance and repair costs are estimated to amount to 2% of the fixed capital investment, or $29,000. Operating supplies costs, such as spare parts, tools, etc., are estimated at 20% of maintenance costs or $6,000.

Laboratory charges, assuming that one half-time shift per operating day is required to complete needed analytical tests, amount to $50,000/yr based on a unit charge of $28/hr.

As a fixed charge, depreciation is evaluated on the basis of a straight line declining value of the direct plant cost over a 10 year period, and amounts to an annual cost of $105,000. Insurance is assumed to be obtainable at about 0.4% of the fixed capital investment, with premiums of $6,000/yr.

General expenses are also incurred, including administrative costs which are estimated at 15% of the costs for operating labor, supervision and

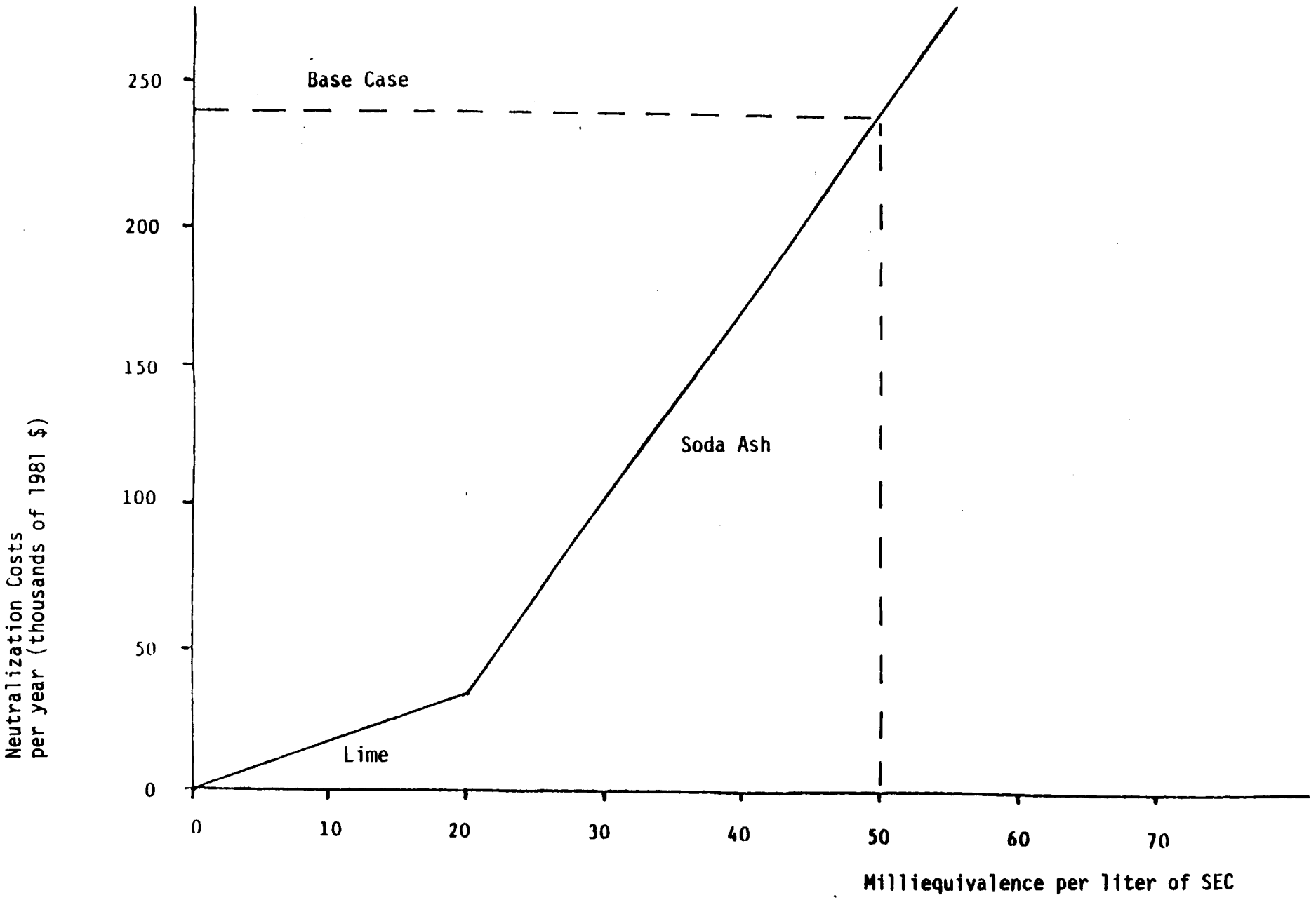


Figure 43. Annual Costs for Bases as a Function of Concentration in SEC Processing.

maintenance, or $19,000/yr. Continuing research, development and consulting activities may cost approximately $15,000/yr. Financing costs are the largest general expense item, and, assuming that a loan in the amount of the total capital investment could be secured at a 15% interest rate compounded annually, the resulting cost is $225,000/yr.

Thus the total general expenses amount to about $259,000/yr and total manufacturing costs to about $543,000, and together these yield $802,000, the total annual cost before income.

Biogas Credit and Annual Costs

Income can be realized from the product biogas (S-16) and the mass balance in Table 11 shows that about 5200 m^3/day (186,000 ft^3/day) of methane is produced. Fuel grade natural gas is valued at $0.16/$m^3$,[15] and thus the credit arising over 360 operating days is about $309,000.

Considering this credit only, and treating the process as separate from other effluent treatments, the final annual costs are estimated to be $493,000, which corresponds to a cost of about $0.041 per pound of COD removed.

Kraft Evaporator Condensates (KEC)

Since recent research in our laboratory indicates that KEC can be fermented anaerobically with a 12 hour or less retention time to produce methane with removal of about 80% of the influent COD, it has seemed worthwhile to make preliminary cost estimates for KEC based upon a flow sheet similar to that shown in Fig. 40.

Compared with SEC, the processing of KEC offers two advantages: because KEC is available at about pH 10, and thus only small amounts of chemicals need to be added to neutralize and increase buffer capacity to provide for

effective operation at about pH 7; and, because the concentration of organic solutes is much lower in KEC than SEC, smaller amounts of sludge are produced per unit volume treated, although, disadvantageously, the yield of methane is correspondingly lower.

As a basis for estimation of KEC processing costs, the following assumptions are made: that KEC is supplied at 35°C, 2 atm pressure, with a chemical oxygen demand of 950 mg L^{-1}, that it is processed at a rate of 3.8 (10^6 gal) per day with a 12 hour hydraulic retention time; that the materials of construction are carbon steel with rubber coatings and stainless steel pumps and fittings as needed; and that 80% of the COD of the influent is removed.

Equipment Costs and Fixed Capital Investment

Equipment and fixed capital investment costs are taken to be the same as those used in the SEC computation except that the lime feeding system is not needed. Thus, the purchased equipment cost is $219,000 in 1979 dollars, and, including a 3% delivery fee, $284,000 in 1981 dollars. The reactor core construction costs are considered to be the same as found for SEC processing, i.e., $255,000.

The ratio factors applied to give estimates of fixed capital investment are the same as those shown in Table 13. Multiplying the delivered equipment costs by the percentages shown for each component of plant construction, and summing, and then adding the cost for reactor core construction, the fixed capital investment amounts to about $1,409,000, not including the start-up costs, purchased land, or service facilties.

Annual KEC Treatment Plant Costs

Costs for raw materials are significantly less for KEC than for SEC while costs for operating labor, supervisory labor, clerical labor, utilities, maintenance, operating supplies and laboratory charges are similar. Costs for insurance and financing are slightly less, while research and development and administration costs are about the same.

When the various expenses are added, the annual cost before income amount to $548,000, very much less than in the SEC case.

However, the credit for product "Biogas" is only about $59,000/yr because of the low concentration of dissolved organic substances in KEC. The overall result is an estimated treatment cost, after credit, of $589,000. The cost per pound of COD removed, is $0.214.

Integrated Anaerobic - Aerobic Processing

Anaerobic processing of SEC should be considered, not as an isolated process, but as one step in the overall treatment of the effluent. Anaerobic processing should probably be followed by aerobic treatment to remove residual odors and organic matter.

In this context 3 additional benefits can be recognized as associated with integrated anaerobic processing of evaporator condensates: (1) whatever neutralization is needed for anaerobic processing would be required, at least in part, for subsequent aerobic treatment and thus the neutralization costs should not be charged entirely to the aerobic step but appropriately apportioned; (2) no aeration is required for the anaerobic treatment, and thus the cost of aeration in the subsequent aerobic system will be reduced by some 50% to 80%; and (3) only about one-fifth to one-tenth as much sludge mass is

produced in the aerobic system with a consequent savings in nutrient requirements and disposal costs.

In future research we hope to evaluate some of these prospective credits, although they may well vary substantially for each mill considered. At present, we can only set forth the above preliminary estimates which should be viewed as conservative compared with what may eventually be possible in optimally integrated systems.

ACKNOWLEDGEMENTS

The authors are grateful for the funds granted in support of our research by the United States Office of Water Research and Technology, and the Boise-Cascade, CH_2M Hill, Georgia Pacific, ITT Rayonier, Scott, and Weyerhauser companies and especially the leadership and counsel of Mr. E. Dahlgren of the Georgia Pacific Company. Our colleagues, Professors Mark M. Benjamin and John F. Ferguson, of the Department of Civil Engineering, and L. Ricker of the Department of Chemical Engineering, have given us valuable advice relative to this paper.

REFERENCES

1. Benjamin, M.M., Ferguson, J.F., and Buggins, M.E. "Treatment of Sulfite Evaporator Condensate with an Anaerobic Reactor," in 1980 Environmental Conference Proceedings, TAPPI PRESS, Atlanta (1980).

2. Blosser, R.O., NCASI, Bulletin No. 310 (1978).

3. Boyle, W.A. Thesis for M.S. in Chemical Engineering, University of Washington (1980).

4. Buggins, M. Thesis for M.S. in Civil Engineering, Univ. of Washington (1981).

5. Chem. Eng. 88(15):7 (1981).

6. Dehaas, G.G. and Clark, L.H. Tappi 52(11):1728 (1969).

7. Fors, R. Thesis for M.S. in Chemical Engineering, University of Washington (1980).

8. Haggerty, P. Thesis for M.S. in Chemical Engineering, Univ. of Washington (1980).

9. Perry, R.H. and Chilton, C.H. Chemical Engineer's Hand κ, 5th edn., McGraw Hill, NY (1973).

10. Peters, M.S. and Timmerhaus, K.D. Plant Design and Economics for Chemical Engineers, 3rd edn., McGraw Hill, NY (1980).

11. Pikulik, A. and Diaz, H.E. Chem. Eng. 84(21): 106(1977).

12. Rexfelt, J. Samuelson, O., Hagglund, S. and Ohgren, T. Svensk Papperstid. 76(12):448 (1973).

13. Ruus, L. Svensk Papperstid. 67(6):221 (1964).

14. Samuelson, O. and Rexfeld, J., Svensk Papperstid. 21:689 (1970).

15. Washington Natural Gas Co., personal communication, April (1982).

CHAPTER 6

ANAEROBIC TREATMENT OF CAUSTIC EXTRACTION WASTE WITH SULFITE EVAPORATOR CONDENSATE[1,2]

David R. Nitchals
Mark M. Benjamin
John F. Ferguson

ABSTRACT

The anaerobic treatment of caustic extraction stage bleaching waste (CE) combined with sulfite evaporator condensate (SEC) has been investigated. This process produces energy as well as reducing the waste loads on aerobic treatment systems. Use of the alkaline CE waste stream to neutralize the acidic condensate improves the cost effectiveness of the process significantly.

The CE/SEC mixture has been characterized with respect to its acid/base properties by titration analysis, and its treatability has been evaluated in batch tests and in a continuous flow reactor. Mixtures with pH as low as 4.6 are treatable, with 70 to 80% BOD removal and 42 to 51% TOC and COD removal. A gas phase containing about 75% methane is produced. Combined anaerobic treament of these two waste streams appears to have both technical and economic promise.

1. Presented at TAPPI Pulping Conference, Houston, TX, October 25, 1983.

2. Submitted for publication to T.A.P.P.I.

INTRODUCTION

Anaerobic biological processes for treating industrial waste streams have received increased interest in recent years. Among the potential advantages of anaerobic treatment compared to the more commonly used aerobic processes are cost savings associated with (a) smaller capital outlays for process equipment, (b) elimination of the need for aeration equipment and the cost of running it, (c) reduced sludge production and reduced requirements for nutrients and sludge processing capability, and (d) the production of methane as a by-product. One drawback to utilization of this technology has been a paucity of operating experience; hence confidence that anaerobic processes are applicable to a broad range of waste treatment problems or that operational problems which arise will be correctable in a timely and cost-effective manner is lacking. Recent laboratory research as well as pilot and plant demonstrations have shown that anaerobic processes can operate reliably, as stably as aerobic ones. As with any biological process, care must be taken to ensure that the process conditions are consistent with the needs of the organisms carrying out the bioconversions.

For the past 5 years we have conducted research to evaluate the feasibility of and limitations on the anaerobic treatability of various waste streams from pulp and paper mills. Studies of evaporator condensates from both the Kraft and acid sulfite processes (KEC and SEC) led us to conclude that anaerobic treatment was a viable option for these streams, and that neutralization of the acidity and provision of alkalinity to SEC would be a major component of the overall treatment cost.[2,6] A cost advantage would be gained if an alkaline waste stream could be mixed with the condensate before

treatment, reducing the need for purchased neutralization chemicals and, in the best case, removing organic pollutants from both waste streams simultaneously in the treatment process. An obvious candidate stream for such a purpose is the effluent from the caustic extraction stage of the bleaching process (CE). This stream may have sufficient alkalinity to neutralize most of the acidity of the condensate, and it represents a significant BOD load. There are also potential problems. In particular, compounds such as chlorinated organics found in the CE may interfere with biological activity in the reactor to the point where anaerobic treatment of the mixed stream becomes uneconomical or impossible. An understanding of the reactions that can occur when these streams are combined and exposed to a mixed anaerobic culture may allow design of an optimal treatment strategy for a given plant. In this paper we report an evaluation of toxicity and biodegradability of a strong CE waste, an assessment of the use of CE to neutralize SEC waste, and results of an anaerobic treatability study of a mixed SEC-CE waste stream.

METHODS AND MATERIALS

Experiments were performed using a laboatory scale submerged media anaerobic reactor (SMAR) of 20 liter gross volume equipped with effluent recycle and gas collection apparatus, all contained within an environmental chamber at 37±1C. The reactor, shown schematically in Fig. 44, is a 122 cm by 14.5 cm acrylic cylinder filled with plastic media of high specific surface area, yielding a void volume of 19 liters. This reactor has been used previously for studies of the anaerobic treatment of SEC.[2,3,4]

Feed to the reactor consisted of combinations of synthetic waste, SEC or CE, tap water and nutrients. Composition of the synthetic wastes is presented

Table 15. Organic Compounds in Synthetic Feed

Compound	Concentration in feed (mg/L)	COD Equivalent (mg/L)
Acetic Acid	2400	2560
Methanol	880	1320
Ethanol	440	920
Acetone	100	220
Phenol	100	240
Total Feed COD		5260

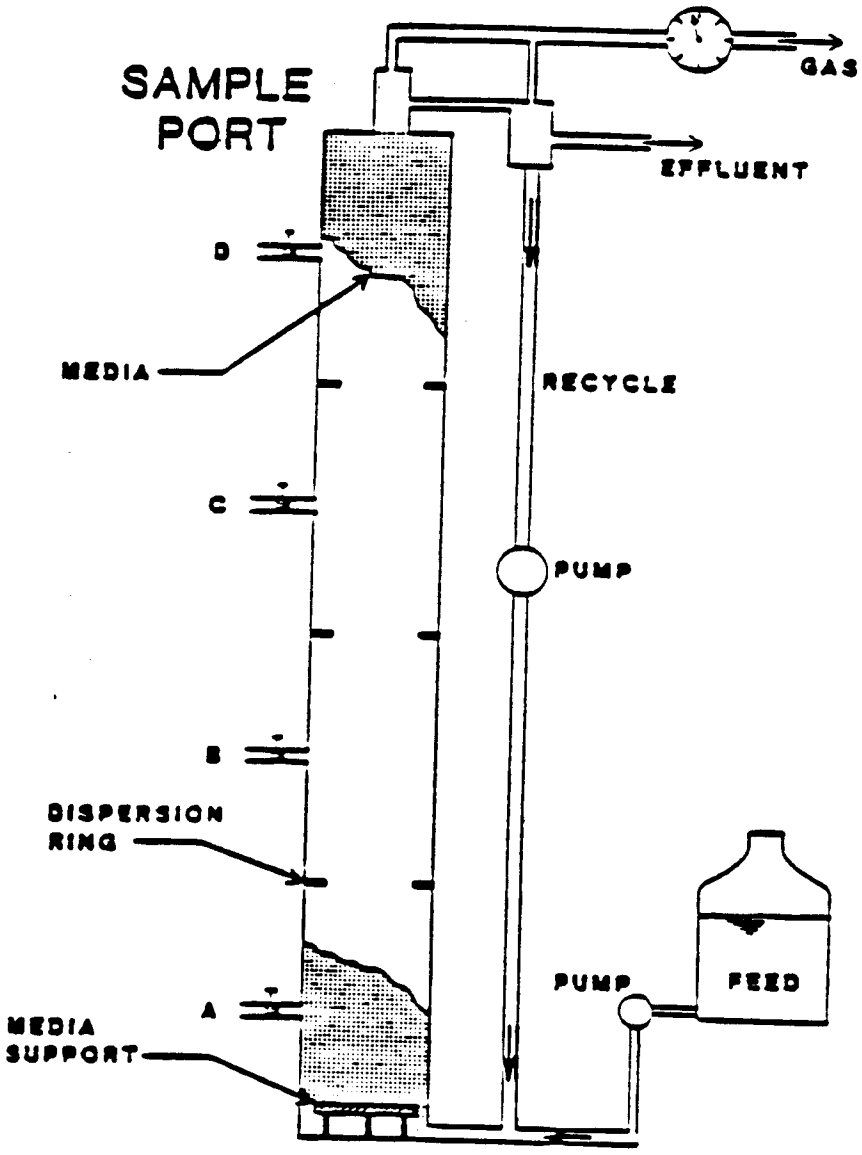


Figure 44. Schematic diagram of submerged media anaerobic reactor.

in Table 15. Except as noted below, the feed was neutralized to about pH 6.9 with Na_2CO_3. Alkalinity additions amounted to 60 meq/l for the synthetic feed and 0 to 25 meq/l when SEC and CE were being fed.

Feed was usually prepared by adding SEC and then CE to an 80 liter storage vessel, but the order of addition was sometimes reversed. While tap water was being added to the vessel, the Na_2CO_3 was mixed in and allowed to dissolve. Although it could not be detected during feed preparation because of dark, opaque vessel walls, a dark precipitate formed in other experiments when CE was acidified.

Reactor performance with 3 fferent feed compositions was studied in detail. In all 3 of these intensive study periods only real industrial waste, as opposed to synthetic waste, was fed to the reactor. During the first test, the feed contained 12.5% CE, 25% SEC, 62.5% tap water (all percentages by volume), nutrients and Na_2CO_3. In the second study period the CE fraction was increased to 19% and tap water was reduced to 56%. During the third period, the CE and SEC concentrations were the same as in the second, but no Na_2CO_3 was added. The CE identified in Table 16 as Mill C, Sample 2 was used in all 3 test periods. A different batch of SEC from Mill A was used in each.

Reactor performance was evaluated daily by measuring the volume and composition of gas produced, effluent and/or reactor pH and effluent alkalinity. Gas production was measured with a wet test gas meter in the environmental chamber. The methane fraction in the gas was determined by gas chromatography. Chemical oxygen demand (COD), biochemical oxygen demand (BOD), total and dissolved non-purgeable organic carbon (TOC and DOC) and alkalinity titration curves were evaluated on feed and effluent samples. In addition, a limited number of samples were tested for suspended solids, volatile acids and alcohols.

RESULTS AND DISCUSSION

Waste Characterization

Composite Organic Analysis

Water quality characteristics of the waste streams, including conventional composite water quality parameters (BOD, COD, TOC) and some analyses related to neutralization are presented in Table 16.

Variations in waste strength among samples from a given mill can be large and relate to the particular operating conditions extant when the samples are taken. Much more dramatic are the variations among mills, particularly if the mills use different pulping processes or produce different quality pulps. In our study, 3 acid sulfite mills were sampled. One, producing dissolving grade pulp, had SEC and CE much more concentrated in almost all constituents than the others, which produced market grade pulp.

The BOD is the conventional measure of SEC and CE most closely associated with anaerobic treatability. The values reported for all mills indicate high strength wastewaters (e.g., the ratio of 5 day to ultimate BOD is usually 0.6 to 0.7). The BOD/COD ratios for the SEC are all about 0.6, indicating a large fraction of the organics present are readily biodegradable. The CE samples on the other hand, have BOD/COD ratios less than 0.3, which would indicate that about half the total organics are biodegradable. Some of the oxygen demand in the COD and perhaps the BOD tests may be exerted by sulfur compounds (S in the -II and +IV oxidation states.)

Chlorinated Organics and Sulfur Compounds

The organics in CE may also include toxic organic compounds which may or may not be anaerobically degradable. The concern about toxicity of CE derives

Table 16. Characteristics of sulfite evaporator condensate and caustic extraction stage effluents.

Sulfite Evaporator Condensates

Source	COD mg/l	BOD_5 mg/l	TOC mg/l	pH	Total Acidity[3] meq/l	Total Conductivity mmhos/cm
Mill A[1,2]	4740 ±390	2860 ±360	1780 ±190	2.3 ±0.2	63.2 ±9.6	3.2 ±1.6
Mill B	8230	4770	-	2.5	92.0	1.8
Mill C	12500	5840	4490	2.3	89.8	6.9

Caustic Extract

Source	COD mg/l	BOD_5 mg/l	TOC mg/l	pH	Total Alkalinity meq/l	Total Conductivity mmhos/cm
Mill A	1220	350	-	10.4	6.5	2.2
Mill B	800	-	-	8.8	4.7	1.6
Mill C[1]						
Sample 1	16500	5260	5510	8.1	-	11.2
Sample 2	29900	8100	12500	8.8	53.1	16.0
Sample 3	18900	-	7360	8.8	44.0	12.8

1. SEC from Mill A and CE from Mill C were used in reactor studies of treatability.
2. Values for Mill A SEC are ± standard error of mean except pH, acidity and conductivity which are ± standard deviation.
3. Acidity to pH 8.3, alkalinity to pH 4.5.

primarily from the presence of chlorinated organics formed during the bleaching process. Concentrations of some of the specific chlorinated compounds detected in a batch of CE used in this study are listed in Table 17. Although none of these compounds is present in a concentration likely to be toxic individually, the combined effects may be significant. Numerous other chlorinated compounds are also undoubtedly present in the waste.

One concern with respect to anaerobic treatment of SEC is that either the influent sulfur (+IV) or the reduced sulfur (-II) formed in the reactor might be toxic to the anaerobic microorganisms essential to methane generation. Previous work has shown that this problem can be overcome, and that organisms can acclimate to relatively high sulfur concentrations.[5]

Titration Analyses

A discussion of the neutralization of SEC with CE requires information about the acids and bases in the waste streams and their possible changes during anaerobic treatment. The major constituents of SEC with respect to its anaerobic treatability and neutralization are acetic acid, methanol, furfural and compounds containing sulfur in the +IV oxidation state (free and loosely combined SO_2). Acetic acid and the sulfur compounds contribute to the acidity of SEC and help lower its pH to the range 2-3. The neutralization of this waste with mineral bases has been discussed by Ferguson et al.[6]. In the anaerobic treatment process, both groups can undergo microbial reactions which convert them to weaker acids. However, these microbial reactions require pH values between about 6.5 and 8. Thus, one requirement for anaerobic treatment is to maintain a near neutral or slightly alkaline pH in the reactor so that entering acids can be degraded and neutralized rapidly by bio-reactions. If the acid balance in the reactor is upset the reactions are slowed, increasing the acidity in the reactor and leading to ultimate failure unless corrective

Table 17. Caustic extract chlorinated phenols content

	ALP Batch 2	ALP Batch 3
o-Chlorophenol	0 µg/l	0 µg/l
m-Chlorophenol	0	0
p-Chlorophenol	16	0
2,4-Dichlorophenol	65	59
2,4,6-Trichlorophenol	301	190
5-Chlorovanillin	430	978
4,5-Dichlorocatechol	96	94
4,5,6-Chloroguaiacol	199	117
Pentachlorophenol	7	8
Tetrachloroguaiacol	166	66
Tetrachlorocatechol	33	21

action is taken. However, previous work in our laboratory has shown that anaerobic reactors can treat chemically neutralized SEC and that upsets due to excessively low pH are avoidable or correctable.

The acid/base behavior of the Mill A SEC and Mill C CE was characterized by titration with strong base or acid. Titration curves (Figs. 45a and 46a) were determined, as well as pH and total alkalinity (pH 4.5 endpoint) or total acidity (pH 8.3 endpoint) as reported in Table 16. Some of the features of the titration curves are accentuated when the slope of the titration curve known as the buffer intensity, is plotted as a function of pH. Figs. 45b and 46b show the buffer intensity of SEC and CE, after subtracting the values for titration of pure H_2O. Such curves have maxima approximately at pH values where the pH equals the pKa of acids comprising the sample. Furthermore, the height of the maxima and the shape of the curve can be used to make inferences about the concentrations and variety of the constituent acids. The SEC buffer intensity curve has a sharp primary maximum at pH 4.7 and a secondary one at pH 7.0. The first is attributable to acetic acid (pKa 4.75), which usually contributes about 60% of the total COD of SEC. The secondary peak is attributable to hydrated SO_2 (H_2SO_3, pKa2 = 7.0). Knowing the pKa's of the constituent acids, one can return to the titration curve to estimate acid concentrations. Using the approximation that 82% of the total concentration of an acid in solution is deprotonated as the solution is titrated from one pH unit below pKa to one pH unit above pKa, we estimate the concentration of acetic acid (or carboxylic acids with pKa's near 4.75) to be 46 mmole/l and that of SO_2 to be 11 mmole/l for the sample shown, with a range of 33 to 75 mmole/l carboxylic acids and 3 to 11 mmole/l SO_2 for all the SEC batches analyzed. These results agree well with volatile acid determinations by gas chromatography and SO_2 measurements by iodometric titration. The results of

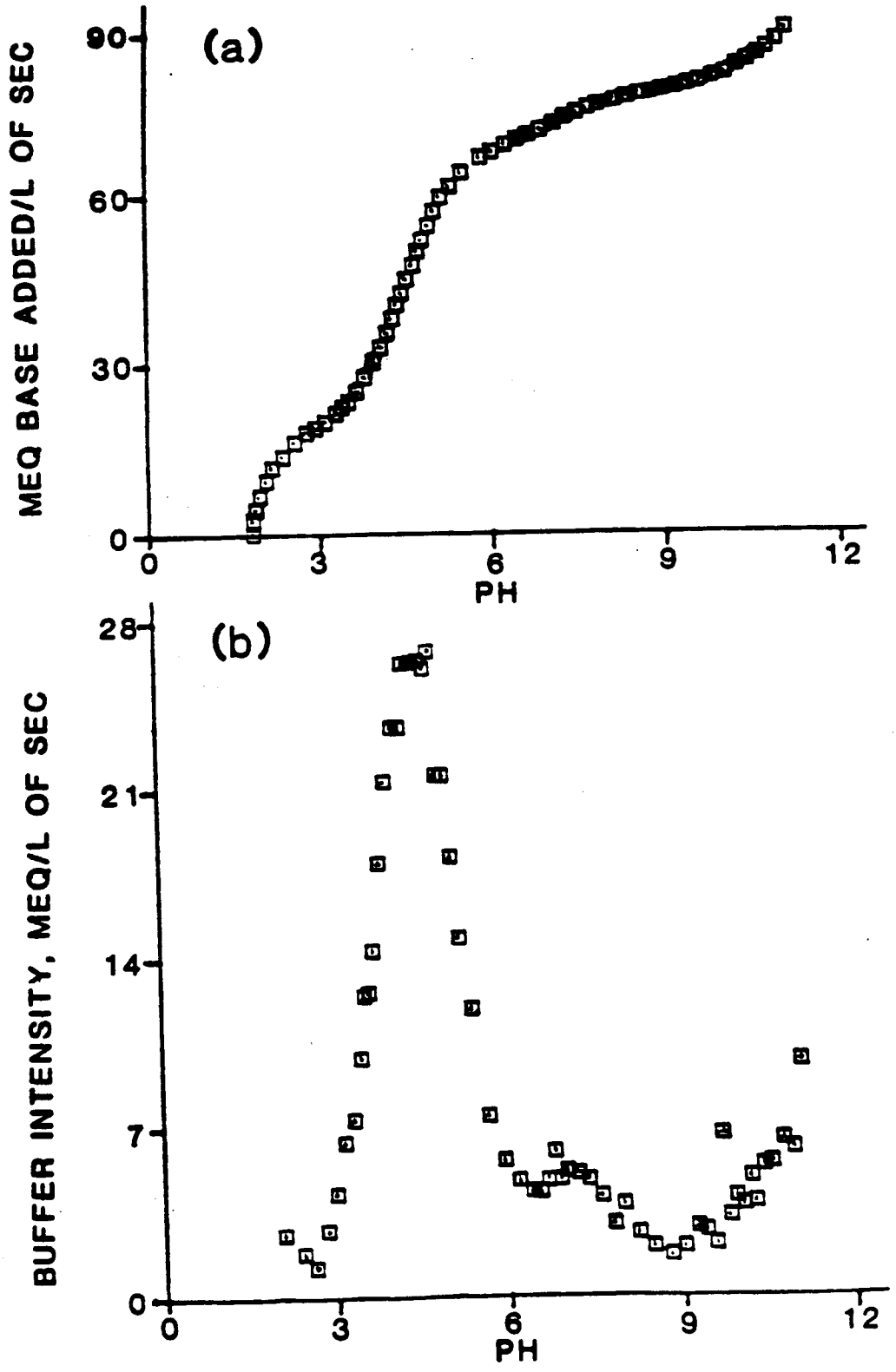


Figure 45. (a) Alkalimetric titration curve for SEC from Mill A.
(b) Buffer intensity for same SEC.

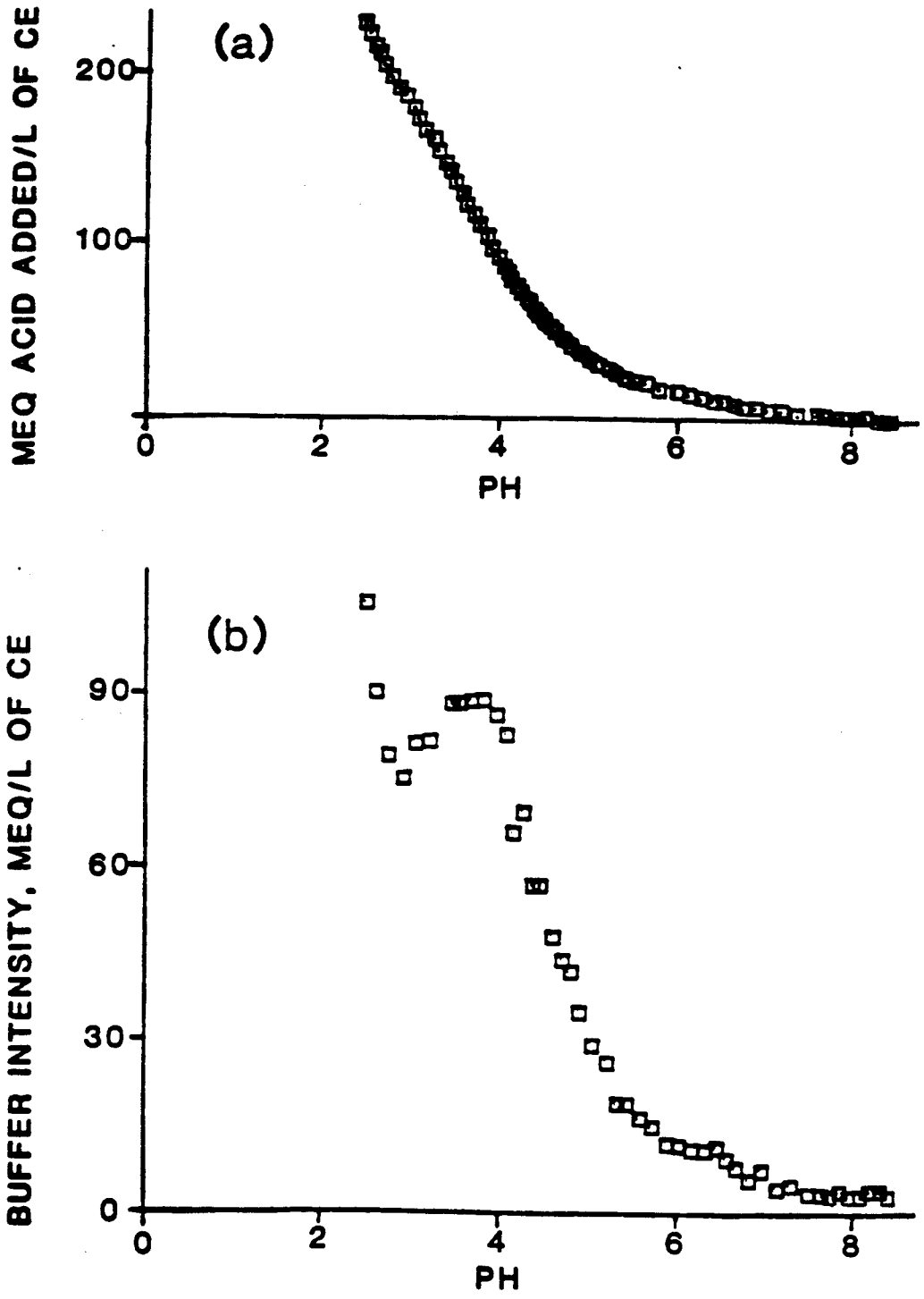


Figure 46. (a) Acidimetric titration curve for CE from Mill C. (b) Buffer intensity for same CE.

this analysis emphasize that while the pH of SEC may be controlled primarily by dissolved SO_2,[3] most of the acid which must be titrated to neutralize the SEC is acetic or other short-chain carboxylic acids. The total acidity to pH 8.3, which is about 75 meq/L, is a good measure of the amount of base required to neutralize all the carboxylic acids and nearly all the SO_2.

Caustic extract is a more complex mixture than SEC, containing numerous small to medium molecular weight by-products of lignin chlorination and hydrolysis, as well as sugars and other organics. Many of the molecules in CE contain organic acid groups such as carboxylates or phenolics. Since each molecular structure has a slightly different effect on the acidities of these functional groups, the acid-base properties of CE tend to be spread over a broader pH range than those of a simple mixture such as SEC containing only 2 or 3 dominant compounds. This property is apparent in the titration curve and the buffer intensity of a batch of CE from Mill C, producing dissolving grade pulp (Fig. 46). There is no sharp alkalinity endpoint at pH 4.5. In fact, the alkalinity to pH 4.5 measures less than half the buffer capacity of CE. The buffer intensity curve has a broad peak extending over a range of more than one pH unit; the decrease in buffer intensity from pH 4 to 6 is less steep than was the case for SEC. The fact that the peak occurs at pH less than 4.0 implies that much of the acidity is provided by stronger acids than acetic acid, such as multi-protic organic acids or carboxylic acids conjugated with an aromatic ring or a phenolic moiety. These organic acids are largely unidentified. Gas chromatographic analysis for volatile acids gave values of 47, 1.3, and 2.1 mM/L for acetic, propionic, and butyric acids, respectively, accounting for only about 12% of the COD in the sample.

Neutralization of SEC/CE Mixtures

The pH of a SEC/CE mixture will depend on both the concentration and pKa values of the acids and bases which comprise the two solutions. The fact that most of the buffer capacity of CE is exerted at low pH means that CE is a relatively weak base. It will be ineffective in raising the pH of the SEC/CE mixture above 4 to 5. Although the pH in the reactor must be greater than about 6.8 for effective treatment, a lower pH in the feed may be acceptable if the reactor contents are well-mixed. This is because biological reactions in the reactor will convert acetate to bicarbonate, effectively destroying acidity (or, equivalently, producting alkalinity) and raising pH.

Only in Kraft mills or in sulfite mills where dissolving grade pulp is being produced does the total alkalinity of the CE approximate the total acidity of the evaporator condensate. In most sulfite mills, CE could be used to partially neutralize SEC leaving a solution with an acidic pH. In dissolving grade mills, neutralization with CE should be nearly complete, although the pH may still be slightly acidic.

The pH of the mixture can be increased, if necessary, by relatively small chemical additions of caustic, soda ash, or lime. The conditions at a given pulp mill, including the relative strengths and flow rates of SEC and CE as well as the desired final pH, would of course determine the exact amount of base required. Fig. 47 illustrates this point for a range of operating conditions. It indicates, for instance, that the requirement for neutralization chemicals can be reduced by 34% if SEC and CE are mixed in 1:1 proportion and mixed pH of 5.5. is acceptable in the solution fed to the reactor. (As will be discussed later, stable reactor operation was obtained with feed pH as low as 4.6 in this study.)

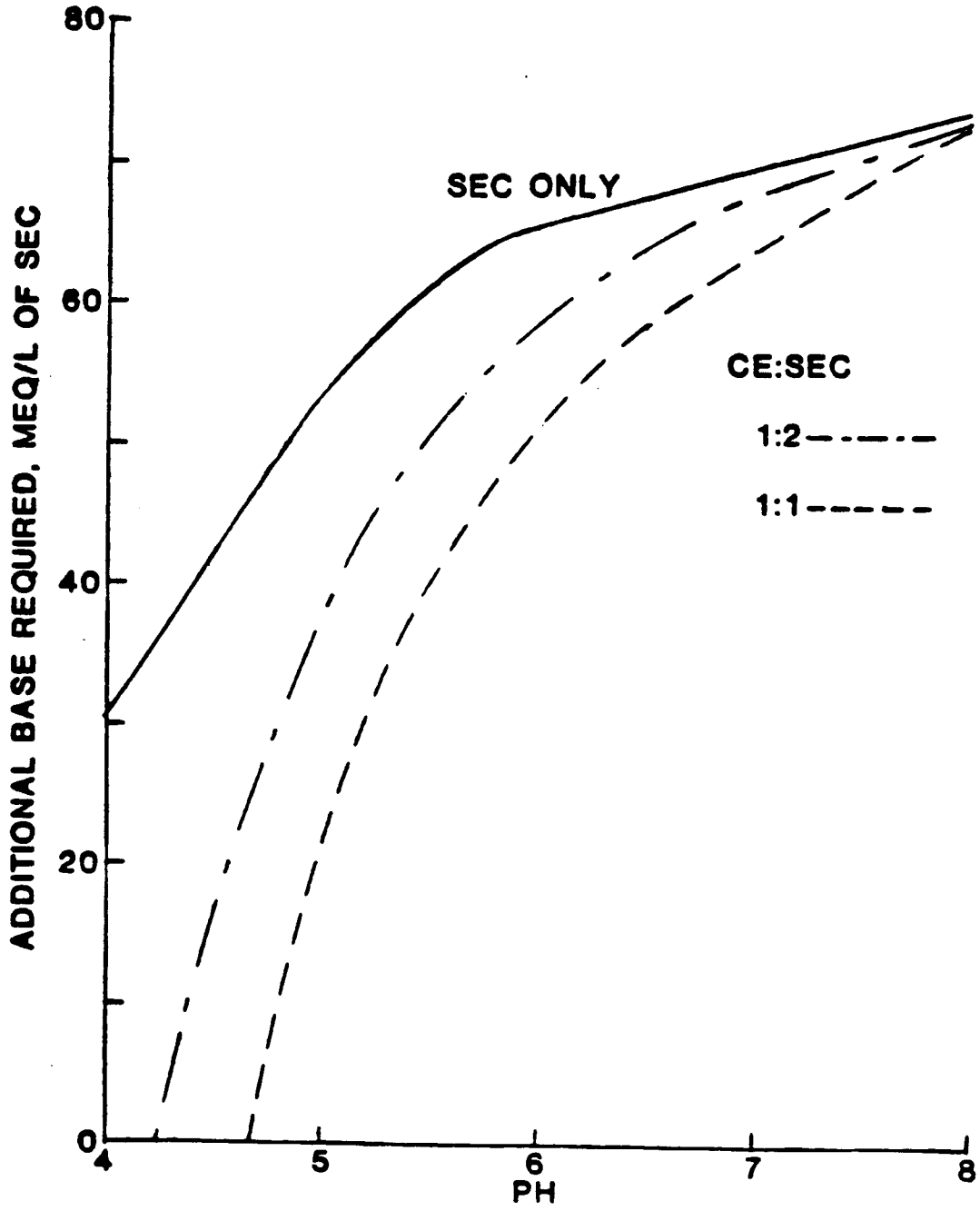


Figure 47. Base addition required to reach feed pH values for mixtures of Mill A SEC and Mill C CE. The SEC:CE ratios are on a volume basis.

Batch Bioassays of SEC and CE

Analysis of the acid-base behavior of SEC/CE mixtures gives an indication of the "best case" scenario. That is, it indicates the potential savings in neutralization costs which could accrue if the presence of CE has no adverse effects on the bacterial metabolism. However, it is possible that the complex mix of compounds, including chlorinated organics, in CE could be either inhibitory or toxic to the microorganisms mediating removal of degradable organics in SEC and CE. The next two portions of this study were designed to address this issue. Batch tests and continous flow tests were conducted to assess the treatability of the SEC and CE individually and of various mixtures of the two.

The batch tests included two anaerobic bioassays: anaerobic toxicity assays (ATA's), in which the rate of degradation of one or more easily-metabolized compounds (acetic acid and methanol in this case) is monitored as a function of the concentration of a suspected inhibitor or toxicant, and biological methane potential assays (BMP's), in which the rate and extent of conversion of the test compound or mixture to methane in the absence of other carbon sources is monitored.

Tests with SEC from Mill A have been performed several times in our laboratory in connection with biodegradability and inhibition studies. Results have previously been reported by Benjamin, et al.[2] and Eis.[4] The SEC was degradable by acclimated cultures, but at a lower rate when the SEC concentration was high. Sulfite reduced the rate and total amount of gas production. In the present study 4 concentrations of SEC were assayed in both ATA's and BMP's, such that the final test solutions contained 17, 33, 50, and 67% SEC by volume.

The ATA's and BMP's using SEC as the test "compound" showed a consistent pattern of gas production, essentially similar to that found before. The presence of SEC caused an inital lag period during which no gas was produced. The higher the concentration of SEC in the test, the longer was the lag period, ranging from about 8 days for 17% SEC to 12 days for 67% SEC. Once the lag period passed, gas was usually produced in two stages. During the first stage, which lasted 1 to 3 days, an amount of gas was produced roughly equal to the amount expected from degradation of the methanol in the SEC and/or in the spike. Then a much more gradual rate of gas production ensued for periods of up to several weeks, after which it ceased altogether. The final cumulative gas production increased with increasing SEC concentration. Fig. 48a shows the amount of methane produced from compounds in SEC in the bottle tests as a function of SEC concentration. Most of the COD in the SEC was utilized by the microorganisms in all cases. Some of the organics which were not converted to methane may have been oxidized during reduction of sulfur(IV).

Caustic extract waste had not previously been investigated for anaerobic toxicity and biodegradability, but the same phenomena were expected that had been found with SEC. ATA's and BMP's for fractions of CE between 8 and 58% are presented in Figs. 49 and 50. The bottles were inoculated with bacteria from a reactor that had intermittently treated 12% or 19% CE waste over several months. Lag periods were found both initially before any gas production and after a first stage of gas production. In the ATA's, the volume of gas produced in the first step decreased steadily with increasing CE concentration. The lag period between the first and second stage varied from a few days for the 8.3% CE test to >210 days for CE concentrations of 50% or more. The second stage was never observed in the ATA with 50% CE or the BMP

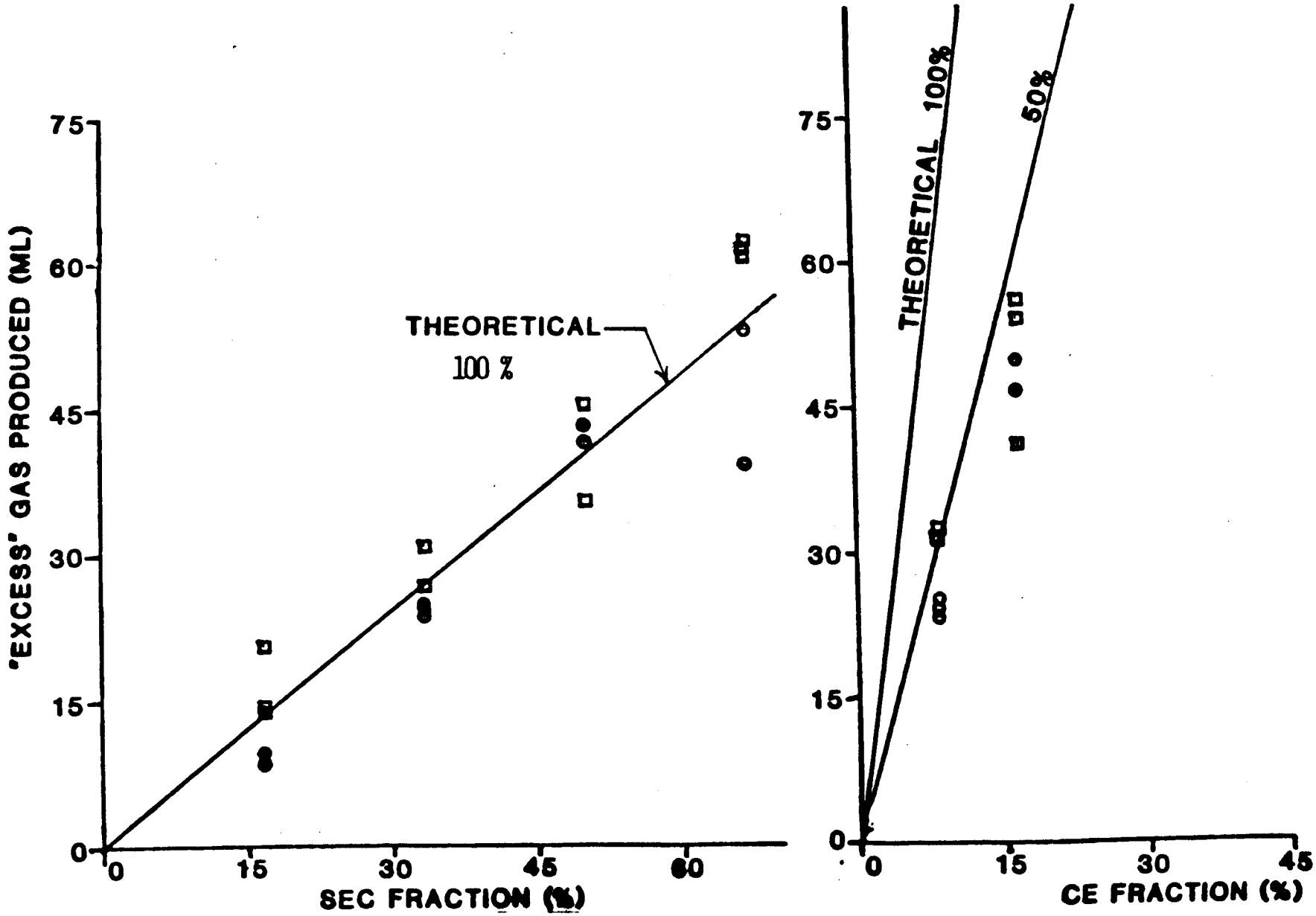


Figure 48. Methane production from compounds in SEC (a) and CE (b). The data points were generated by subtracting the methane produced in controls from that in the test bottles. Only bottles which had stopped producing gas at the end of the test are included. Lines represent the theoretical gas production for 50% or 100% conversion of COD to methane, assuming 85% CH_4 in the gas phase.

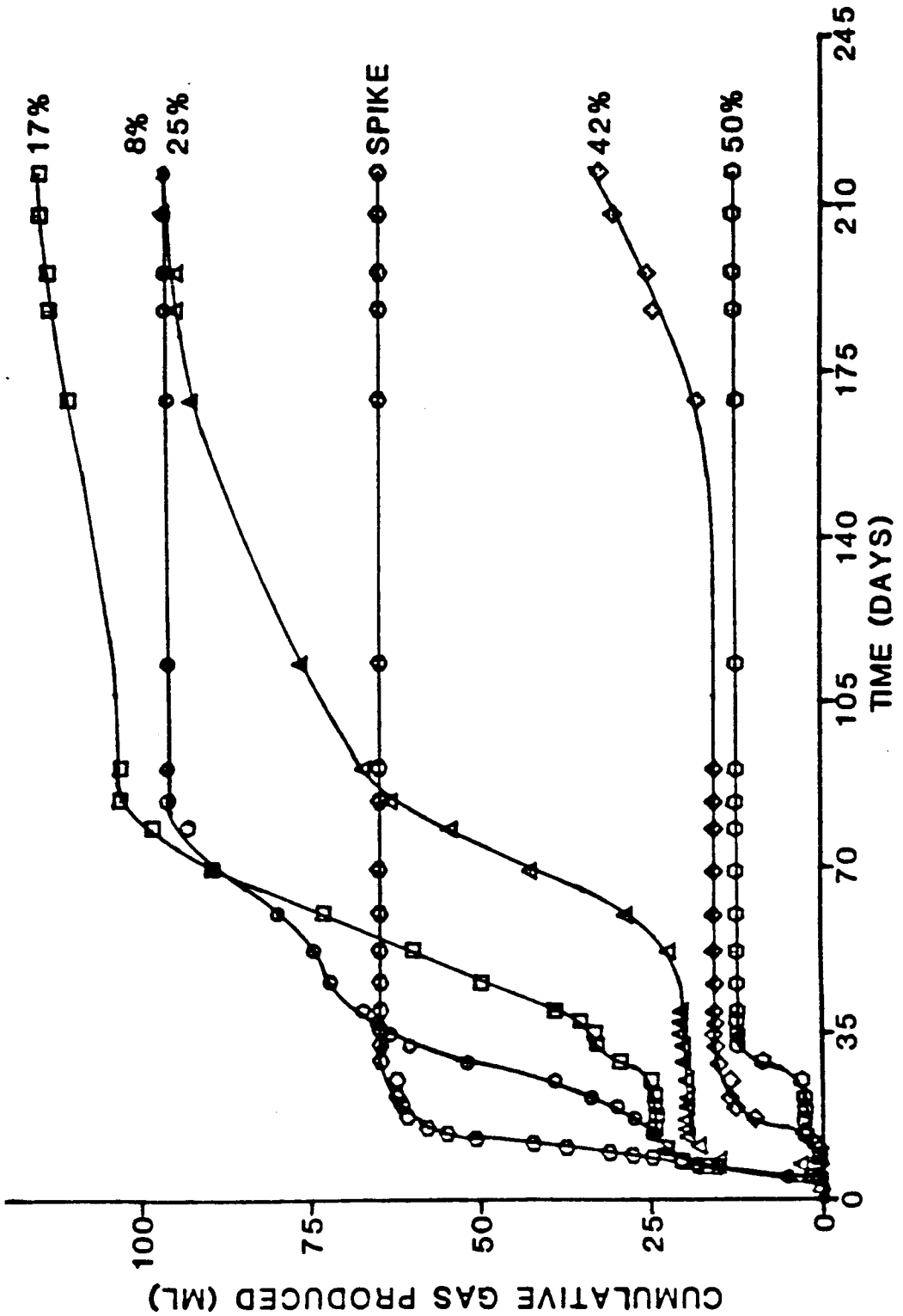


Figure 49. Anaerobic toxicity assay for Mill C CE. The numbers represent the volume fraction CE in the test solution.

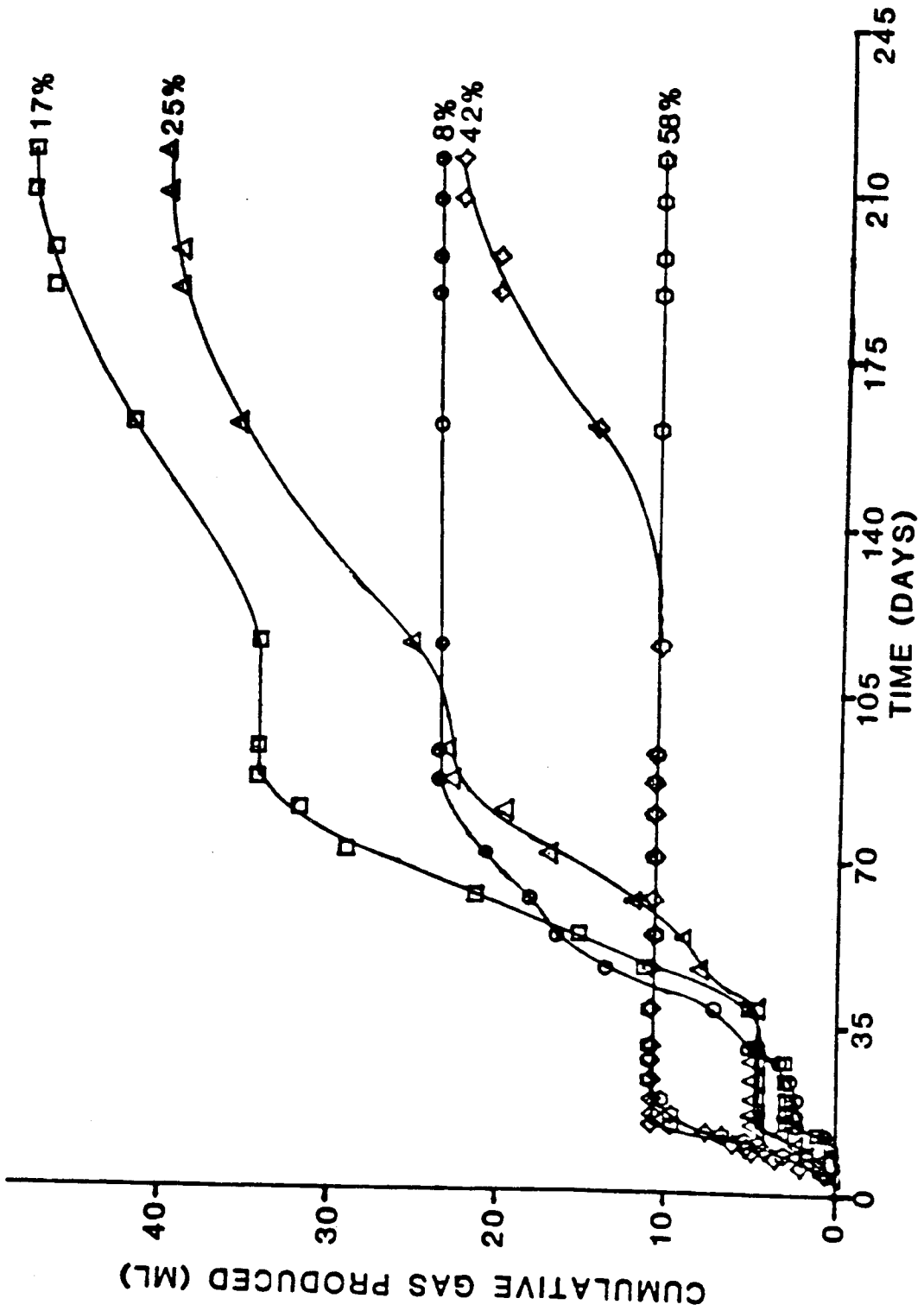


Figure 50. Biological methane potential assays for Mill C CE. The numbers represent the volume fraction CE in the test solution.

with 58% CE, since the tests were terminated after 220 days. For the ATA's with CE, the rate of gas production during the second stage appeared to decrease with increasing CE concentration, but no such trend was evident in the BMP's.

Significant amounts of total gas production in the BMP's and amounts in excess of that produced by the spiked blank in the ATA's indicated that some of the organic matter in the CE was being converted to CO_2 and CH_4. Fig. 48 shows that this fraction is substantially smaller for CE than for SEC. In the two most dilute solutions, analysis of residual COD at the end of the assay indicated that almost 3/4 of the COD originally injected with the CE had been removed. Estimates of COD removal based on gas production for these same bottles indicated approximately 50% removal. These results give a range of COD removal efficiencies that can be taken as a tentative upper limit on the anaerobic degradability of CE. Based on the BOD_5 of this sample, the maximum attainable is also about 50% of the BOD. The waste is quite inhibitory and must be diluted considerably prior to treatment.

There appears to be a significant correlation between the inhibitory effects of the CE on anaerobic microorganisms and their prior exposure to CE. The organisms used in both the ATA's and BMP's were taken from a continuous flow reactor which had been fed a solution containing 19% CE for 6 weeks and a solution containing 12% CE for 4 weeks prior to that. Thus the organisms may have "acclimated" to compounds present in a 19% mixture of CE. (We use the term "acclimation" in an operational sense here indicating the ability of a culture to biodegrade compounds in a solution after some exposure period, if the compounds are not degradable by organisms which have not been previously exposed to the solution.) Significantly, the first stage of gas production in ATA's was not inhibited at all by CE concentrations up to 19%, but was

inhibited, i.e., there was a lag period, by higher concentrations. Furthermore, in both ATA's and BMP's with CE concentrations up to 19% the organics in CE were degraded to the apparent maximum possible extent (75% reduction of the COD) within 90 days, with the 17% CE BMP taking somewhat longer. In none of the tests with more concentrated CE solutions did cumulative degradation reach this 75% limit within the 7 month test period.

Significant differences between the tests at less than and greater than the acclimated concentration are also apparent from analyses of the residual short-chain (volatile) acids remaining in solution after 220 days incubation. In a healthy, non-inhibited culture these compounds should be present in low concentrations. The volatile acids in the original solution would be utilized early in the test, and volatile acids produced from the breakdown of more complex substances would be catabolized shortly after they are formed. However, in an inhibited system volatile acids may accumulate. Consistent with the earlier observations about bacterial acclimation, Table 18 shows that volatile acids were present in negligible concentrations in the assays containing 17% or less CE, but were present in much higher concentrations in the assays with 25% or more CE. In many of the more concentrated assays, there was net production of propionic and butyric acids during the test period. These results call attention to the sequential nature of the methane generation process and emphasize the fact that a bottleneck at any step can control the rate of conversion of complex organics to methane.

Summarizing the batch bioassays of CE, some compounds in CE apparently inhibit the breakdown of short-chain acids and methanol. The breakdown of larger, more complex molecules may be inhibited as well. The inhibition involves a lag period during which no gas is produced, and this period gets progressively longer as the CE concentration increases. There is also a

Table 18. Volatile acids concentrations before and after batch bioassays of caustic extract.

Anaerobic Toxicity Assay

	Calculated Initial Concentration (mg/l)			Measured Final (216 days) Concentration (mg/l)		
Bottle	Acetic	Propionic	Butyric	Acetic	Propionic	Butyric
Spike	1750	-	-	38 ± 6	<10	<8.8
8.3% CE	1990	8.5	16	32 ± 2	<10	<8.8
17% CE	2220	17	32	30	<10	<8.8
25% CE	2460	26	48	230	156	<8.8
42% CE	2930	42	81	2350 ± 440	252 ± 7	601 ± 1
50% CE	3170	51	97	2770 ± 90	253 ± 6	684 ± 1

Biochemical Methane Potential

	Calculated Initial Concentration (mg/l)			Measured Final (218 days) Concentration (mg/l)		
Bottle	Acetic	Propionic	Butyric	Acetic	Propionic	Butyric
8.3% CE	236	8.5	16	32	<10	<8.8
42% CE	1180	42	81	678 ± 218	228 ± 85	432 ± 85
58% CE	1651	51	97	1230	280	583

Note: Value are mean ± standard deviation; < indicates no peak occurred on the chromatogram output. Value given is from standard curve for zero area.

decrease in gas production rate once the lag period ends, but it is not clear whether this rate reduction becomes more severe with increasing CE concentration.

There may be significant advantages to be gained by exposing organisms to incrementally higher concentrations of CE to allow acclimation of the organisms to inhibitors or toxicants in the solution. Acclimation to higher concentrations may allow more rapid utilization of organics fermented during both the first and second stages of gas production and may increase the fraction of the COD ultimately fermentable to methane. Further work is required to test this hypothesis and to determine the limits of its applicability.

Continuous Flow Treatability Studies

Batch tests provide useful information about the degree of treatment that may be attained and about possible problems of toxicity and their mitigation by acclimation of the microbial culture. However, they are not completely reliable as predictors of the performance of continuous flow reactors. Usually continuous flow tests are required at both a bench and pilot plant scale to establish design parameters and demonstrate feasibility of anaerobic treatment of industrial wastes.

Bench scale continuous flow tests were conducted with the reactor illustrated in Fig. 44 over a period of about 5 months. During portions of the time synthetic waste was used at loading rates of 5 to 10 g COD/L day. However, for a duration of 3 months, various mixtures of Mill A SEC and Mill C CE were fed to the reactor after dilution with tap water and addition of nutrients and base. Loading rates for the real waste mixtures were also in the range of 5 to 10 g COD/L day. It should be kept in mind, though, that a

significant portion of the CE waste is not biodegradable; the 5 day BOD loadings were in the range of 2 to 4 g/l day. The dilution of the SEC/CE mixture with tap water was initiated when preliminary attempts to switch from synthetic waste to an undiluted mixture of CE and SEC were unsuccessful. Treatment efficiency dropped markedly when the CE fraction reached 25%. It is possible that with longer acclimation periods, more concentrated solutions could have been treated. The results reported here are for "pseudo-steady state" periods of reactor operation, i.e. periods during which the feed composition and operating conditions were held constant, and the performance of the reactor was stable. Characteristics of the feed solution and operating conditions during each test are summarized in Table 19, and the performance of the reactor in each case is summarized in Table 20. In each test, about 75% to 85% of the COD in the feed was contributed by the CE. Nutrients and alkalinity were added to the feed solutions to support biological growth and to attain feed pH of 7.0 in the first 2 tests.

The results during the steady-state periods show 70 to 80% removal of BOD, lower than often found with aerobic processes treating readily degradable, non-toxic wastes. In the first trial, volatile acids were found to include about 150 mg/L acetic, 35 mg/L propionic, and 10 mg/L or less butyric. Propionic and perhaps butyric acids were produced during treatment, while acetic acid decreased by about 80% from the feed concentration. The volatile acids, which are readily degradable, accounted for a large fraction of the effluent BOD in the first trial.

Removal of COD and TOC were in the range of 42% to 51%, reflecting the substantial fraction of non-degradable organics in the CE waste. Our prior estimate was of anaerobic degradability of CE COD, which is that roughly 50% of the COD and most of the BOD in caustic extract is anaerobically or

Table 19. S.M.A.R. steady states: operating conditions.

Parameter	Steady State Designation 1	2	3
Organic Loading[1]			
g COD/l reactor void vol/day	6.3	6.5[2]	7.8
g BOD_5/l reactor void vol/day	2.9	3.4	3.6[3]
Average Hydraulic Loading (l/hr)	1.1	1.0	0.93
Feed Composition	12.5% CE	19% CE	19% CE
	25% SEC	25% SEC	25% SEC
Na_2CO_3 Added (meq/l)	17.5-21.0	17.0-20.8	NONE
Feed pH	6.7	6.9	4.6
Recycle Ratio (Q recycle/Q feed)	4.2-5.0	5.0-5.2	5.4
Number of Sampling Days	5	5	2

NOTE: Values are averages, or range.

1. Loadings calculated from average feed COD or BOD_5 and hydraulic loading may not agree with the above values due to differences in feed batch duration.

2. COD values for steady state 2 are low due to contaminated silver catalyst.

3. BOD_7 basis.

Table 20. S.M.A.R. steady states: results.

Parameter		Steady State Designation 1	2	3
BOD_5 (mg/l)	Feed	2070 ± 40	2570 ± 100	3050[1] - 3070
	Effluent Total	450 ± 20	760 ± 30	650[1] - 750
	Soluble	450 ± 80	720 ± 30	730[1]
	% Removal Total Soluble	78(78)	71(72)	77(76)
COD(mg/l)	Feed	4680 ± 150	5190[2] ± 50	6270 - 7300
	Effluent Total	2330 ± 80	3000[2] ± 30	3290 - 3700
	Soluble	2090 ± 60	2750[2] ± 80	3290
	% Removal Total Soluble	50(53)	42(47)	49(52)
TOC(mg/l)	Feed	1800 ± 60	1980 ± 80	------
	Effluent Total	1000 ± 100	1050 ± 30	------
	(Soluble)	890 ± 70	1000 ± 30	------
	% Removal Total (Soluble)	44(51)	47(50)	------
Normalized Gas Production				
1 gas/g BOD_5 fed		0.50 ± 0.03	0.42[3] ± 0.07	0.52[1] - 0.54
1 gas/g COD^5 fed		0.22 ± 0.003	0.22[3] ± 0.01	0.22 - 0.26
Gas Composition (% methane)		-----	75 ± 2	-----
Effluent pH		7.4 ± 0.1	7.4 ± 0.1	7
Effluent Alkalinity (meq/l to pH 4.5)		40.0 ± 1.3	52.2 ± 2.0	about 29

COD, BOD, and TOC values are mean ± standard error. The rest are mean ± standard deviation.

1. BOD_7 basis
2. COD values are low due to contaminated silver catalyst
3. Value is high due to errors in COD values.

aerobically degradable. There were insufficient data to refine this estimate. However, there was also no evidence that removal occurred by any process other than aerobic fermentation to methane and carbon dioxide.

The trials substantially verified the observations from the bottle tests about the toxicity of CE. There were similar BOD removal efficiencies with 12.5% and 19% CE. However, the BOD effluent concentrations increased significantly at the 19% CE fraction, perhaps indicating incipient inhibition or toxicity to the methane-formers. Bottle tests showed inhibition of gas production and COD removal at a similar CE fraction.

A major objective of the continuous flow studies was to investigate the neutralization of SEC with CE. In the first 2 trials, about 20 meq/L of alkalinity were added to the SEC/CE mixture; the effluent pH was always well above 7, and the effluent alkalinity was about 20 to 30 meq/L higher than in the feed. In the third trial, at CE and SEC percentages of 19 and 25, respectively, the feed pH was 4.6. The effluent pH was very close to 7 and stable. The effluent alkalinity was 29 meq/L. The titration curves and calculated buffer intensities are shown for feed and effluent for this trial in Fig. 51.

The pH and alkalinity increases are caused by the biodegradation of a major portion of the carboxylic acids. This can be noted as a decrease in buffer intensity at pH values below 5 in the effluent. There is destruction both of strong carboxylic acids (those providing buffer intensity at pH below 4 in the CE) and acetic acid (with maximum buffer intensity at pH 4.7 in the SEC). Carbon dioxide, bicarbonate, and carbonate appear as major contributors to the effluent buffer intensity with peaks at pH 6.3 and 10. The minimum amount of CE needed to neutralize SEC has not been precisely determined. It has already been noted that CE alkalinity to pH 4.5 is an imprecise indicator

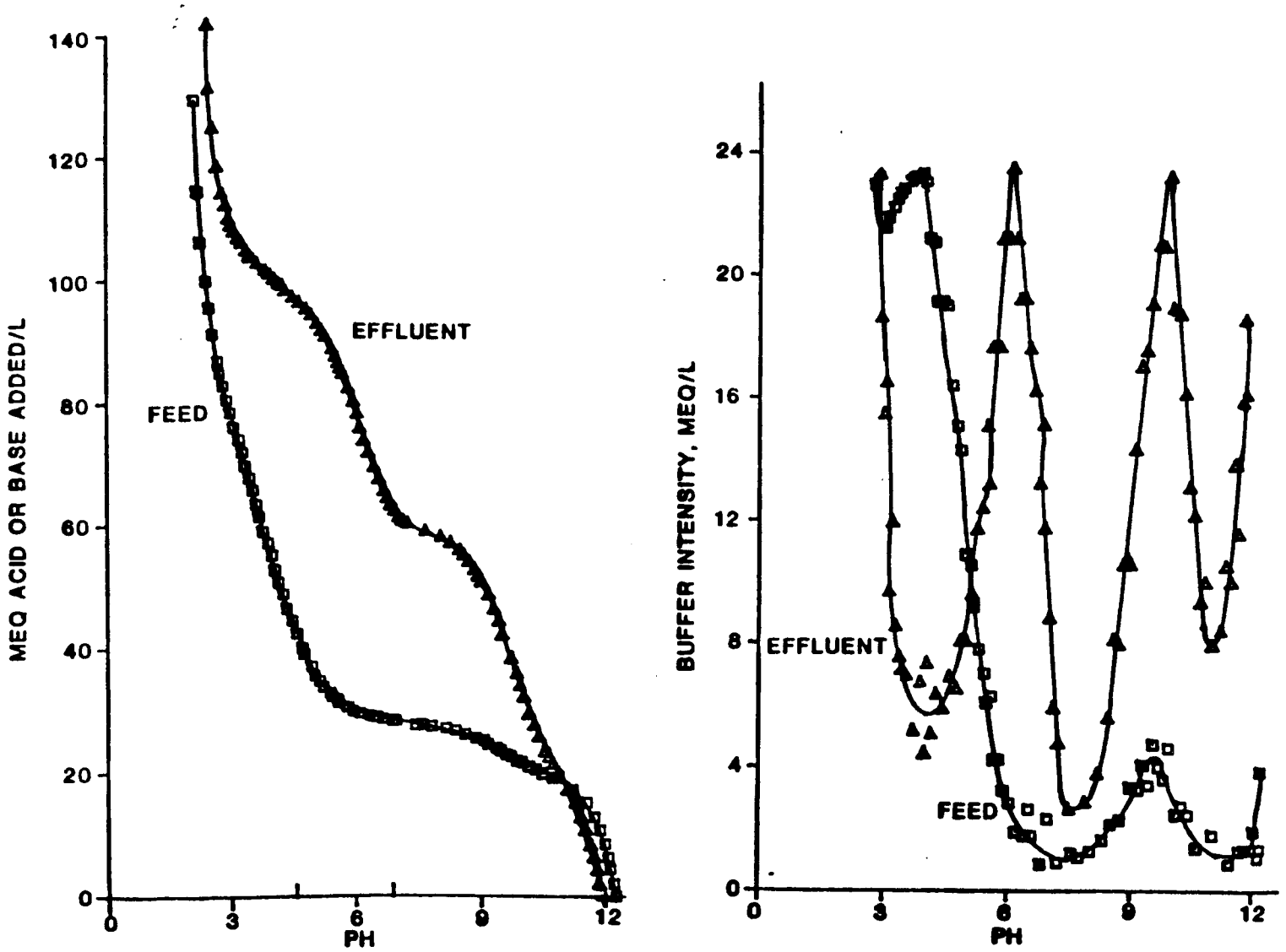


Figure 51. (a) Titration curves for steady state #3 feed and effluent samples. (b) Buffer intensity for same samples.

of neutralizing capacity because there is no reasonably sharp endpoint anywhere near pH 4.5. In addition, the amount of neutralization provided and the process efficiency are implicitly related. On one hand, a near-neutral pH is required for effective process performance. At the same time, improved process performance means more of the acids in the feed will be converted to carbon dioxide and bicarbonate. Whereas, the acids would require neutralization, the carbonate species do not. Thus, increased neutralization improves process performance, which in turn reduces the need for neutralization. Empirically, a feed pH of 4.6 or so is probably near the minimum tolerable. The SEC mineral acidity (to pH 4.5) is then a good estimator of the amount of neutralization needed in the feed. To a first approximation, CE alkalinity (pH 4.5) and base addition should balance the mineral acidity of the SEC. Bioconversions should result in an increase in reactor pH and alkalinity suitable for maintaining anaerobic treatment. The pH in the influent zone must also be in the neutral range, so a high recycle ratio or backmixing are required.

Some properties of the anaerobic reactor effluent were characterized further by using it in ATA and BMP tests. The test results were consistent with inferences drawn based on both the reactor performance and tests on mixtures of SEC and CE prior to treatment. The inhibitory substances which cause a lag between inoculation and utilization of methanol and a further lag period before utilization of acetate are apparently unaltered by passage through the reactor. Each of these lags is observed in the ATA of reactor effluent, and the duration of each lag period increases with decreasing dilution of the sample (Fig. 52). Even after 70 day's incubation there was no evidence that any of the organics in the reactor effluent were being fermented to methane, supporting the suggestion that 50% COD removal and 80% BOD removal

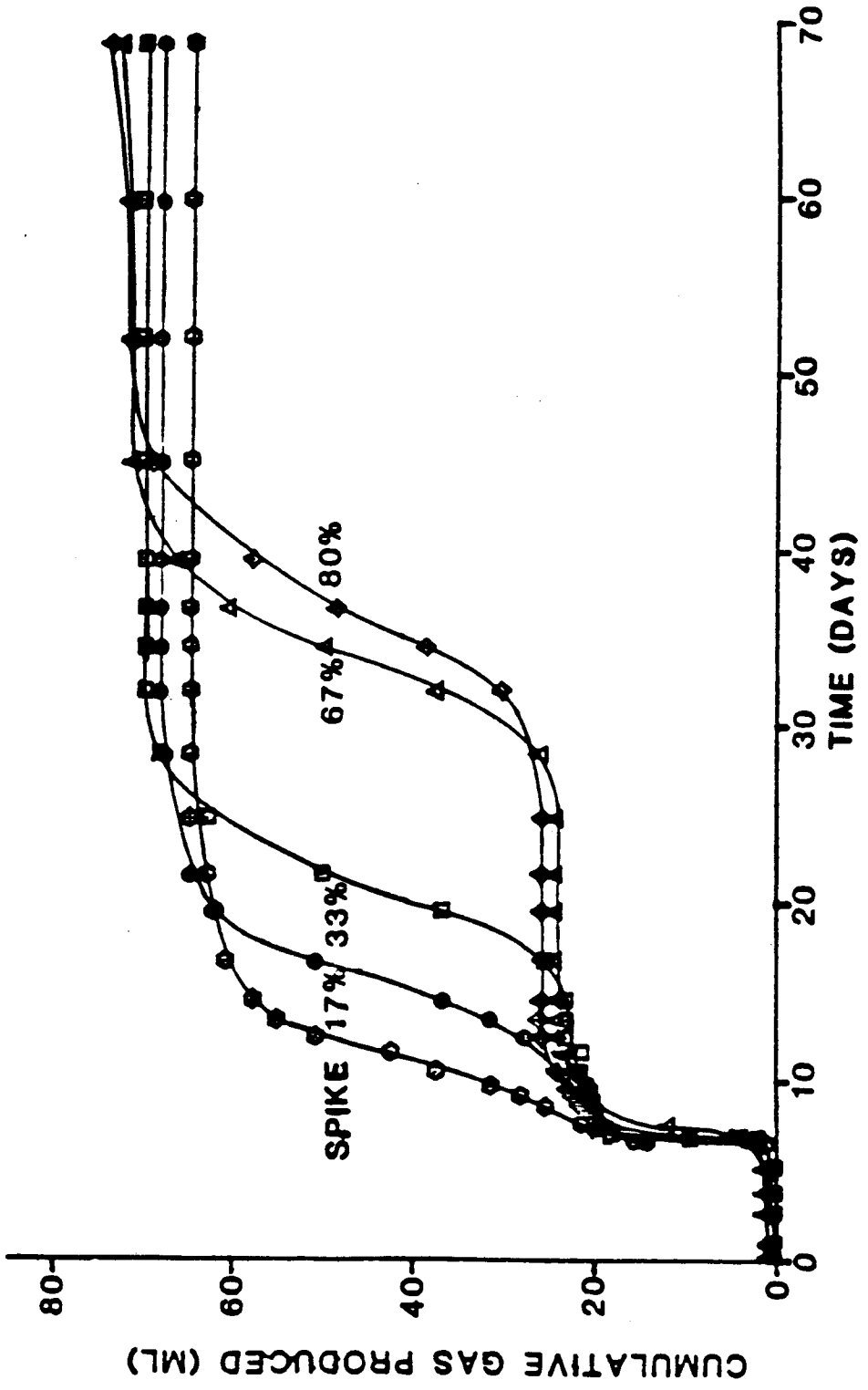


Figure 52. Anaerobic toxicity assay for steady state #3 effluent. Numbers represent concentration (% by volume) of effluent used in the test.

may be the maximum attainable efficiency for the CE/SEC mixture in this type of reactor. However, the result is still somewhat at odds with the results of the BMP's of SEC and CE individually, which showed that given sufficient time and dilution, the SEC was nearly 100% degradable. Other workers have also noted differences between the results of batch and continuous tests.[9] The reasons for such apparent anomalies are not well-understood.

Overall, the similarities in reactor performance among the 3 steady-state tests are probably more significant than the differences. While COD removals ranged from 40% to 50%, BOD removals were significantly better and were all between 70% and 80%. In the 2 tests where it was measured, TOC removal was about 50%. Significantly, the reactor was able to achieve these removal efficiencies in the third test with a low pH influent (4.6) and with no alkalinity added beyond that in the CE. While there was some suggestion that reactor performance deteriorates with higher organic loadings (test 2) or with higher concentrations of CE (data not presented), these observations cannot be generalized at this time. Optimization of operating conditions and bacterial acclimation may allow improved efficiency at higher loadings. Thus, these experiments demonstrate the applicability of anaerobic treatment to a CE/SEC mixture and represent minimum attainable process performance.

CONCLUSIONS

Caustic extraction waste is treatable in anaerobic systems after about five-fold dilution. About half the COD can be removed by conversion to methane and carbon dioxide. BOD removals are in the range of 70 to 80%. A significant portion of the carboxylic acids that provide the high buffer intensity at pH below 5 are removed in anaerobic treatment. At lower

dilutions, CE is inhibitory to methane formation, and short chain volatile acids accumulate.

CE waste is suitable for neutralizing SEC prior to anaerobic treatment. The relatively high alkalinity needed to maintain a stable pH in anaerobic systems may be a significant treatment cost in SEC treatment at some mills. CE can partially or completely eliminate the need for other base addition. CE alkalinity plus base addition in an amount equal to the mineral acidity of SEC is believed to approximate the minimum necessary neutralization.

Several phenomena were noted in the toxicity assays. CE caused discernible separate inhibitions of methanol and acetic acid fermentations to methane. Lag periods and decreases in rate and perhaps in extent of bioconversion were observed for methanol, first, and then for acetic acid. CE also inhibited the bacteria capable of degrading its own constituents. Organic conversion was about 50% complete at dilutions below 20% but decreased rapidly so that conversions were negligible at a 50% dilution.

REFERENCES

1. American Public Health Association, Standard Methods for the Examination of Water and Wastewater, 1980.

2. Benjamin, M.M., Ferguson, J.F., and Buggins, M.E., TAPPI, 65:96 (1982).

3. Buggins, M.E., MSE Thesis, University of Washington, Seattle, WA (1981).

4. Eis, B.J., MSCE Thesis, University of Washington, Seattle, WA (1982).

5. Eis, B.J., Ferguson, J.F., and Benjamin, M.M., Jour. Water Poll. Control Fed., accepted for publication (1983).

6. Ferguson, J.F., Eis, B.J., and Benjamin, M.M., Proc. IAWPR Specialty Conference on Anaerobic Treatment, Copenhagen (1982).

7. Owen, W.F., Stuckey, D.C., Healy, J.B., and Young, L.Y., Water Research. 13:485 (1979).

8. Sawyer, C.N. and McCarty, P.L., Chemistry for Environmental Engineering, McGraw-Hill, New York, 1978.

9. Stuckey, D.C., Owen, W.F., McCarty, P.L., Parkin, G.F., Jour. Water Poll. Control Fed., 52:720 (1980).

Chapter 7

TRANSIENT RESPONSE OF AN ANAEROBIC ROTATING DISK BIOREACTOR

Neil L. Ricker
Colin C. Felton
Joseph L. McCarthy

ABSTRACT

We describe the operation of 4 bench-scale rotating disk bioreactors used for the anaerobic treatment of a synthetic sulphite pulp mill wastewater. The primary organic constituents of the wastewater were neutralized acetate and methanol at 3 and 1 kg/m^3, respectively. The rotating disk design was effective in this research application although it was impossible to accurately determine the concentration of bacteria within the reactor during normal operation.

Both steady-state and transient modes of operation were studied. Steady-state kinetic parameters were within the range of those found in previous work. The transient response of the effluent methanol concentration indicated a slow adjustment in bacterial metabolism in response to changes in methanol availability. A simple dynamic model is proposed and used to simulate the transient responses. The model is as representative as more complex models and may be useful in future process control studies.

INTRODUCTION

Recent research has demonstrated that anaerobic treatment of industrial effluents can be an attractive alternative to the more common aerobic treatment processes (e.g., the activated sludge process). Haggerty et al.,[8] Benjamin et al.,[2] Priest,14 and Brune et al.[3] have studied the use of anaerobic treatment for sulphite and kraft pulp mill effluents, and Henze and Harremoes[9] and Olthof and Oleszkiewicz[12] have reviewed other applications. Recognized advantages of the anaerobic process are:[11] 1) low production of waste biological sludge; 2) low nutrient requirements; 3) no oxygen requirement (the provision of which is the major operating cost of the aerobic process); and 5) methane is the primary

degradation product and is a potential source of energy for use in the treatment process or in other unit operations. Disadvantages are the need to operate at elevated temperature, typically around 40C, and the slow reproduction rate of the anaerobic bacteria. The latter implies that a treatment process, once upset, may require days or weeks to recover, depending on the nature of the disturbance. A robust process control system is thus an important requirement for an indusrial application. Design of such control systems depends to a large extent on a fundamental understanding of the process dynamics.

The dynamics of the anaerobic treatment process are complex. The bacterial population is typically a consortium of different species working together to convert the organic matter in the effluent from large molecules into smaller fragments and, ultimately, to carbon dioxide and methane. The overall process efficiency is heavily influenced by the relative amounts and efficiencies of the various species present. Other important factors are

temperature, pH, waste concentration, and the presence or lack of inhibitory compounds.

The impact of these variables on the process dynamics has been considered by Graef and Andrews,[7] who developed a computer simulation of an anaerobic digestion system. Their model was able to reproduce the important qualitative features of the response of this process to disturbances, but it requires the specification of parameters representing the kinetics of bacterial growth and substrate utilization, many of which are not well established. The objective of the present work was to measure the transient response of a representative, well-characterized anaerobic reactor so that such parameters could be determined and the accuracy of alternative dynamic models could be verified.

THE EXPERIMENTAL SYSTEM

The Rotating-Disk Biological Reactor

The biological reactors used in the present work were similar to the rotating-disk reactor described by Tait and Friedman.[15] A side-view schematic of one of our reactor units is shown in Figure 53. Each reactor unit contains 2 well-mixed, cylindrical chambers separated by an internal wall. The cylindrical shell is plexiglass pipe, 25 cm diameter, with plexiglass end-plates. Each chamber contains a plexiglass disk with a diameter of approximately 23 cm and a thickness of 6 mm that is fixed to an axial stainless-steel shaft. The shaft passes through o-ring seals in the end plates. It can be coupled to a variable-speed motor (not shown) and rotated at speeds up to 20 rpm.

Ports are provided for the continuous addition of feed, removal of effluent, and removal of the gas produced by the bacteria. All internal

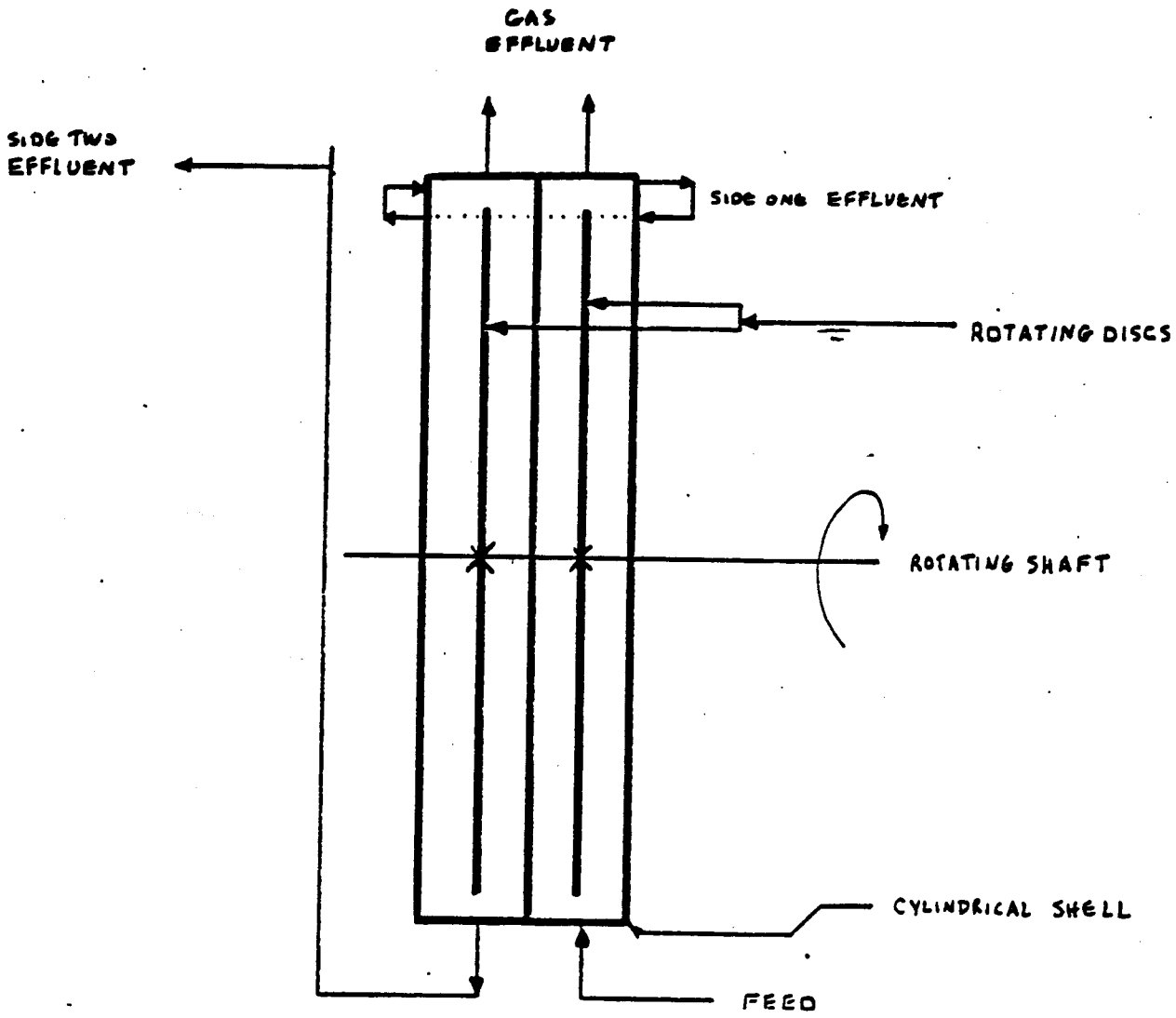


Figure 53. Schematic of Reactor

surfaces are roughened with sandpaper to promote attachment and growth of a bacterial film. Stable films could be obtained after a start-up period of about one month. The films were black and opaque at this point. The normal operating mode was to meter fresh feed into one chamber of the unit (with a Fluid Metering, Inc. positive-displacement pump). The effluent from that chamber flowed by gravity through external tubing to the other chamber to provide 2 continuously stirred tank reactors (CSTR's) in series. Each chamber was kept full of liquid; liquid level was controlled by the placement of an overflow leg. The reactor was kept horizontal as shown in the Figure.

The advantages of this design as a research unit are: 1) the disks provide for a degree of mixing in the fluid phase that is independent of the feed rate (and recycle rate, if any); 2) bacteria can be grown as a fixed film on the internal surfaces and/or as a suspension in the fluid phase; 3) gas disengagement is straightforward and each chamber's gas production can be measured independently; and 4) influent and effluent concentrations can be measured for each chamber. Tracer studies with the reactor full of liquid (but without bacterial growth) confirmed that each chamber did indeed act as a single CSTR in the range of rotational speeds used.

The Synthetic Wastewater

The primary organic constituents of the synthetic wastewater used in the present work were acetic acid and methanol. The former is a key intermediate in the anaerobic breakdown of more complex organics,[11] and it and methanol are the dominant organic substrates in sulphite pulp mill evaporator condensates.[5] We normally used concentrations of 1000 mg/l methanol and 3000 mg/l acetic acid in Seattle tap water, which has less than 40 ppm total dissolved solids. The feed was neutralized and buffered to approximately pH 6.8 and

trace nutrients were added. Standard amounts of all chemicals added are shown in Table 21.

Analytical Methods

The gas production rate and composition, and the effluent pH, temperature, composition and suspended-solids content were measured routinely in both steady-state and transient experiments. Gas was collected and its total volume measured by displacement of acidified water. The production rate was measured at appropriate intervals using a gas-bubble flow meter. The accuracy of this instantaneous rate could be checked against the collected gas volume. Proportions of methane and carbon dioxide in the gas were determined by FID gas chromagtography.

The reactors were housed in a temperature controlled room and the liquid feed was preheated to the desired operating temperature by passing the feed line through a water bath maintained at 38C. The pH of the effluent was measured continuously with an in-line pH probe attached to an Orion digital pH meter. In all experiments, the buffers in the feed solution kept the reactor pH between 6.8 and 7.2.

Samples of the feed and effluent were taken at appropriate intervals, acidified to pH 2, and stored at in a cold room at 1C for subsequent off-line analysis. This included the determination of the methanol and acetic-acid concentrations via FID gas chromatography (using a glass column, 1 m long and 2 mm i.d., packed with Porapak Q and operated at 160C) and the measurement of total suspended solids by filtration on Whatman GF/C filters followed by weighing (Standard Methods, 1971). COD measurements were also made at each steady-state. Overall material balances based on the GC analyses of the steady-state feed, effluent and gas streams agreed with the COD analyses to

Table 21. Composition of Synthetic Wastewater

COMPONENT	CONCENTRATION (kg/m^3)
Methanol	1.00
Acetic Acid	3.00
$NaHCO_3$	1.50
NaOH	1.82
NH_4Cl	0.126
$MgSO_4$	0.010
$(NH_4)_2HPO_4$	0.022
$FeCl_3*H_2O$	0.006
$COCl_2*2H_2O$	0.0008
$MnCl_2*4H_2O$	0.0016
$CaCl*2H_2O$	0.002
$ZnCl_2$	0.0008
Vitamin B_{12}	0.00002

within 5%, suggesting that the GC analyses were detecting all major oxidizable components and that flowrate measurements were accurate.

Other analyses were performed to better characterize the nominal steady-state operation of each reactor. These were done on a non-routine basis because it was necessary to shut down the reactor and remove a plug in each end-plate, allowing access to the reactor internals. The fluid contents of the reactor were drained and homogenized and the total mass of suspended solids in the drained fluid was determined as described above. The thickness of the biofilm on internal surfaces was then determined by pressing the edge of a microscope coverslip against the biofilm, allowing the coverslip to dry, and measuring the impression of the biofilm thickness with a hemocytometer. Biofilm densities were measured by scraping a sample of the film from measured surface area and weighing. Samples of the biofilm and the effluent from each chamber were examined microscopically to determine the relative proportions of the various bacterial species present.

EXPERIMENTAL RESULTS AND DISCUSSION

Steady-State Conditions

Steady-state measurements were performed on the 4 independent reactor units numbered 1, 2, 4 and 5. Note that the internal surface to volume ratio in reactor 5 is about twice that for reactors 1, 2 and 4. $R_{i,j}$ refers to the j^{th} chamber of reactor i, where 1 is the upstream chamber and is rightmost in Fig. 53. All of these runs used the nominal feed composition shown in Table 21. A reactor was deemed to be operating at steady-state when the routinely measured variables were constant over a period of 2 days. Table 22 summarizes the major results. Detailed results are given by Felton.[6]

TABLE 22. Steady-state Results

	REACTOR						
	R1,1	R2,1	R2,2	R4,1	R4,2	R5,1	R5,2
Residence time (h)	5.7	7.6	7.6	1.7	1.7	1.3	1.3
Surface area (cm^2)	2077	2077	2077	2077	2077	1920	1920
Volume (cm^3)	1660	1660	1660	1660	1660	707	707
Eff. acetate (kg/m^3)	0.44	0.71	0.05	2.72	1.63	2.33	1.03
Eff. methanol (")	.009	.003	0.00	.242	0.00	.065	.003
Effluent VSS (")	.096	.162	.055	.098	.045	.073	.143
Acetate consum. ($kg/m^3/d$)	10.8	7.2	2.1	3.9	15.4	12.4	24.1
rate (kg COD/kg VSS/d)	1.1	3.1	1.4	1.1	1.3	3.5	2.3
CH_3OH consumpt. ($kg/m^3/d$)	4.2	3.1	0	10.7	3.4	13.5	0.5
rate (kg COD/kg VSS/d)	0.62	1.8	0	4.4	0.40	6.8	0.07
Net VSS prod. ($kg/m^3/d$)	0.40	0.51	-0.33	1.36	-0.72	1.4	1.3
rate (kg VSS/kg COD)	0.022	0.041	-0.15	0.067	-0.03	0.036	0.049
Biofilm thickness (mm)	0.5	0.4	0.2	n.a.	5.0	0.2	0.1
Total reactor dry solids (g)	17.0	4.2	2.5	6.1	21.0	2.7	7.8
Est. VSS in react. (kg/m^3)	9.3	1.8	1.1	n.a.	3.3	2.93	11.0

NOTES

1) COD is chemical oxygen demand calculated from molecular structure
2) VSS is mass of volatile suspended solids, dry basis
3) (g/l/d) is grams substrate consumed (or grams VSS produced) per liter of reactor volume per day
4) (kg COD/kg VSS/d) is kg of COD of substrate consumed (see note 1) per kg VSS in the reactor per day
5) (kg VSS/kg COD) is the mass of VSS produced per kg total COD consumed, i.e., the yield coefficient.
6) n.a. means the measurement or calculated value was not available
7) a methanol concentration of zero in the effluent implies that the actual concentration was too small to detect accurately
8) a zero rate of methanol consumption implies that the feed was too dilute for calulation of the actual consumption rate.

Removal Efficiencies and Kinetic Parameters

Overall removal efficiencies for acetate (per chamber) ranged from a high of 93% in $R_{2,2}$ at a residence time of 7.6 hours to a low of 9% in $R_{4,1}$ at a residence time of 1.7 hours. The average efficiency was 54%. Removal efficiencies for methanol were generally much higher than for acetate, averaging 95%. Only $R_{4,1}$, where the removal was 76%, exhibited a methanol removal below 90% and in 2 cases ($R_{2,2}$ and $R_{4,2}$) the methanol was removed to below detectable limits.

For both substrates, removal efficiency increased with increasing residence time. We could easily have attained high removal efficiencies by operating at longer residence times, but this would have made it difficult to follow transients in the effluent concentrations, which were already approaching the lower limit of detectability in some cases.

The dimensions used in Table 22 to report the acetic acid and methanol consumption rates and the net solids production rates are those in common use in the anaerobic-treatment literature. Pooler[13] and others[13] have summarized values reported by previous researchers. For methane-formers, values of the net solids production rate range from 0.02 to 0.14 kg VSS per kg COD consumed, with an average value of 0.04. If we ignore the negative values shown in Table 21, our results are completely within the expected range and our average value is also 0.04.

In both cases in which we observed a negative net solids production rate, the chamber in question was the second of 2 in series and the methanol concentration in the effluent from that chamber was very low. It is possible that bacteria specific to methanol consumption were being carried over from the first chamber, and, lacking a significant amount of substrate, were being consumed.

Pooler[13] also reports maximum substrate consumption rates for methane-formers. These range from 0.4 to 12.3 kg of COD per kg of VSS per day. The maximum consumption rate of acetate observed in our steady-state experiments was 3.5, and the maximum rate for methanol was 6.8. We are still analyzing our steady-state and transient data for the values of other kinetic parameters, such as the Michaelis-Menten constants. Our steady-state data alone are insufficient to determine these constants with the necessary accuracy.

Previous researchers have suggested that anaerobic bacteria of the type considered here will consume methanol preferentially if both methanol and acetate are readily available. Some evidence of this can be seen in our results. In the second chamber of both reactors 4 and 5, the specific acetate consumption rate is 2 or more times larger than in the first chamber, where most of the methanol is being consumed, even though the acetate concentration is higher in the first chamber. This competitive utilization of substrate makes the system difficult to model in a simple manner.

Reactor Bacterial Population

Measured biofilm thicknesses varied by more than an order of magnitude, as shown in Table 22. Our values are typical of those measured by previous researchers.[13] Films in the first of 2 chambers, i.e., having the higher methanol concentration, appeared more dense than those in the downstream chamber. Microscopic examination of the former indicated a large population of Methanosarcina, which metabolizes both acetate and methanol.[17] These bacteria have a characteristic disk shape. The downstream chamber, on the other hand, contained mainly filamentous bacteria, tentatively identified as Methanothrix soehngenii. This species metabolizes acetate but not methanol.[10] The fila-

mentous character of the downstream bacteria was especially notable in $R_{4,2}$, where the 5mm film consisted of long seaweed-like strands. Brune et al.[3] observed similar bacterial populations in their experiments.

It is obvious from a comparison of the VSS in the effluent with the VSS in the reactor that solids are preferentially held up within the reactor. The internal VSS concentration is always 1 to 2 orders of magnitude greater than that in the effluent. During steady-state operation we could see large flocs of bacteria moving in a stable circular orbit within each chamber. The cross flow of liquid from the feed to the effluent was apparently insufficient to sweep these out of the chamber.

This was especially troublesome in the transient runs in which we had hoped to estimate the VSS in the reactor by measuring that in the effluent. We attempted direct measurement of reactor VSS during steady-state operation but it proved impossible to obtain consistent results. In future experiments we plan to recycle a portion of the effluent from a chamber to the feed inlet in order to provide more uniform washout of the bacteria.

Effect of Variations in Disk Rotational Velocity

We also ran a series of steady-state experiments at constant feed rate and concentration to determine the effect of variations in the disk rotational speed. We used reactor 1 for each of the 5 steady-states. In each run the disk speed was set to a value between 4 and 20 rpm and the reactor was allowed to come to steady-state. The order of the experiments (i.e., the variation in speed settings) was chosen randomly. The results showed a small but significant increase in the percent removal of COD with increases in rotational speed up to the limit of 20 rpm (further increases caused large sections of the attached film to be sheared off the reactor surfaces).

One possible reason for the above trend is an increase in the limiting mass transfer coefficient with increases in rpm. A more likely explanation, however, is an increase in the holdup of suspended bacteria due to the orbiting phenomena described above. Again, we were unable to measure the concentration of bacteria in the reactor with sufficient accuracy to distinguish between these 2 possibilities.

Transient-Response Experiments

Figs. 54 through 57 summarize the main results of 6 transient-response experiments. Three types of variations in reactor operating conditions were made: 1) a variation in the aqueous feed rate at constant feed composition, 2) a variation in the concentraion of acetate or methanol in the aqueous feed, and 3) a variation in feed rate with a simultaneous change in feed concentration so as to maintain a constant feed rate (i.e., "organic loading") for each chemical species. The response of the effluent concentrations of methanol, acetate and suspended solids is shown for each experiment. The plotted dependent variables are the concentrations of each component in the effluent normalized by the effluent concentration for that component at the initial steady-state. The independent variable is the elapsed time normalized by the space time. For experiments involving a step change in the space time (e.g., those in Fig. 54), the space time used for normalization is that after the step change. The initial concentrations and the residence time used for normalization are given in Table 23.

We also measured the transients in other variables such as pH, and gas production rate and concentration, but these variables were generally much less sensitive to process variations than the 3 shown in the plots. Detailed data are available in Felton.[6]

Transients in Effluent Suspended Solids Concentration

Any change in the operating variables resulted in an initial increase in the concentration of suspended solids in the effluent. Depending on the nature of the change, this concentration would then continue to increase with time or, in other cases, decrease to a value less than the initial concentration. For example, Figs. 54b and 57c both show that the response to an increase in aqueous feed rate at constant feed composition is a rapid increase of about 30% in the solids concentration, followed by a decrease to about 80% of the original value. Fig. 54c, on the other hand, shows that a decrease in the feed flowrate causes a gradual increase in the effluent solids. The same type of behavior is shown in Fig. 55a and 55b, which show the response to an increase and a decrease in feed rate at constant organic loading. In both cases the effluent solids concentration first increases by more than 100% and then gradually decreases to a value approximating the original steady-state condition.

In general, these transients were not what we would consider to be a "normal" response to the given disturbance. We expected responses like those reported by Brune et al.,[3] in which, for example, an increase in organic loading at constant feed flowrate caused a gradual increase in solids concentration, whereas a decrease in organic loading caused a gradual decrease in solids concentration. In our equivalent experiment, shown in Fig. 56, an increase in feed methanol concentration at constant feed flowrate caused an initial sharp 20% increase in effluent solids followed by a gradual decrease to a value 20% below that at the original steady-state. The overall COD removal rate increases by 30% over the course of the experiment, so the observed behavior does not appear to be due to substrate inhibition.

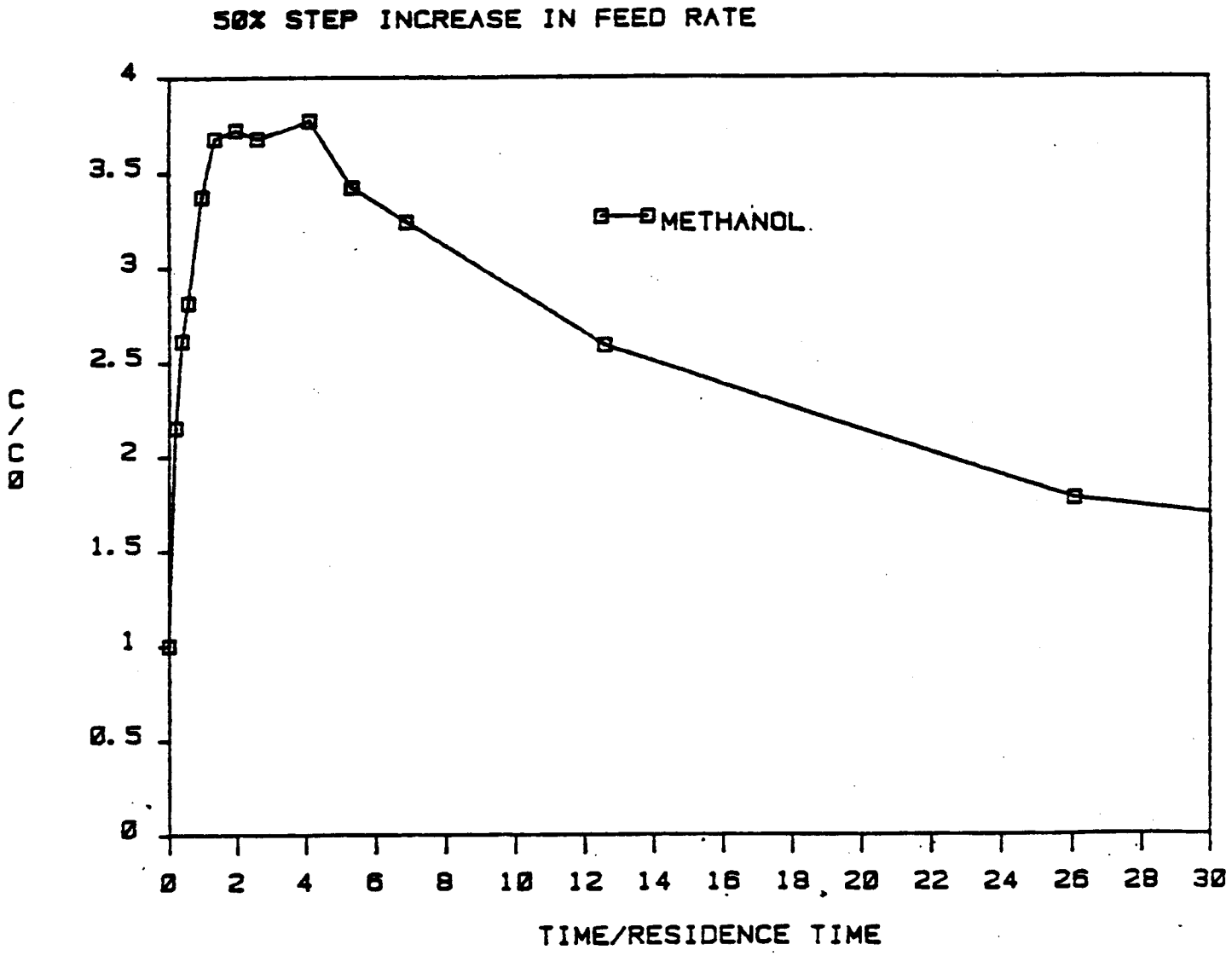


Figure 54a. Transient Response of Effluent Methanol Concentration to 50% Step Increase in Aqueous Feed Rate (Reactor 5,1).

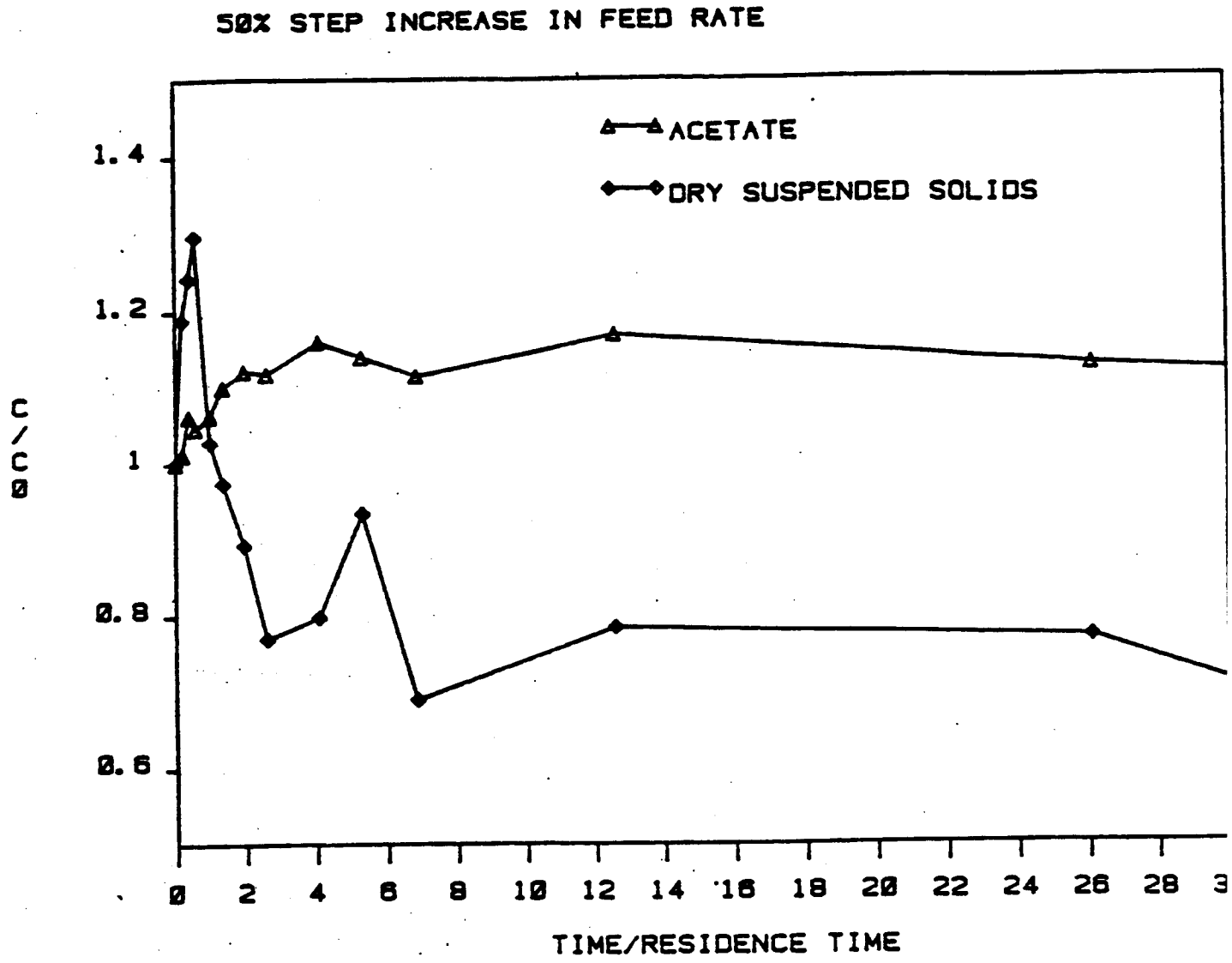


Figure 54b: Transient Response of Effluent Acetate and Dry VSS Concentrations to 50% Step Increase in Aqueous Feed Rate (Reactor 5,1)

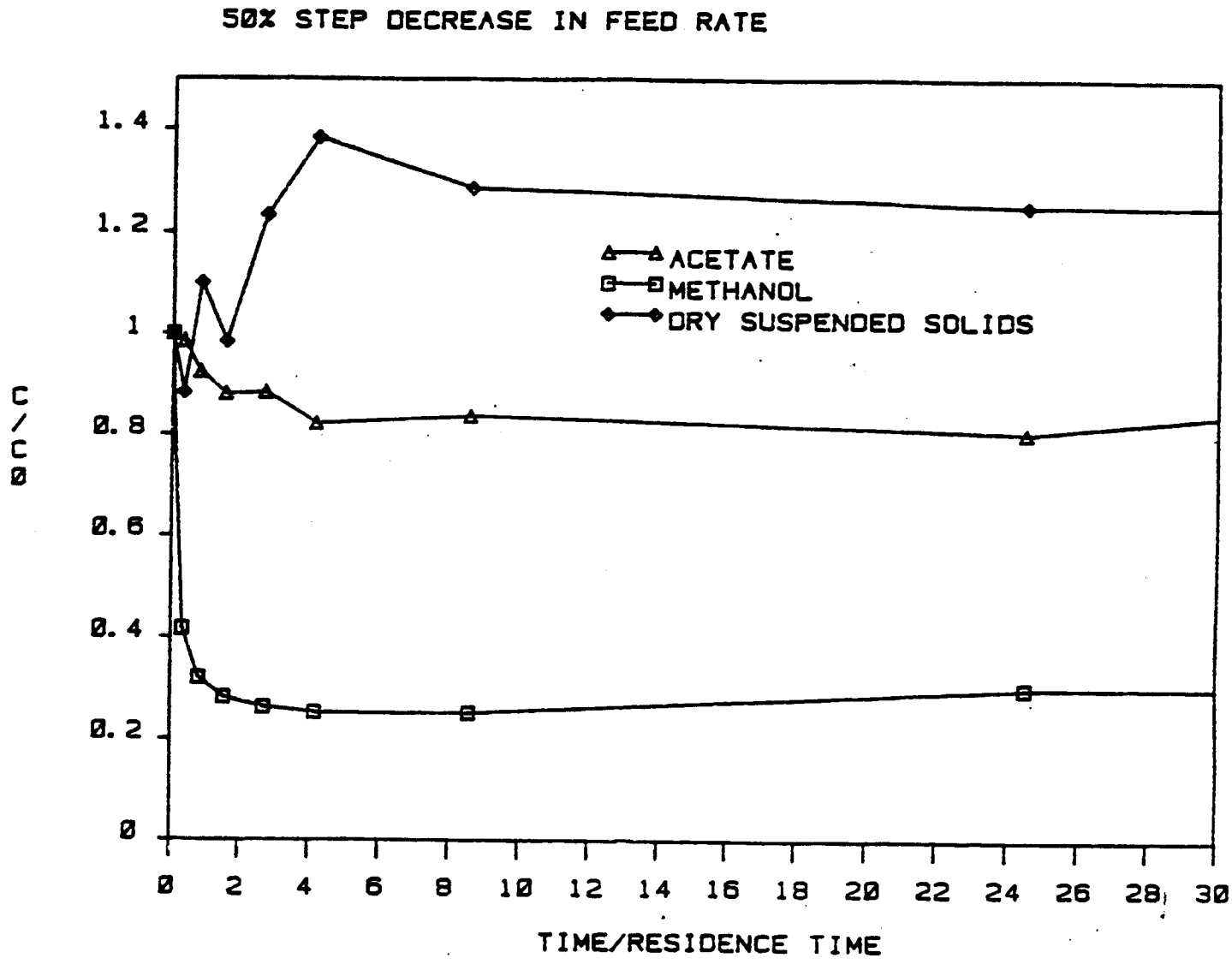


Figure 54c. Transient Response of Methanol, Acetate, and Dry VSS Effluent Concentrations to 50% Step Decrease in Aqueous Feed Rate (Reactor 5,1)

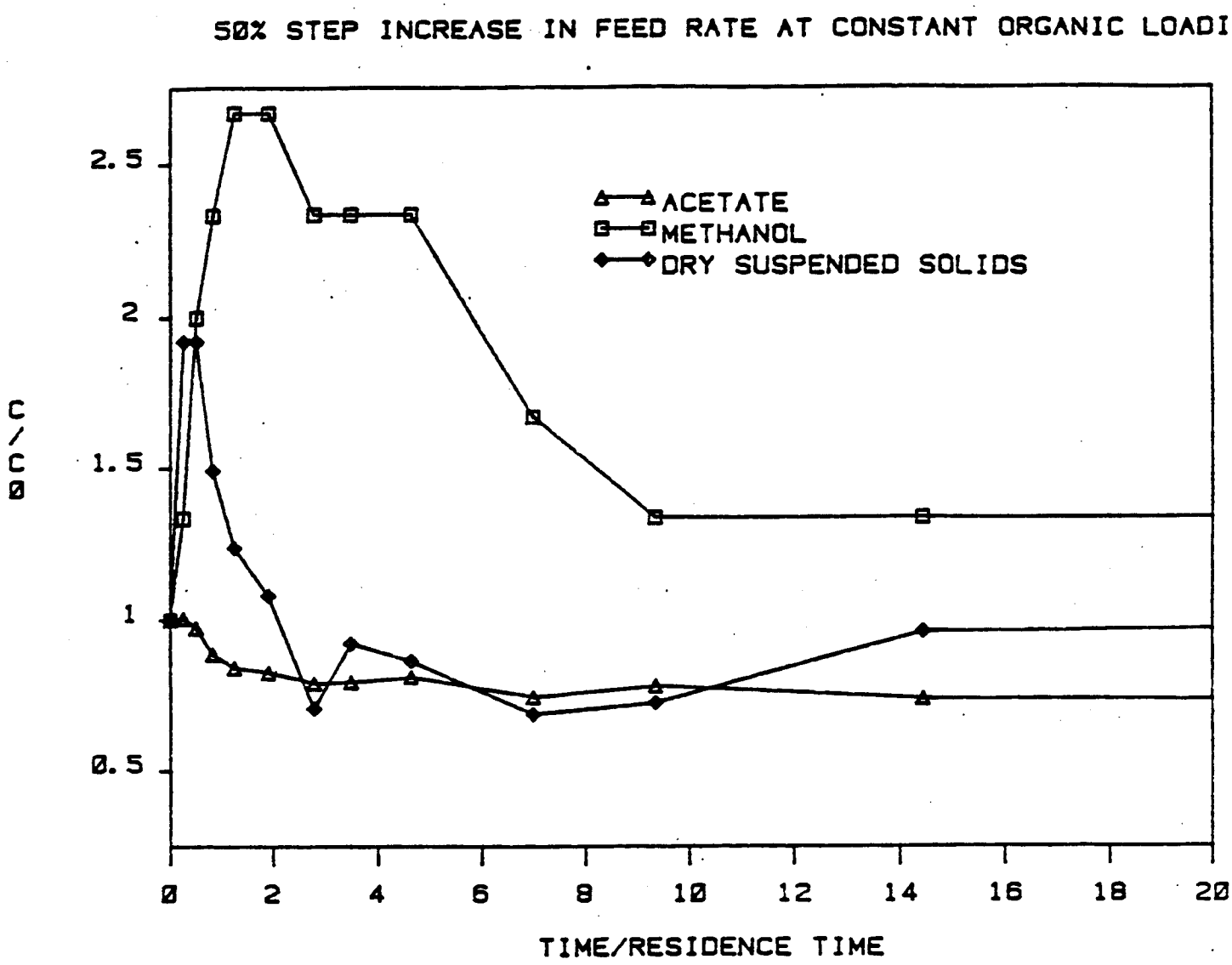


Figure 55a. Transient Response to 50% Step Increase in Aqueous Feed Rate at Constant Organic Loading (Reactor 5,1)

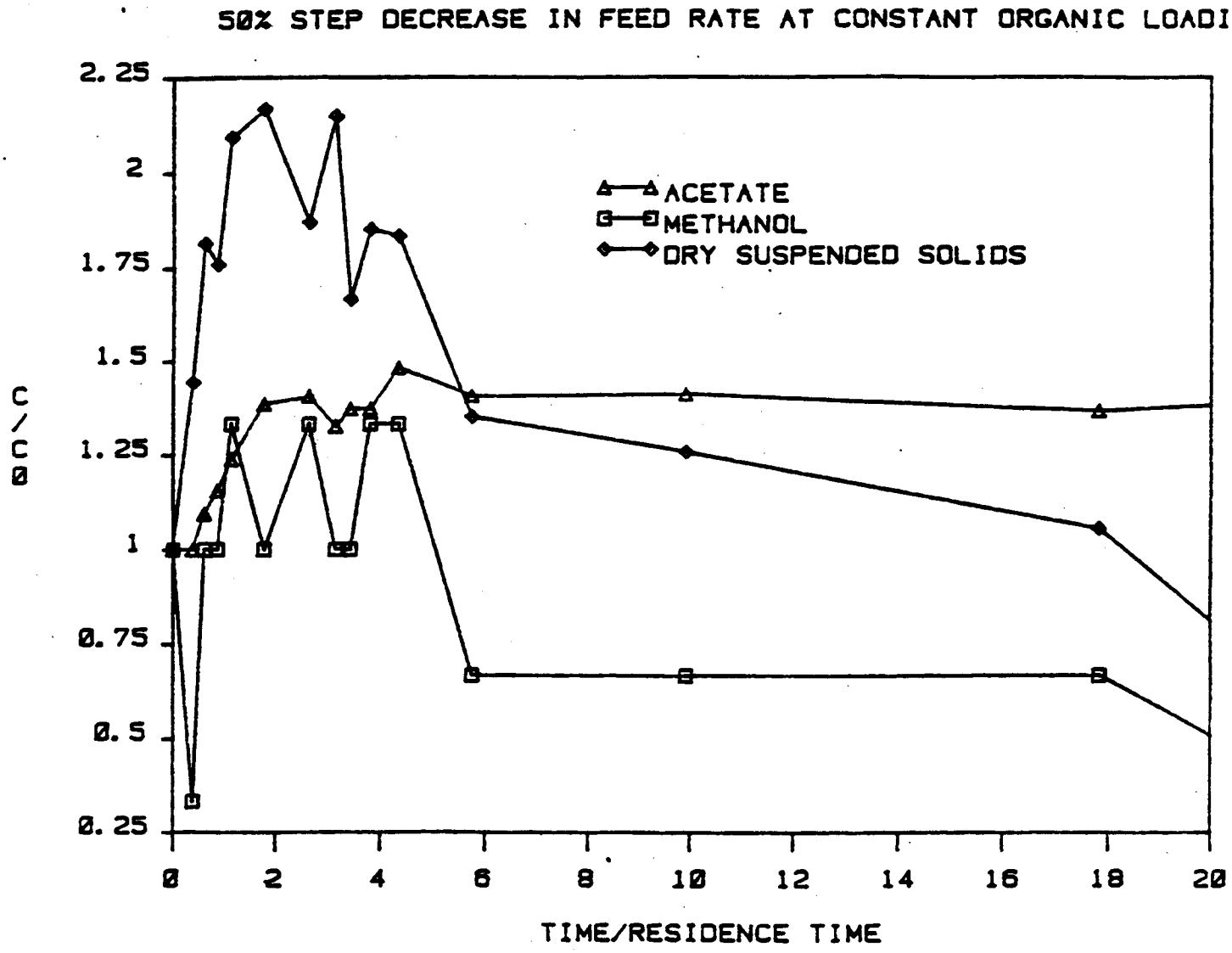


Figure 55b. Transient Response to 50% Step Decrease in Feed Rate at Constant Organic Loading (Reactor 5,1).

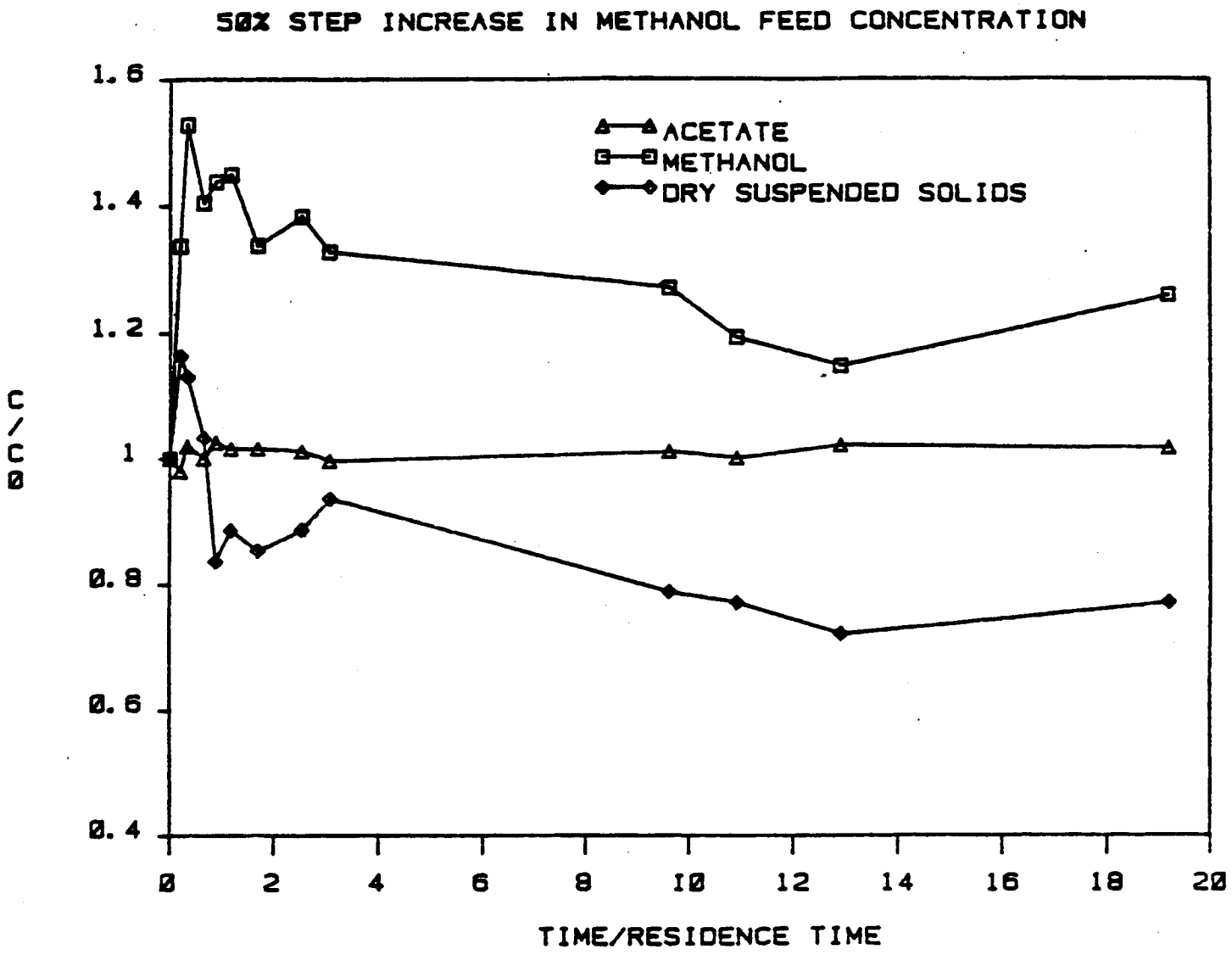


Figure 56. Transient Response to 50% Step Increase in Methanol Feed Concentration (Reactor 5,1).

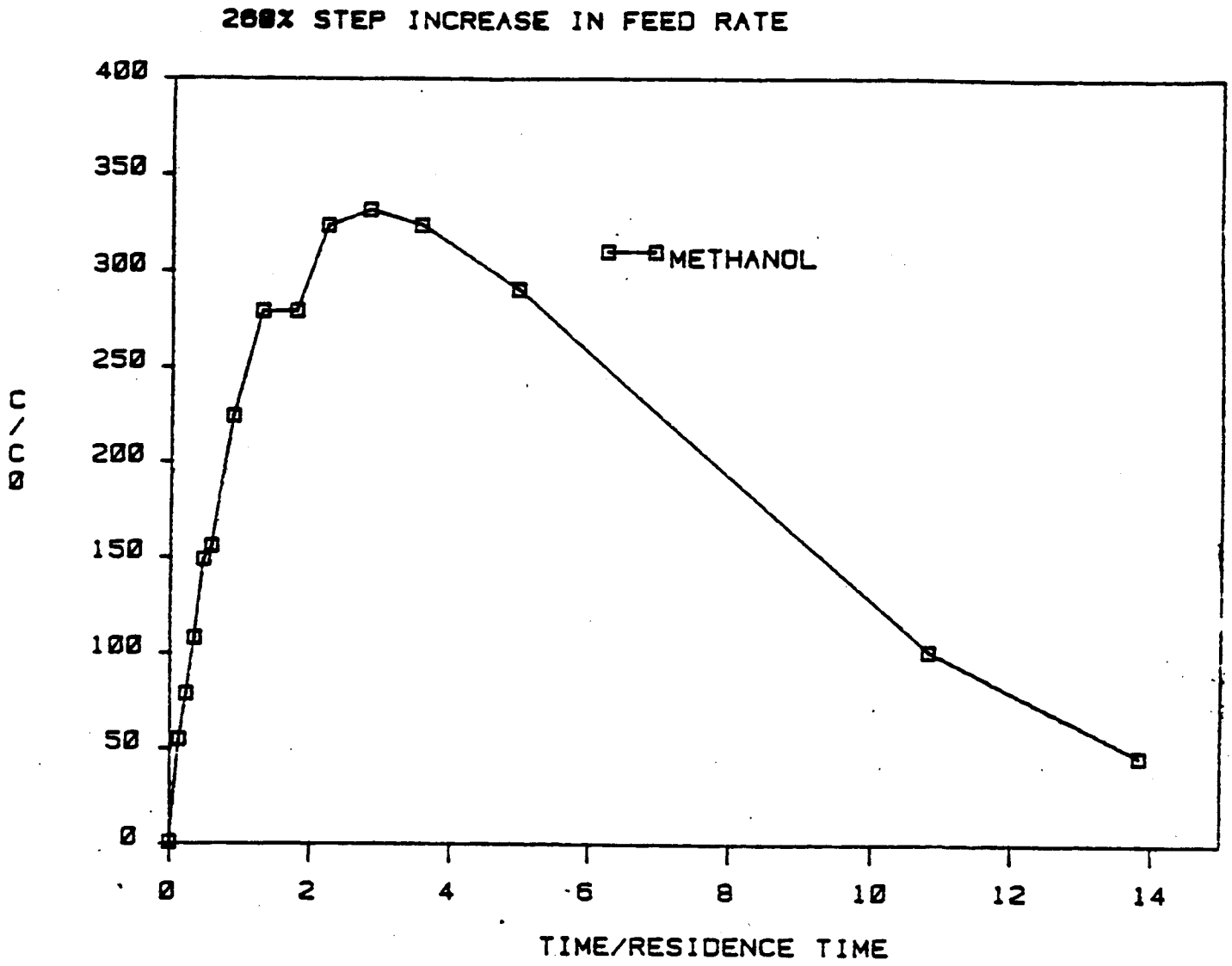


Figure 57a. Transient Response of Methanol Concentration to 260% Step Increase in Aqueous Feed Rate (Reactor 1,1).

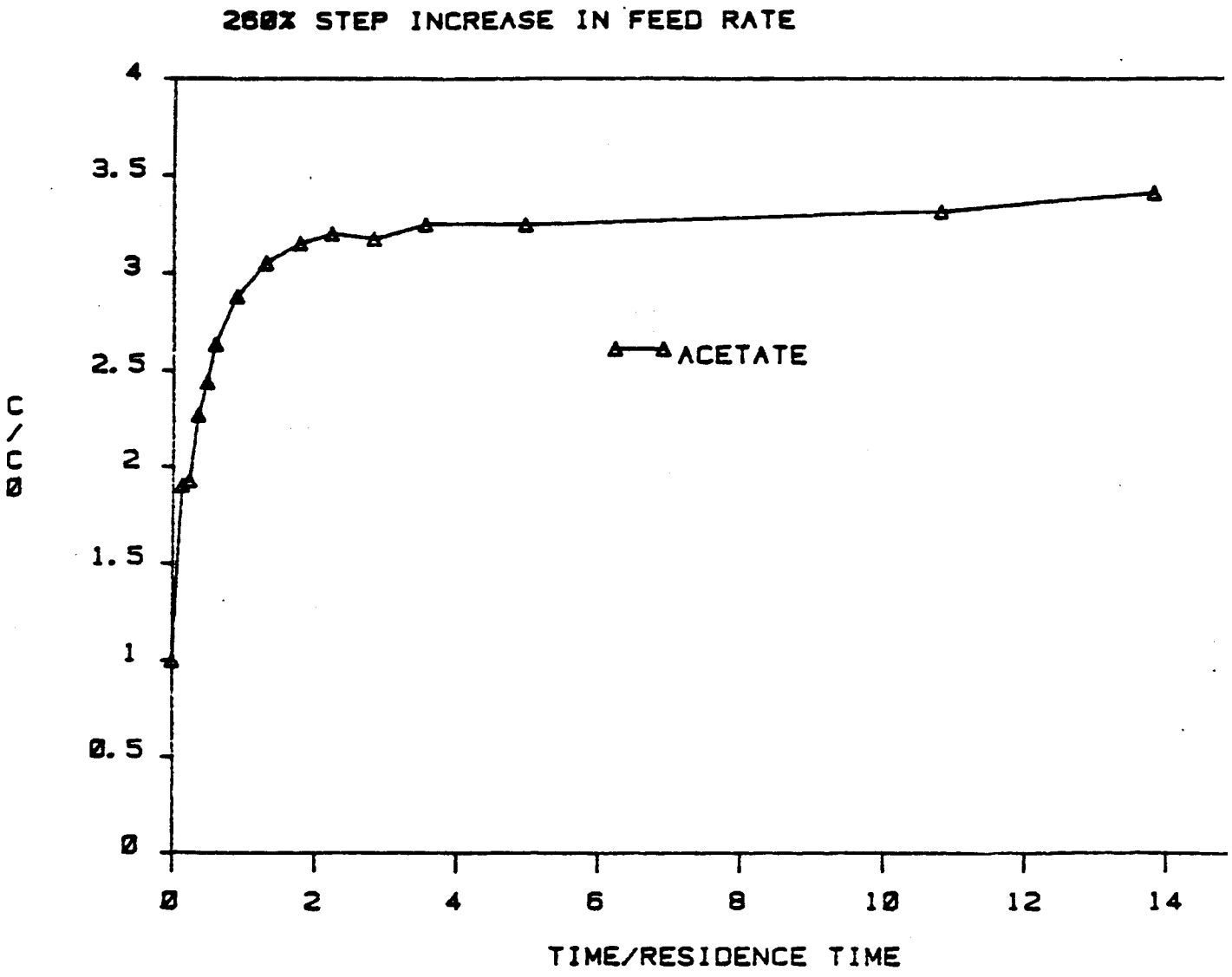


Figure 57b. Transient Response of Acetate Concentration to 260% Step Increase in Aqueous Feed Rate (Reactor 1,1).

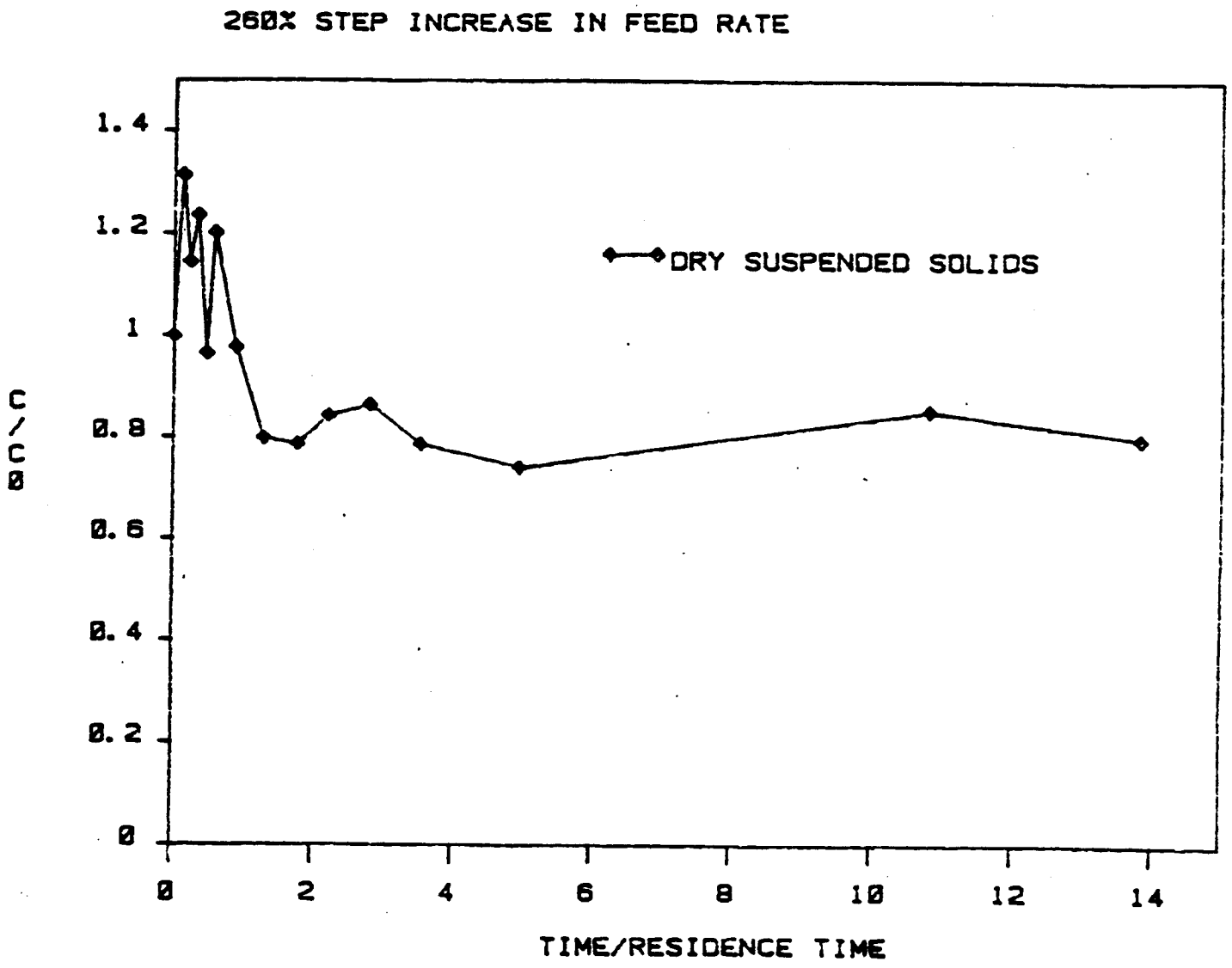


Figure 57c. Transient Response of Dry VSS Concentration to 260% Step Increase in Aqueous Feed Rate (Reactor 1,1).

TABLE 23. Summary of Conditions for Transient Runs

Figure	Step Change		Initial Concentrations			Res. Time (h)	Removal (or prod.) Rates			Chng. in Yield coef.
	Flow	COD Load	MeOH (kg/m^3)	Acet. (kg/m^3)	Solids (kg/m^3)		MeOH (mass)	Acet. (mass)	Total COD	
2a,b	+50%	+50%	0.065	2.39	0.074	0.91	+42%	+18%	+32%	-24%
2c	-50%	-50%	0.114	2.53	0.056	1.36	-27%	+33%	-3%	-58%
3a	+50%	const.	0.003	1.95	0.051	1.26	-3%	-23%	-11%	+70%
3b	-50%	const.	0.039	1.46	0.056	1.26	+2%	+8%	+4%	-36%
4	const.	+16%	0.089	1.94	0.061	1.33	+50%	0%	+30%	-39%
5	+260%	+260%	0.001	0.41	0.089	2.19	+150%	+60%	+110%	0%

Other possible explanations include: 1) variations in the rate of reproduction during the transient, 2) variations in relative amounts of the different bacteria, each having different fundamental (and roughly constant) reproduction rates, and 3) variations in floculation behavior of the suspended bacteria resulting in a change in the concentration of suspended bacteria in the reactor relative to that in the effluent. It is unlikely that explanations 1) and 2) are the cause of the consistently observed initial increase in effluent concentration. These increases could be seen almost immediately, e.g., within 15 minutes for the experiments shown in Figs. 55a and 55b. It is more likely that such sudden changes in operating conditions shock the bacteria, causing bacterial mass to be released from the attached biofilm or from the orbiting flocs.

Let us next consider the longer term effects. If we assume that the bacterial population is at steady-state at the beginning and end of each transient, then the mass flowrate of bacteria leaving in the effluent must equal the net mass rate of reproduction, (the feed is free of bacteria in the transient runs). Table 23 shows reproduction rates calculated in this manner along with the relative consumptions of each substrate. In each case, the value shown is the production (or consumption) rate at the end of the transient divided by that immediately preceding the step change. Table 23 also gives the apparent change in the "yield coefficient" from the beginning to the end of the experiment. The yield coefficient is defined as the mass of bacteria (or suspended solids) produced per mass of COD consumed and is calculated using the measured effluent concentrations. Note that the apparent yield coefficient decreases or remains constant in 5 out of the 6 cases. Moreover, there does not appear to be a correlation between the variation in the apparent yield coefficient and variations in other operating conditions, e.g., the relative

rates of consumption of methanol and acetate. This would seem to rule out 2) as an explanation for the longer term changes in apparent yield.

A more likely explanation is that variations in operating conditions shock the bacteria in a way that both causes the short-term sloughing of cells described above and longer term changes in overall metabolic processes. This, in turn, implies that the bacteria are not at a metabolic steady-state at the end of the transient, which is supported by other evidence to be discussed below.

Transients in Substrate Consumption and Effluent Concentrations

Transients in the effluent acetate and methanol concentrations were more informative than transients in effluent solids because we were able to demonstrate that the fluid phase within the reactor was well mixed. Figs. 54a and 54b show the substrate-concentration transients for a 50% step increase in feed flowrate at constant feed concentration in $R_{5,1}$. Approximately 30 hours after this initial disturbance, the feed flowrate was returned to its original value. Fig. 54c shows the resulting transients. Fig. 57 shows transients for a 260% increase in the volumetric flowrate entering $R_{1,1}$.

It is interesting to contrast the behavior of methanol and acetate in the 3 experiments. For both increases in feed flowrate (i.e., Figs 54b and 57b) the acetate concentration increases to a new level with only minor oscillations and exhibits approximately the reverse behavior for the decrease in feed flowrate. In all 3 cases, the effluent acetate concentration reaches what is essentially a constant value within 4-6 residence times after the start of the transient.

For methanol, however, an increase in flowrate (Figs. 54a and 57a) causes a sharp increase in the effluent concentration to a peak that occurs after

about 2-4 residence times, and the concentration then gradually decreases to a value that is more than 50% lower than the peak value. Such peaks in the methanol concentration also occurred in the transients shown in Figs. 55a and 56. In Fig. 54c, however, the methanol concentration drops sharply to 30% of its initial value within about 2 residence times and stays at that level for the next 24 residence times, a period of about 32 hours.

One explanation for the peak in the methanol concentration is that an increase in the availability of methanol causes a slow increase in the population of methanol-consuming bacteria. If the time constant for the change in population were substantially larger than the hydraulic residence time, which is likely in the case of the short residence times (about 1 hour) used in our experiments, then we might expect such a peak. There was, however, no evidence for an increase in the bacterial population. Figs. 54b and 57c, for example, show that the concentration of suspended solids in the effluent is actually less than the initial value during all but the very beginning of the transient period.

A more plausible explanation is that the methanol peak is due to a gradual change in the metabolic processes of the existing population. An increase in the availability of methanol could, for example, initiate the production of additional cell proteins needed in the degradation process. Chi and Howell[4] derived a dynamic model of aerobic phenol degradation in which they accounted for this type of phenomenon. The data and model predictions in their Fig. 56a (corresponding to an increase in feed flowrate, as in our Figs. 54 and 57) are very similar to our methanol transients.

Chi and Howell also compared their predictions with the more common type of dynamic model in which the specific substrate consumption rate is a static function of substrate concentration, e.g., as in Michaelis-Menten

kinetics or the cell-growth model of Williams.[16] The resulting transient in the substrate concentration is similar to that for acetate in the present work, i.e., there is no peak in the concentration.

The lack of a peak in the methanol transient in our Figure 54c suggests that the protein production process is not reversible in the usual sense. In other words, having built up protein levels in response to increased methanol availability, the bacteria are slower to decrease these levels in response to a subsequent decrease in methanol availability. We would, however, expect the methanol to gradually come back to the concentration that was obtained at the beginning of the transient in Fig. 54a (which corresponds to a value of 0.57 in Fig. 54c), as suspended bacteria wash out and film bacteria slowly change their metabolism.

MATHEMATICAL MODELING AND ANALYSIS

One of the initial goals of the present work was to derive a dynamic model of the anaerobic treatment system that could be used for control studies and as a way of gaining insight into the biological mechanisms. Unfortunately, it is difficult if not impossible to derive a model that is truly representative of all the behavior observed in our transient response experiments. The transients in effluent solids concentration, in particular, are poorly understood, as discussed previously, and are at variance with the established, simple models of bacterial growth. Transients in the substrate concentrations, however, are at least qualitatively similar to those of previous researchers.[4] We have investigated the characteristics of the Chi and Howell model and several variations. What follows is a relatively simple model of substrate

degradation that fits the data as well as the more complex Chi and Howell model and may be useful in process-control studies.

The instantaneous rate of consumption of substrate and the instantaneous growth rate are assumed to obey the following relationships:

$$R = \frac{1}{Y}\,\mu \tag{1}$$

$$\mu = Q\,\mu_{max} \tag{2}$$

where R is the instantaneous rate of substrate consumption [kg/kg bacteria/d], s is the substrate concentration in the bulk fluid and in the bacteria [kg/m^3], K_s and μ_{max} are the usual Monod parameters,[1] Q is a metabolic activity that depends on the past history of the population, μ is the instantaneous specific growth rate [d^{-1}] and Y is the yield coefficient [kg bacteria produced/kg substrate consumed]. We assume that at steady-state the expression for μ takes the standard Monod form so that $Q = s/(K_s + s)$ at steady-state.

We next determine the way in which Q approaches its steady-state value. We assume that the driving force for a change in Q is the difference between the current value of Q and the value that could ultimately be attained if the substrate concentration were to stay at the current value. If we assume that the rate of change of Q is first-order with respect to this driving force, then we get the following differential equation:

$$\tau \frac{dQ}{dt} = \frac{s}{K_s + s} - Q \tag{3}$$

where τ is a time constant that characterizes the speed with which the metabolism of the bacteria can shift. Equation 3 is merely a simple way to model a metabolic lag in the growth rate and substrate consumption. The virtue of equations 1-3 is that they reduce to the Monod form in the steady-

state and yet can simulate the rather complex transients exhibited by the effluent methanol concentration in Figs. 54a, 55a, 56 and 57a.

In order to simulate the experimental reactor, we assume that the reactor fluid is well-mixed and combine equations 1-3 with material balances for the substrate and the mass of suspended bacteria:

$$V \frac{dS}{dt} = F(s_i - s) - MR \tag{4}$$

$$V \frac{dx_s}{dt} = M \mu - F x_s \tag{5}$$

$$M = V x_x + A x_f$$

where V is the volume of fluid in the reactor [m^3], F is the volumetric feed rate and effluent rate [m^3/d], s_i is the substrate concentration in the inlet fluid, M is the total mass of bacteria in the reactor, x_f is the mass of fixed bacteria per unit of reactor surface area [kg/m^2], and x_s is the mass of suspended bacteria per unit volume of fluid [kg/m^3]. The value of x_f is assumed to be constant over the short transients considered here. All bacteria are assumed to be equally active and mass-transfer limitations are neglected. The bacteria are also assumed to degrade both substrates independently, i.e., equations 1 to 4 are written for each substrate, requiring 2 sets of values of the kinetic parameters. The growth rate term in equation 5 is taken as the sum of the rates for the consumption of the 2 substrates.

The adjustable parameters in the above model were fit to the transient-response data shown previously in Figs. 57a and 57b. Figs. 58a and 58b show the data and the resulting model predictions. The K_s and μ_{max} parameters were determined so as to provide a good fit at the beginning and end of the transient. Values used are shown in Table 24.

It was impossible to fit the 2 ends of the acetate transient exactly since this would have required a K_s value less than zero. A value of zero was therefore used in the model predictions. We note that literature values for K_s are on the order of 0.01 to 0.1 kg/m^3 for acetate utilization by methanogens, whereas the acetate concentrations in our experiments were much higher, on the order of 2 kg/m^3. Consequently, the predictions are insensitive to assumed K_s values in the range at or below the literature values.

This also means that the value chosen for the time constant in equation 3 is unimportant in the case of acetate. When s is much greater than K_s, the value of Q approaches 1.0 and is essentially constant unless s decreases dramatically for some reason. In other words, the bacteria are initially at their maximum metabolic potential with respect to acetate, and small changes in the operating conditions have little effect on their rate of acetate utilization. Therefore, the shape of the predicted acetate transient is unaffected by large changes in the value of the time constant, e.g., over the range of 0.1 hours to 100 hours. We therefore arbitrarily used the same value as was used for methanol. The resulting transient is of approximately the right shape, suggesting that the acetate transient is indeed dominated by the hydraulic time constant (the residence time) rather than the kinetic parameters.

The time constant for metabolic changes in methanol utilization was determined by a best fit to the transient portion of the curve in Fig. 58a In this case, variations in the time constant had a large effect. Smaller values than the one used for the predictions shown in the Figure resulted in a smaller, sharper peak with oscillations in the approach to the new steady-state. With a single adjustable parameter it was impossible to fit both the

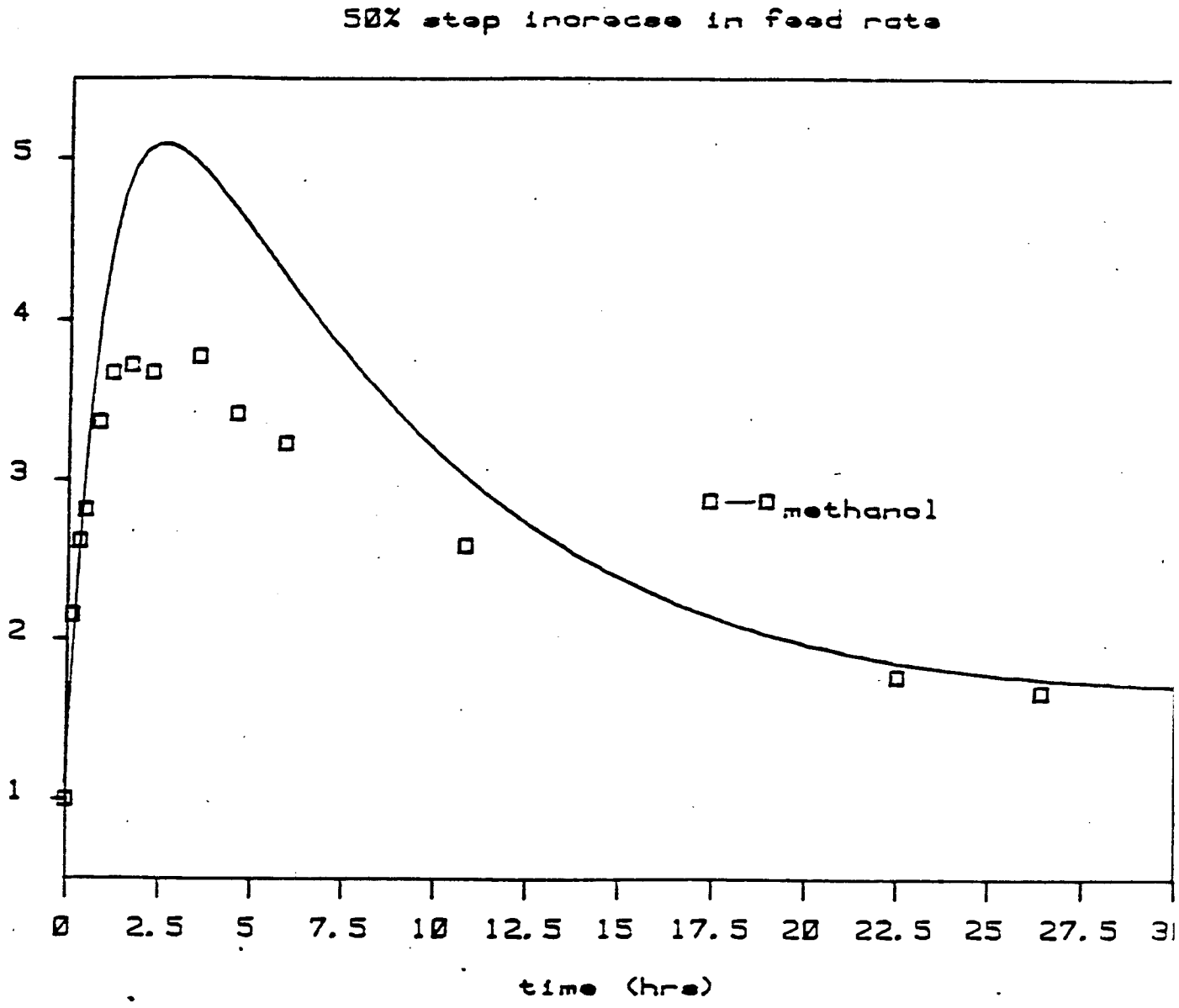


Figure 58a. Transient in Effluent Methanol Concentration for 50% Step Increase in Feed Flowrate. Data and Model Prediction.

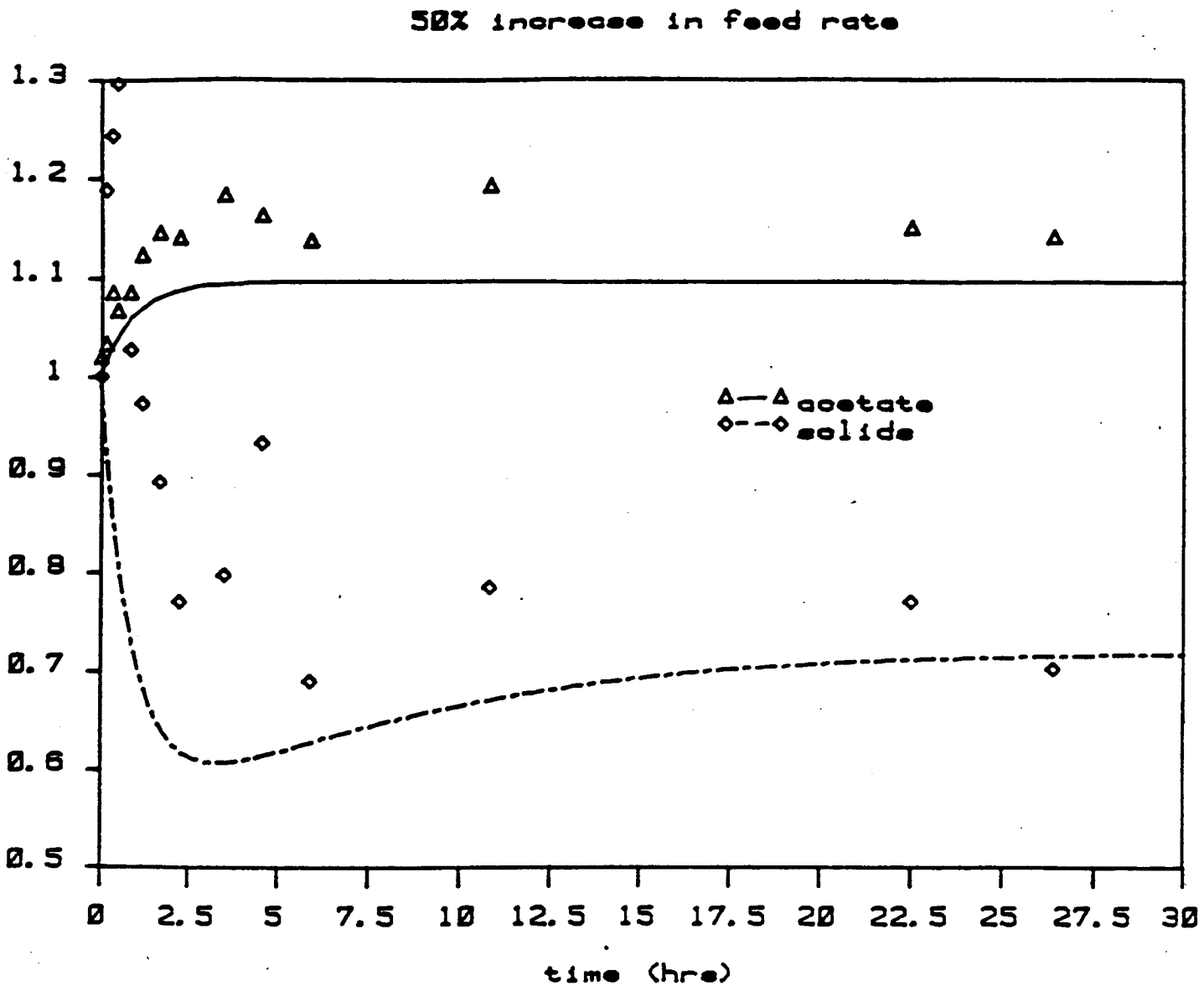


Figure 58b. Transient in Effluent Acetate and VSS Concentrations for 50% Increase in Feed Flowrate. Data and Model Predictions.

TABLE 24. Parameters Used in Simulation, Figs. 6a,b

	Yield Coef.	μ_{max} (d^{-1})	K_s (kg/m^3)	τ (h)
Acetate	0.04	0.0051	0	40
Methanol	0.04	0.0305	0.210	40

peak height and the speed of the transient; the result shown in Fig. 58a is a compromise. In any case, the model does a good job of reproducing the qualitative features of the methanol transient.

The representation of the effluent-solids transient is less satisfying, especially in the initial response where, as discussed previously, the data and the model move in opposite directions. This was to be expected, however, and the fit is much better at the 2 steady-states.

We are presently re-examining all of our transient and steady-state data in order to provide a uniform treatment with a single model. We also plan to perform experiments at lower acetate concentrations to see whether evidence of metabolic changes begins to show up as it does for methanol.

CONCLUSIONS

The rotating-disk biological reactor can be used effectively in the study of both steady-state and transient behavior of bacteria found in anaerobic wastewater treatment systems. Steady-state kinetic parameters determined from the experimental data were within the range found in previous research. The only difficulty encountered was the inability to measure the concentration of suspended bacteria contained in the reactor during normal operation. It appeared that bacterial flocs were held up in stable orbits in the rotating fluid and were not washed out by the cross flow of fluid from the feed inlet to the effluent port. This complicated the analysis of the results, because the concentration of suspended bacteria in the reactor was generally one or more orders of magnitude higher than that in the effluent at steady-state. We are considering a number of design changes that would provide a more uniform washout of bacteria in research applications. Preferential holdup could

actually be an advantage, however, in an industrial application, where one generally would like to maintain as large a population of bacteria as possible within the reactor

The transient response of the effluent solids concentration consistently deviated from what would be predicted by simple models of bacterial growth. It is postulated that sudden changes in operating conditions shock the bacteria in a manner that causes a release of bacteria from the attached film or from the orbiting flocs.

The transient response of the effluent acetate concentration was primarily influenced by the hydraulic residence time; the acetate concentration was nearly always in the range of zero-order Michaelis-Menten kinetics. By contrast, the transient response of the effluent methanol concentration was much more heavily influenced by the bacterial kinetics. There is clear evidence that the bacteria slowly adjust their metabolism in response to changes in availability of methanol.

A simple dynamic model is proposed and used to simulate the transient response to changes in availability of methanol. The model requires only a single adjustable parameter beyond the usual Michaelis-Menten parameters. This parameter is a time constant characterizing the rate at which the bacteria can adjust their metabolism to accomodate changes in methanol concentration. The model is as good at representing the unusual qualitative features of the methanol transients as more complex models and may be useful in process control studies.

ACKNOWLEDGEMENTS

We are grateful for the support of grants from the United States Office of Water Research and Technology, and from the Boise-Cascade, CH_2M Hill, Georgia Pacific, ITT Rayonier, Scott, and Weyerhaeuser companies. Our colleagues, Mark M. Benjamin and John F. Ferguson, of the Department of Civil Engineering were enthusiastic and a wealth of information on anaerobic treatment processes.

REFERENCES

1. Bailey, J.E.; Ollis, D.F. Biochemical Engineering Fundamentals 1977, McGraw-Hill, New York, p501.

2. Benjamin, M.M.; Ferguson, J.F.; Buggins, M.E. Tappi, 1892 65(8), 96.

3. Brune, G.; Schoberth, S.M.; Sahm, H. Process Biochem. 1982, 17, 20.

4. Chi, C.T.; Howell, J.A. Biotech. Bioeng. 1976, 18 63.

5. Eis, J.E. MS Thesis in Civil Engineering, 1982, University of Washington, Seattle, WA.

6. Felton, C. MS Thesis in Chemical Engineering, 1983, University of Washington, Seattle, WA.

7. Graef, S.P.; Andrews, J.F. Chem. Eng. Prog. Symp. Ser. 1974, 70(136), 101.

8. Haggerty, P.D.; Wines, B.; McCarthy, J.L. Tappi 1983, 66(5), 75.

9. Henze, M.; Harremoes, P. Symp. on Anaerobic Treatment of Wastewater in FixedFilm Reactors, IAWPR-Specialized Seminar, Copenhagen, Denmark, June, 1982, p1.

10. Huser, B.A. Arch. Microbiol. 1982, 132 1.

11. McCarty, P.L. Public Works 1964, 95, Sept., 107; Oct., 123; Nov., 91.

12. Olthof, M.; Oleszkiewicz, J. Chem. Engr. 1982, 89(23), 121.

13. Pooler, T.W. MS Thesis in Civil Engineering, 1983, University of Washington, Seattle, WA.

14. Priest, C.J. Pulp and Paper 1983, 57(4), 125.

15. Tait, S.J.; Friedman, A.A. "Anaerobic Rotating Biological Contactor Treatment for High Strength Carbonaceous Wastewaters" 1979, paper presented at the 52nd Ann. Conf. Water Poll. Control Fed., Houston, Oct. 11, 1979.

16. Williams, F.M. J. Theoret. Biol. 1967, 15, 190.

17. Zeikus, J.G. Bacteriological Rev. 1977, 41 514.

APPENDIX

STUDENT THESES AND REPORTS

Buggins, Mark Edward, (1981) MSE, Civil Engineering. "Treatment of Sulfite Evaporator Condensate with a Submerged Media Anaerobic Reactor."

Eis, Brian Jeffery, (1982) MSCE, Civil Engineering. "Limiting Factors in the Anaerobic Treatment of Sulfite Evaporator Condensate."

Felton, Colin C., (1983) MS, Chemical Engineering. "The Transient and Steady State Response of an Anaerobic Rotary Disc Bioreactor in Waste Water Treatment."

Fors, Rodney Robert, (1979) MS, Chemical Engineering. "Biochemical Engineering Processing of Sulfite Pulp Mill Evaporator Condensate Streams to Produce Methane and Reusable Process Water."

Gerboth, Mark (1984, expected) MS, Chemical Engineering. "Transient Response of Anaerobic Water Systems."

Haggerty, Peter D., (1980) MS, Chemical Engineering. "The Anaerobic Treatment of Sulfite Pulp Mill Evaporator Condensate."

Jurgensen Shirley L., (1984, expected) MSCE, Civil Engineering. "Anaerobic Treatment of a Thermomedimal Pulping Waste."

Kuenzi, Michael S., (1983) MSCE, Civil Engineering. "Chemical Neutralization Effects on Aerobic Lagoon Treatment Performance."

Poling, Mark A., (1984, expected) MS, Civil Engineering. "Anaerobic Treatment of Kraft Evaporation Condensate."

Pooler, Theodore Warren, (1983) MSCE, Civil Engineering. "A Simulation Model of the Submerged Media Anaerobic Reactor."

Woods, Sandra, (1980) MSCE, Civil Engineering. "Assessing the Toxicity of Sulfite Evaporator Condensate to Methanogenic Bacteria."