FINAL REPORT

Project No. B 338

A STUDY OF SLUDGE DIGESTION WITH SODIUM CHLORIDE AND SULFATE

by

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REPORT ON PROJECT B 338

ABSTRACT

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The work on the grant was divided into two parts. Most of the time was spent in studying the poor digestion which results from the use of salts by the carpet industry in coloring natural fibers or tufts. The rest of the time was used for studying waste water treatment in which the waste contains the surfactants required to color the synthetic fibers which are now used by the same industry.

For many years the tufted textile or carpet industry was centered in Dalton, Georgia, where many dye houses contributed their waste water to city sewers. Digestion at the combined waste water treatment plant was very poor in spite of periodic pH adjustments with lime. The mixed waste water of the city had a salt content of several thousand milligrams per liter (mg/l). Most of the salt was sodium chloride, but a portion was sodium sulfate. Furthermore, sodium sulfide was used from time to time at the dye houses and may have entered the digester directly. However, chlorine, which was also present intermitently, may have oxidized it. Because of the unsatisfactory digestion, a synergism of sodium chloride and sodium sulfide (from sodium sulfate) was proposed as being responsible for the low pH in the digester.

When work was finally begun on the project, the salt content of Dalton waste water was only 100 mg/l, but the aeration tank had a high foam layer. Instead of the salts which make the natural fibers take up dye, the new synthetic fibers take up dye in the presence of surfactants or carriers. The waste water from an individual mill may well contain 200 to 300 mg/l surfactant.

Thus, part of the grant was devoted to a study of the new problems which arise in treating waste water from the synthetic carpet industry.

For the digestion experiments, an effort was made to reduce variations in toxic response which might be caused by differences in digester sludge samples from variable sampling procedures. All sludge samples were obtained from the same plant in the City of Atlanta. Precautions were taken to get active samples by using only primary stage sludge which was warm and transferred directly into a graduated cylinder and then into the actual digesting flask. In spite of precautions, large variations occurred in the original pH values, in the capacity of sludge to accept food on a unit-volume basis, in the production of gas per unit weight of food added, in the ability to maintain a pH near 7.0, and in the manner of response to the added sulfide.

In studying the proposed synergism of sodium chloride and sodium sulfate, it was assumed that neither salt was toxic per se, but that the sulfate would be toxic only after conversion to sodium sulfide. Thus several digestion runs were performed to study the direct toxicity of sulfide and compare it with the toxicity of sulfate. Without pH adjustment sodium sulfide is extremely toxic. At room temperature and with adjustment of pH, an initial dose of 190 mg/l showed no toxic effect for three weeks, while 380 mg/l caused a sharp drop in gas production after five days. However, at 32°C the 190 mg/l sulfide dose created a sharp decrease in gas production in five days. Thus, sulphur as sulfide appears to be more toxic at higher temperatures.

Since nitrates reduce gas production in proportion to concentration, a similar reduction was hypothesized for sulfate. Observations of sulfate at room temperature showed a much lower toxicity or reduction in gas production than that of an equivalent molar concentration dose of sulfide. (Hence,

procedures were developed for determining both sulfate and sulfide concentrations in the digesting mixture). At 32°C, however, the toxicity of sulfate appeared to be greater than that of sulfide at equal molar concentrations. In another experiment at room temperature, 160 mg/1 sulphur as sulfide caused a reduction in daily gas production which returned in ten days to the same daily gas volume as the control.

The last two sludge samples are an excellent illustration of the variations in sludge from a waste water treatment plant. Thus, one had an initial pH 7.6 and the other a pH 6.8. The first of these could accept 1.7 g food per liter per day at 32°C with no change in pH for 20 days while producing 100 percent of the theoretical gas yield. On the other hand, the second sludge would accept no more than 0.6 g glucose without a drop in pH and produced between 60 and 100 percent of the theoretical gas. The toxic responses were also very different. The first sludge was dosed daily with 45 mg of sulfide per liter sludge, which accumulated to 700 mg/1 at which time there was a sudden failure in gas production accompanied by a sudden pH drop to 4.0. The other sample was dosed daily with 35 mg sulfide sulphur per liter of sludge, and showed a gradual loss in daily gas production with a slow drop in pH to 6.2 in two weeks. This sample lost some hydrogen sulfide both in the gas and through reaction in solution such that the sulfide concentration never exceeded 100 mg/1. The response of the sample with sulfide and sodium chloride was not distinguishable from that of the sample with sulfide (no synergism). When dosed with chloride and the same amount of sulfate as sulfide the previous experiment, the sludge responded slowly (very little sulfate was reduced in the first five days). There was evidence of some synergism with sodium chloride and sulfate from day six to day fifteen, but none was evident during an additional two weeks.

With the establishment of an equilibrium among food addition, pH and gas production, it was obvious that methane fermentation was no longer the principal mechanism in equilibrium. It would be interesting to study the new flora which can consume food with a steady pH 6.2 while producing small quantities of gas with a normal methane content. That study, however, might contribute primarily to science and not water pollution control. Actually, it was pure coincidence that the sludge referred to above (initial pH 6.8) had such a different flora and used such different metabolic pathways to different end products. It most nearly approximates, however, Dalton's earlier digester problems.

When feeding and sulfate additions were discontinued, white granules accumulated in the sludge-supernate interface and much of the black color of ferrous sulfide disappeared. These granules were assumed to be sulphur, but they dispersed easily and so disappeared before a specific test could be run. If one can assume that sulphur was produced by oxidation of the sulfide, then this would have contributed to the new equilibrium mechanism. It should be mentioned that although these white granules could well have been produced during the feeding period, they were observable only after a prolonged period of quiescence.

No sulfate or sulfide was detected during the 30 days observation of the control of the samples with initial pH 6.8. In this group the peculiar behavior of the samples dosed with sulfide indicates that the original flora apparently had the capacity to use sugar in a metabolic pathway that produces products other than volatile-acids. On the other hand, the other group of sludge samples (initial pH 7.6) had no flora for controlling the sulfide concentration or for changing metabolic pathways. Hence, when the methane

bacteria ceased functioning, the pH dropped to 4.0 quickly because of an accumulation of volatile acids.

The question arises as to whether the final study demonstrates toxicity, competition between the methane organisms and the sulfide oxidizing organisms, or a changeover to an essentially unusable by-product of the first stage organisms through a different metabolic pathway. The data are not sufficient to fully answer the question, but it is my reaction that either successful competition by the sulfur organisms or a changed metabolic pathway is the primary cause for the decrease in the methane production with steady sulfide concentrations and pH equilibrium values. This does not contradict an apparent sulfide toxicity, but does offer an explanation for the recovery of gas production, after dosing, to a level which is much higher than that previously reported for a non-toxic level. Such a theory might well account for the repeated failures in methane fermentation following pH adjustment when conditions remained favorable for sulfur-organism competition or production of an altered by-product.

The work with surfactants as one of the current problems in carpet mill waste water treatment was taken on as a second area of research under the grant support. Observations were made of treatment under both aeorbic and anaerobic conditions. Concentrations of surfactants in such waste waters can attain 250 mg/l because a very high concentration of surfactant or carrier is required to disperse the dyes and to help them penetrate the synthetic fibers. While the dyes are present in only a few mg/l concentration, they are toxic and are only slowly degraded biologically. The synthetic surfactant is generally non-ionic so that several dyes can each react with, or be absorbed from, one bath by a specific fiber when two or three different fibers are woven in one carpet.

At concentrations less than 5 mg/1, the non-ionic surfactants exerted a higher rate of biological oxygen demand (BOD) than at higher concentrations. Studies of both aerobic and anaerobic degradation were undertaken. Without seeding, aerobic treatment brought about little degradation of 175 mg/1 surfactant. However, after the establishment of a well acclimated seed, twenty-two hours of aeration effected significant reduction in the chemical oxygen demand (COD) exerted by surfactant doses of 900 mg/1 (actual dye-beck discharge). At one half this concentration, or with 46 hours aeration, degradation was more rapid and efficient.

Anaerobically the surfactant was not detectably degraded during a thirty-day digestion period. When normal sugar/peptone feeding was discontinued, the sludge dosed with surfactant ceased gas production, while the control continued to evolve gas. Anaerobic treatment of actual dye beck discharge was also completely ineffective.

INTRODUCTION

Special problems in waste water treatment are generated by specific industries. The carpet industry with its tufted textile mills has been concentrated in North West Georgia and centered in Dalton where it has caused many special problems over the years. As in all industries, the development of modern synthetic chemicals (e.g. fibers) has changed the character of the problems as soon as new ideas and materials were adopted.

With natural dyes and fibers large quantities of salt were used to enable the fiber to take up the maximum amount of dye. The discharging of spent dye baths caused the mixed domestic/industrial waste water to have two to three grams per liter (g/l) of salt in solution when it reached the treatment plant. In spite of the copious amounts of organic matter present for digestion, very little gas was produced and the pH would not maintain the 7.0 required for good methane production. Several programs of pH adjustment with lime were carefully instituted. The pH would remain at 7.0 for only a few days before gradually falling off again. Since sulfates were used heavily, along with small quantities of sulfides, it was postulated that a sulfide toxicity (both directly from sulfide salts and indirectly from sulfate salts) might exist which could be aggrevated by a synergism with sodium chloride.

After the research support was obtained no appreciable quantity of salt was found in the mixed waste water at Dalton, where the earlier trouble was observed. The tufted textile mills had begun using synthetic fibers for tufts except in several isolated cases. The synthetic fibers require new kinds of dyes which in turn require either surfactants or carriers (such as paradi-

chloro-diphenyl) for inducing dye uptake by the fibers. Hence, a study of treatment requirements for reducing the high biological oxygen demand (BOD) produced by surfactants and carriers under aerobic and anaerobic conditions was undertaken as a portion of the grant research. This study is contained in a separate report which follows the report on salt toxicity.

SECTION ON DIGESTION STUDIES

Robert S. Ingols, Richard Robert, and Popet Vira

INTRODUCTION

The anaerobic digestion process is commonly assumed to produce methane and carbon dioxide in amounts proportional to the quantity of food added in the absence of toxic substances. When a toxic compound interrupts methane fermentation or when too much food is added, an excess of lower fatty acids (ethanoic, propanoic and/or butanoic) accumulates. The accumulation of these acids occurs because the methane organisms fail to metabolize the acids fast enough to methane and carbon dioxide. The increase in concentration of these acids is generally evidenced by a sharp reduction in pH. Alcohols which are also used by methane organisms would also accumulate with a falling pH but would not be detected except by direct analysis of the sludge liquor.

High sodium chloride concentrations are not found generally in wastewater but have been observed in Dalton, Georgia. Salts of sulfuric acid were also used in Dalton. Sulfates are not toxic under aerobic conditions, but are decomposable to sulfides under anaerobic conditions. Sulfides have been reported by Aulenbach and Heukelekian (1) as toxic at concentrations in excess of 100 mg/1. Nitrates are also known to reduce methane fermentation in proportion to the nitrate oxygen which in the absence of gaseous oxygen reduces the amount of acidic and alcoholic compounds produced in the first stage of digestion. It is necessary to know whether the sulfate oxygen will also reduce the food available to the methane organisms in proportion to its concentration. At Dalton, some dye houses use hydrogen sulfide in their dying

processes so that the city wastewater had both sulfates and sulfides as a source of sulfides in the digester to interfere with methane fermentation.

In order to study digestion, four important parameters of normal digestion have been assumed to be (1) the quantity of gas production per day, (2) the ratio of actual gas production to the anticipated gas production (based on the quantity of food added daily), (3) the ratio of methane to carbon dioxide in the evolved gas and (4) the pH of the sludge mixture.

Other factors of importance in evaluating the experimental data will include (1) the sulfide and sulfate concentrations in the sludge and the hydrogen sulfide in evolved gas, (2) the temperature of sludge during digestion and (3) the initial pH of sludge. A study of the identity of the flora in the sludge might well provide essential information on understanding the responses to sulfides, but no identification or counting of bacteria has been attempted in this research.

METHODS

Digestion experiments were performed using sludge samples from the South River Water Pollution Control Plant of the City of Atlanta. The vessels which were to hold the digesting sludge samples during experimentation were carried to the facility. The sludge was measured as withdrawn and added in the desired quantity to each vessel in order to introduce the least possible amount of oxygen. The plant has two stage digestion, so an effort was made to obtain the most actively digesting sludge by withdrawing samples from the line which transferred sludge from the first to second stages. The transfer pump was operated for several minutes until fresh, warm sludge flowed from the faucet before sampling.

Throughout our studies the initial toxic dose was added only after active digestion was established. The food was added in solution and consisted of glucose, peptone or a mixture of the two. In the preliminary experiments, feeding was done daily, but no sludge or supernatant was withdrawn. In the last two experiments, a portion of the sludge was withdrawn daily which was equal in volume to the daily food plus toxic dose. After all vessels had attained similar daily gas production values, the food dose was modified or salt addition was initiated along with the daily feeding. The vessel was shaken to assure uniform distribution of food and/or salt in the sludge.

Since the sodium sulfide solution as originally dissolved was quite alkaline, the pH was adjusted to 7.5 - 8.0 before its addition to the various sludge samples under study (after one disasterous observation).

Gas analyses were carried out with a gas chromatograph using molecular sieve as substrate. Figure 1a shows the chromatograms for a day's observation of 5 samples. Small oxygen and nitrogen peaks appear on the chromatograms of the control which were caused by the minute quantities of air that enter the sampling syringe during transfer. Though hydrogen sulfide was observed by smell in the wasted gas from some of the digesters, no separate peak developed in the chromatograms. A different column was installed to detect hydrogen sulfide. Its substrate was 10 percent triton X-305. However, hydrogen sulfide still did not give a separate peak, but rather merely increased the magnitude of the oxygen peak. On the molecular sieve chromatogram, hydrogen sulfide introduced artificially into a portion of digester gas increased the peak for nitrogen commensurately. Since air is approximately 20% oxygen it was assumed that the volume of nitrogen in the air "contaminant" should be four times the volume of the oxygen. When the "nitrogen" peak was more than four times the

oxygen peak, it was assumed to be, and is reported as, hydrogen sulfide. A set of curves showing various amounts of hydrogen sulfide is given in Figures 1a, b, c, d, and e.

Titrations for sulfide ion and sulfate ion along with measurement of pH were performed on the daily sample of sludge which was withdrawn from each digester before feeding. Silver sulfate was used to titrate one aliquot for sulfides using an ion specific electrode for observing the end-point. To determine sulfate, a second aliquot was titrated with a barium chloride solution using alizarin dye for end-point detection. The sulfate end-point was difficult to determine visually, but with experience a technician could obtain reasonable results (10%) on standard solutions and, hence, presumably on samples.

At concentrations of less than 5 mg/1, the non-ionic surfactants studied exerted a high rate of biological oxygen demand (BOD). At higher concentrations several days were required for the development of a floc which would produce a higher rate. Studies of both aerobic and anaerobic degradation were undertaken. Without seeding aerobic treatment brought about little degradation of 175 mg/1 surfactant. However, after the establishment of a well acclimated seed, twenty-two hours of aeration effected significant reduction in the chemical oxygen demand (COD) exerted by surfactant doses of 900 mg/1 (actual dye-beck discharge). At one half this concentration, or with 46 hours aeration degradation was more rapid and efficient.

Anaerobically the surfactant was not detectably degraded during a thirty-day digestion period. When normal sugar/peptone feeding was discontinued, the sludge dosed with surfactant ceased gas production, while the control continued to evolve gas. Anaerobic treatment of actual dye beck discharge was also completely ineffective.

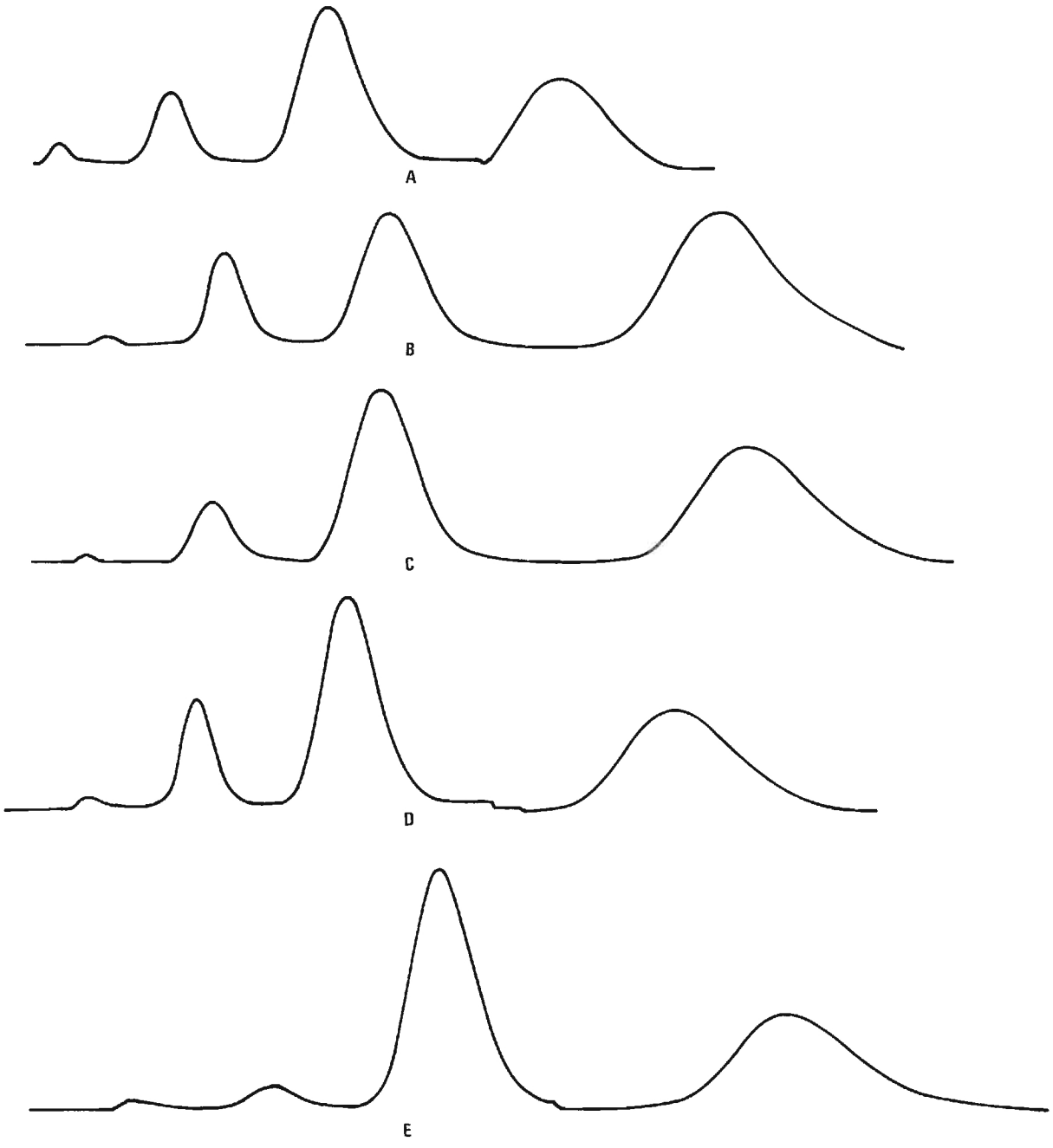

Figure 1. Gas Chromatograms of 5 Daily Gas Samples from First Run.

RESULTS

Our initial experiments on sulfide and sulfate toxicity were performed with a range of different initial doses at two different temperatures. After using the wide range of doses to determine overall response, a group of samples was prepared with which we attempted to arrive at a 50 percent toxicity value. Two temperatures were chosen: room temperature (22-23°C) and 32°C. Each sludge sample was acclimated until the gas production was steady from day to day and uniform among sludge samples at each temperature. No supernatant was withdrawn so that there was a gradual increase in sludge volume but no change in quantity of food added. According to the data in Table I and Figure 2 the addition of a single dose of 200 mg sulfide-sulfur at room temperature caused a temporary decrease in the amount of daily gas production. Gas production reattained normal levels in eight days. With the higher dose of 330 mg per liter, there was a longer period of decreased gas production, but still no permanent loss in the ability to produce gas. However, at 32°C, a dose of 290 mg sulfur per liter of sludge caused a sharp drop in gas production with no apparent recovery (see Figure 3). (This was the lowest dose chosen for that temperature on the basis of a previous set of data).

Because we had no values for the sulfide or sulfate concentrations in the sludge phase, it was decided to study only one sludge sample for sulfide and one for sulfate and to assay for each of these ions in the sludge. An amount of supernatant was removed daily which was equal to the volume of food and sulfide or sulfate to be added. The data for the sample dosed with sulfate which are shown in Table II and Figure 4 indicate that very high concentrations of sulfide sulfur can develop before the methane organisms fail and the pH drops to 4.0.

Table I. Effect of a single sulfide dose upon daily gas production.

Days After Dose	Dose of Na_2S sulfur per liter sludge				
	(1) Incubated at 23°C			(2) At 32°C	
	Control	200 mg S	330 mg S	Control	290 mg S
	ml gas/l sludge	ml gas/l sludge	ml gas/l sludge	ml gas/l sludge	ml gas/l sludge
0	1160	1080	1160	1340	1340
1	1020	420	340	1220	480
2	1080	580	540	1220	600
3	1060	720	600	1260	640
4	1060	800	640	1300	620
5	880	840	660	1260	500
6	820	780	580	1300	380
7	820	780	620	1320	300
8	900	880	700	1420	280
9	880	900	740	1460	200
10	940	980	800	1360	140
11	920	980	860	1360	100
12	920	980	880	1380	100
13	920	920	900	1360	100
14	940	940	880	1300	40
15	920	920	880	1340	80
16	840	880	820	1280	120
17	800	820	800	1240	140
18	820	800	740	1220	200
19	780	760	600	1220	200

Fed Daily (1) 0.9g glucose and 0.5g peptone - 125% of theo. gas yield for glucose.

(2) 1.6g glucose and 0.4g peptone - 100% of theo. gas yield for glucose.

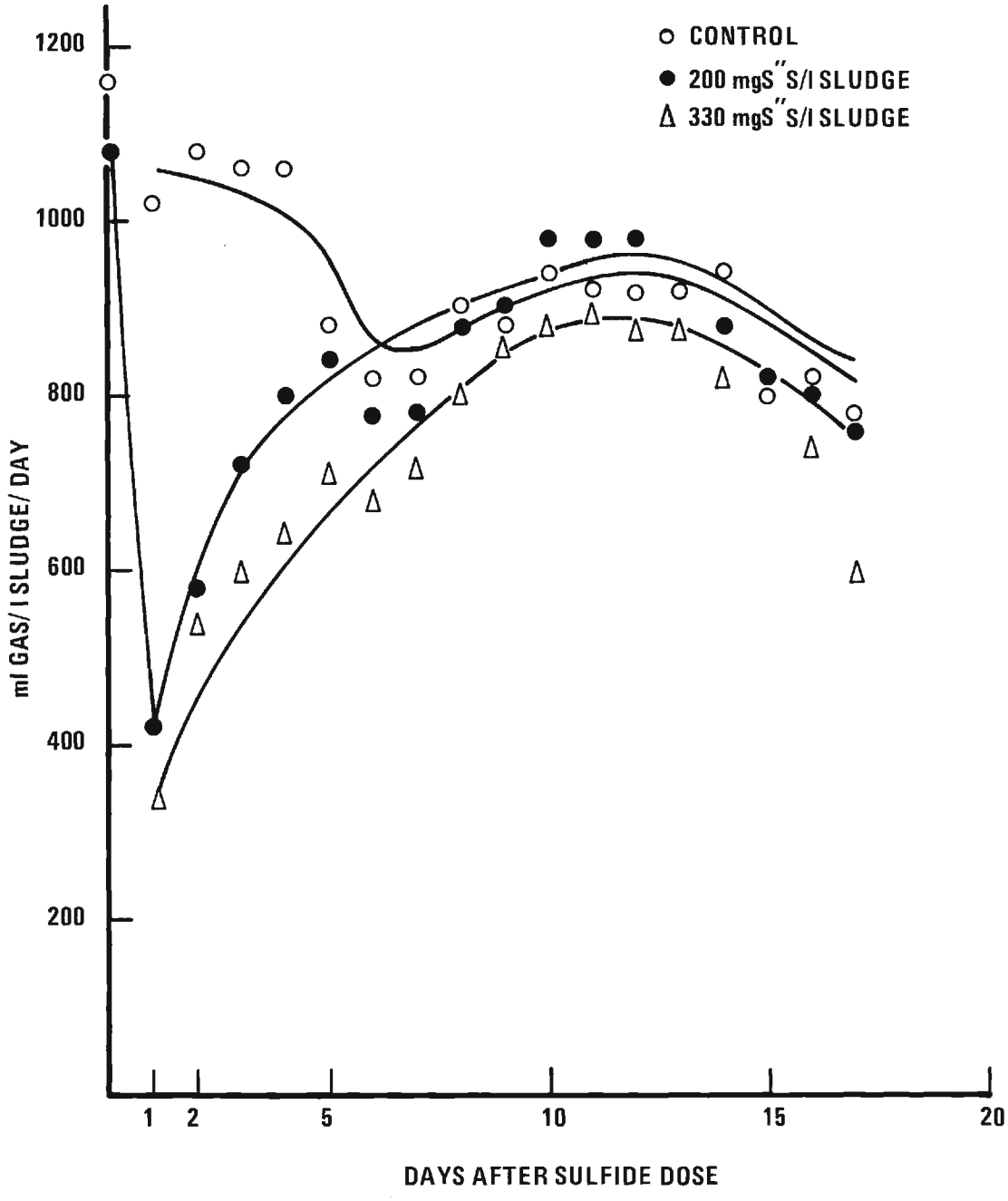

Figure 2. Effect of Single Dose of Sulfide on Gas Production when Incubated at Room Temperature.

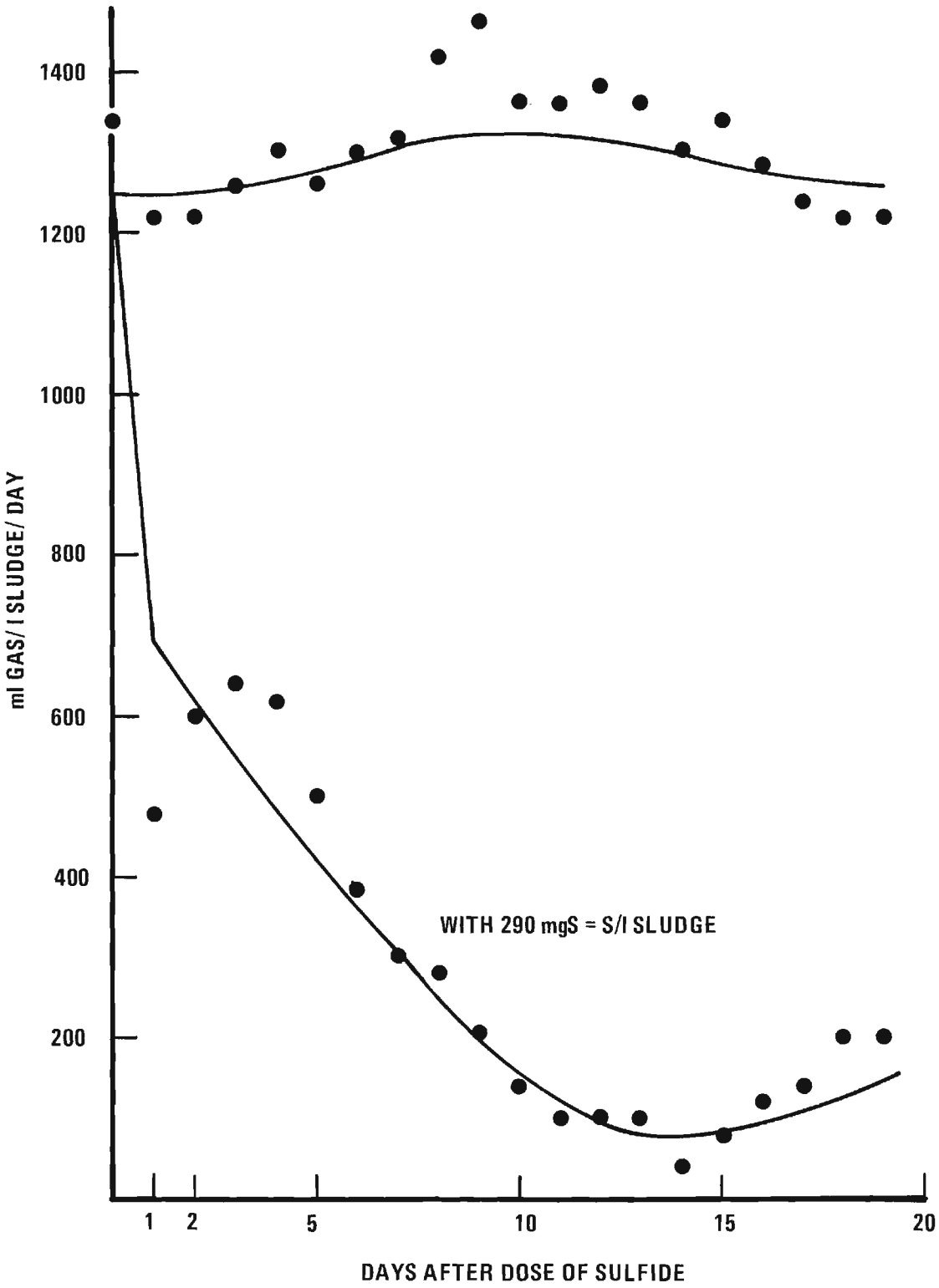

Figure 3. Effect of Single Dose of Sulfide on Gas Production when Incubated at 32° C.

Table II. Effect of daily sulfate additions upon digesting sludge with daily feed.

Control			Sludge Plus Sulfate Sulfur 1g/day/1 Sludge				
Days After Sulfate Dose	Gas Production in ml/day/1 Sludge	pH	Gas Production in ml/day/1 Sludge	pH	Sulfate Theor. g/1	Sulfate Obs. g/1	Sulfide Obs. g/1
0	1350	7.6	1320	7.6	1.0	---	---
1	1300	7.6	1200	7.6	1.9	---	---
2	1250	7.4	1170	7.5	2.8	---	---
3	1370	---	1200	---	3.6	---	---
4	1340	---	1310	---	4.4	---	---
5	1360	7.4	1160	7.7	5.2	---	---
6	1270	7.5	1290	7.5	5.9	---	---
7	1270	7.5	1280	7.5	6.7	---	---
8	1250	7.4	1250	7.5	7.4	---	---
9	1340	7.4	1270	7.4	8.0	---	---
10	1430	---	1230	---	8.7	---	---
11	1470	---	1080	---	9.3	---	---
12	1380	7.5	870	7.5	9.9	---	0.6
13	1490	7.5	910	7.3	10.4	1.0	0.7
14	1390	7.4	960	7.3	11.0	0.9	0.8
15	1450	7.4	1050	7.1	---	1.2	0.7
16	1320	7.2	1030	6.0	---	1.3	1.3
17*	550	7.1	830	5.6	---	---	---
18	400	7.1	930	4.0	---	---	---
19	----	7.3	----	4.0	---	---	---

*feeding discontinued

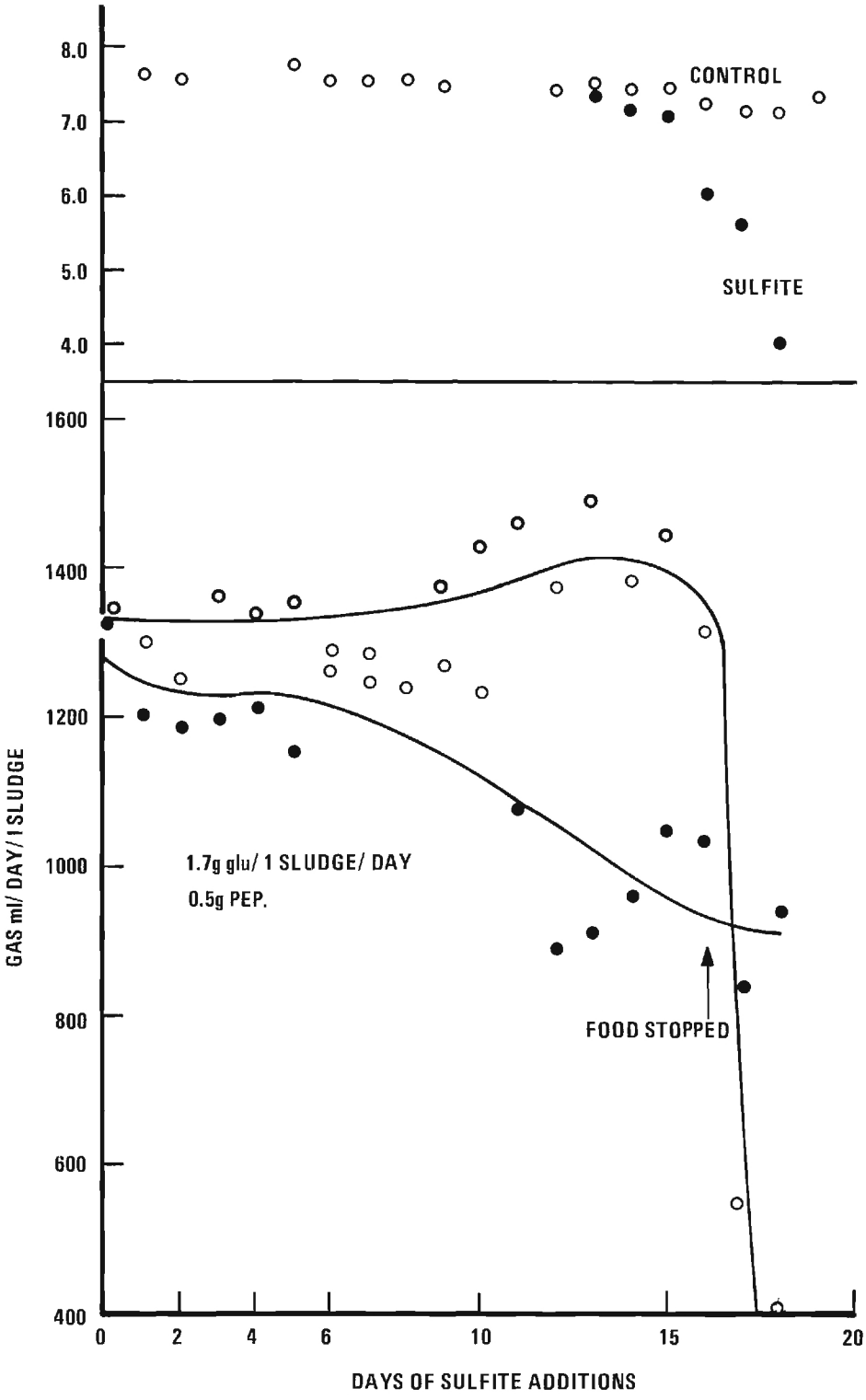

Figure 4. Effect of Daily 45 mg/1 Doses of Sulfide on Gas Production and pH.

It should be noted that a large amount of sulfate remained in solution untouched although conditions for its reduction had changed only slightly from the period during which part of it had been reduced.

The percent toxicity can be calculated as the ratio of the daily gas production values of the sulfate dosed aliquot versus the control. There was little initial decrease in gas production, but after 15 days there was a sharp drop in pH and the experiment was terminated after 19 days. At the end of 14 days, a residue of 10.4g sulfate per liter sludge (74 millimoles per liter) should have developed had there been no chemical change during that period. Actually 7 millimoles of sulfate remained and 10 millimoles of sulfide were found. This means that 57 millimoles sulfur disappeared. Because the digester gas had the characteristic sulfide stench, it was realized that some hydrogen sulfide was lost in the gas phase. However, the gas chromatograms did not develop a new peak, but rather an unexpectedly large nitrogen peak "appeared" in the gas chromatogram as shown in Figure 1.

A final experiment was set up with 5 samples: (1) control (2) sulfate (3) sulfate plus chloride (4) sulfide (5) sulfide plus chloride. Daily dosing of food and salts was used. Gas volumes were observed daily and analyses of the gas samples were made frequently. Sludge samples were withdrawn daily before feeding. The samples were observed for pH, sulfide and sulfate when applicable. The data are summarized in Table III. Gas production for the control (Figures 5 and 6) followed an unexpected and disturbing pattern. Although the control received no toxic substance, its gas production, which started at a rate approximating 100 percent of theoretical, fell for a two week period to only 70 percent of the theoretical and then returned to 100 percent theoretical for the final six day period. Because of the variable gas

Table III Summary of Data of Salt Observations With pH 6.8 Sludge Sample.

	CONTROL 1.25g Glucose, 0.50g Peptone/Day						SET I 1.25g Glucose, 0.50g Peptone, 0.75g Na_2SO_4/Day						SET II 1.25g Glucose, 0.50g Peptone, 0.75g Na_2SO_4, 0.75g NaCl/Day					
Day	pH	Daily gas ml/day	CH_4 : CO_2 ratio	H_2S %	Sulfur as: $SO_4^=$ mg/l	$S^=$ mg/l	pH	Daily gas ml/day	CH_4 : CO_2 ratio	H_2S %	Sulfur as: $SO_4^=$ mg/l	$S^=$ mg/l	pH	Daily gas ml/day	CH_4 : CO_2 ratio	H_2S %	Sulfur as: $SO_4^=$ mg/l	$S^=$ mg/l
1	6.8	890	2.0	0.0			6.7	940	2.0	0.0	430	10	6.7	750	2.1	0.6	390	10
2	6.9	1050	---	---			6.9	900	---	---	---	--	6.9	730	---	---	---	--
3	7.0	1040	---	---			6.9	890	---	---	---	--	6.9	650	---	---	---	--
4	7.1	960	1.70	0.0			7.0	680	5.4	0.9	1800	20	6.8	490	2.2	2.9	1600	10
5	7.0	810	2.6	0.0			7.0	620	2.1	0.0	1900	20	6.9	430	1.6	1.2	1800	20
6	7.1	620	2.3	0.0			6.9	600	2.1	0.0	2400	20	6.7	370	1.8	0.0	2000	30
7	7.1	720	2.3	1.4			6.9	620	1.8	0.0	2600	30	6.7	410	2.1	0.0	2200	50
8	7.0	850	2.2	0.0			6.9	510	1.6	0.0	2700	40	6.6	310	1.3	0.0	2200	50
9	7.0	580	---	---			6.9	390	---	---	---	--	6.7	390	---	---	---	--
10	7.1	730	---	---			6.8	320	---	---	---	--	6.6	310	---	---	---	--
11	7.0	720	---	---			6.8	250	---	---	2500	40	6.5	280	---	---	2700	50
12	7.0	650	1.5	0.0			6.7	280	2.3	3.4	2600	70	6.5	240	1.3	2.0	2500	50
13	7.1	790	2.4	1.6			6.8	230	0.6	0.5	1900	50	6.6	200	1.1	3.4	2600	60
14	7.0	770	3.1	0.0			6.7	150	1.7	0.0	2200	60	6.5	150	1.6	2.7	3000	30
15	7.1	650	---	---			6.7	160	---	---	2800	70	6.5	160	---	---	2600	50
16	7.1	560	---	---			6.6	170	---	---	---	--	6.5	160	---	---	---	--
17	7.0	710	---	---			6.6	260	---	---	---	--	6.4	250	---	---	---	--
18	6.9	590	3.5	0.8			6.5	240	1.6	0.0	2900	100	6.3	270	1.6	8.2	2800	50
19	7.0	770	2.7	1.2			6.5	180	1.1	1.6	2900	110	6.3	200	1.2	6.3	2800	50
20	7.0	760	1.7	0.0			6.5	210	1.2	0.0	3300	100	6.4	230	1.1	9.6	2700	60
21	7.1	770	1.9	0.7			6.5	290	0.9	0.8	3000	90	6.4	210	0.8	11	3000	100
22	7.0	800	---	---			6.4	230	---	---	---	--	6.4	170	---	---	---	--
23	7.0	1290	---	---			6.4	310	---	---	---	--	6.3	220	---	---	---	--
24	6.9	960	---	---			6.4	200	---	---	---	--	6.2	130	---	---	---	--
25	7.1	1000	1.1	0.0			6.4	260	0.9	0.0	3300	140	6.2	210	0.6	8.3	3400	100
26	7.1	840	1.5	0.2			6.3	170	0.8	2.2	3600	150	6.3	200	0.6	11	3500	100
27	7.1	840	1.4	0.3			6.3	160	1.1	6.7	3900	140	6.3	210	0.6	10	3400	100
28	7.1	830	1.7	2.9			6.3	120	0.7	5.1	3800	--	6.3	170	0.5	14	3400	--
29	7.0	---	1.4	0.0			6.3	---	0.5	5.7	3700	130	6.3	---	0.5	17	3200	100

	SET III 1.25g Glucose, 0.50g Peptone, 0.40g Na_2S/Day						SET IV 1.25g Glucose, 0.50g Peptone, 0.40g Na_2S, 0.75g NaCl/Day					
Day	pH	Daily gas ml/day	CH_4 : CO_2 ratio	H_2S %	Sulfur as: $SO_4^=$ mg/l	$S^=$ mg/l	pH	Daily gas ml/day	CH_4 : CO_2 ratio	H_2S %	Sulfur as: $SO_4^=$ mg/l	$S^=$ mg/l
1	6.6	390	2.3	0.0		30	6.7	500	2.3	0.0		10
2	6.8	410	---	---		--	6.8	470	---	---		--
3	6.7	460	---	---		--	6.7	410	---	---		--
4	6.7	370	2.9	0.0		20	6.7	390	2.7	4.4		10
5	6.6	300	1.7	1.2		30	6.7	300	2.0	3.2		20
6	6.6	280	1.6	0.0		30	6.7	290	2.3	3.5		30
7	6.6	390	2.6	2.7		70	6.6	310	2.1	2.9		30
8	6.5	360	1.2	1.4		40	6.5	470	1.9	3.1		30
9	6.5	470	---	---		--	6.6	410	---	---		--
10	6.5	350	---	---		--	6.6	300	---	---		--
11	6.4	330	---	---		80	6.5	330	---	---		50
12	6.4	450	1.2	1.7		30	6.5	270	1.1	0.5		30
13	6.5	390	1.7	2.7		80	6.6	320	1.7	3.7		50
14	6.5	390	1.7	0.0		70	6.5	200	1.6	3.6		40
15	6.5	430	---	---		80	6.5	270	---	---		50
16	6.5	350	---	---		--	6.4	490	---	---		--
17	6.4	340	---	---		--	6.4	200	---	---		--
18	6.2	330	2.1	3.1		80	6.2	220	2.1	6.9		30
19	6.3	250	1.5	1.0		60	6.3	230	2.4	5.5		40
20	6.3	260	1.6	0.5		120	6.3	270	1.7	4.9		100
21	6.2	270	1.4	3.3		90	6.3	220	1.0	6.5		90
22	6.2	220	---	---		--	6.3	180	---	---		--
23	6.2	180	---	---		--	6.3	230	---	---		--
24	6.1	240	---	---		--	6.1	120	---	---		--
25	6.1	180	0.9	5.1		100	6.2	220	1.5	7.2		100
26	6.1	230	1.0	8.7		100	6.2	230	1.0	11		100
27	6.1	170	0.8	4.4		--	6.2	130	1.1	10		--
28	6.1	170	0.9	7.9		--	6.2	230	1.0	8.0		--
29	6.0	---	1.0	9.9		90	6.3	---	1.0	10		100

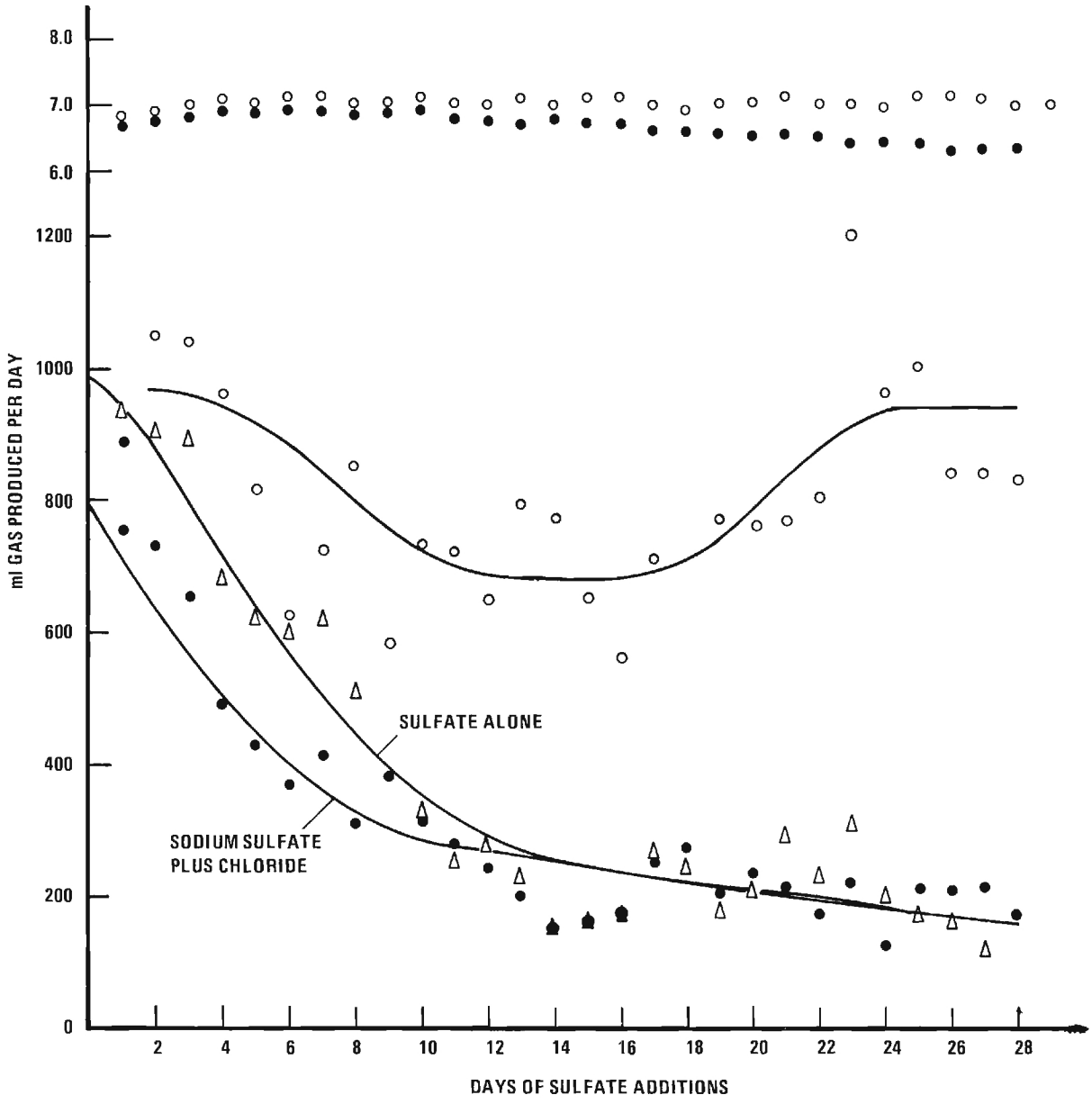

Figure 5. Effect of Daily Additions of Sodium Sulfate and Sulfate plus Chloride upon pH and Gas Production.

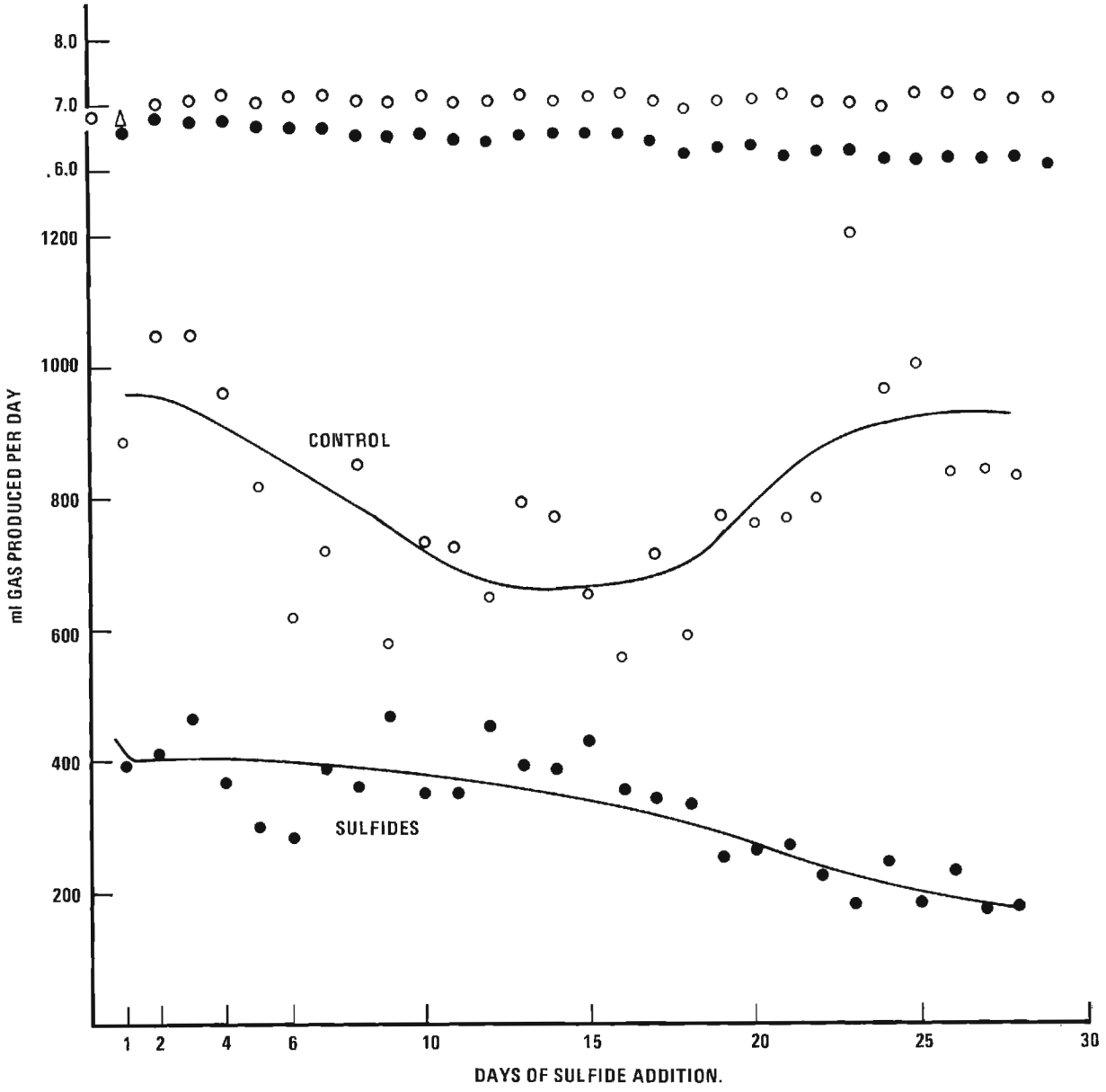

Figure 6. Effect of Daily Additions of Sodium Sulfide upon Gas Production and pH.

production of the control, only raw data is plotted in Figures 5 and 6. The ratio of the gas production of a dosed sample versus the unusual gas production of the control does not produce an easily understood pattern. The two columns of data for sulfate from Table III (which are also summarized in Figure 5) show that sulfates accumulate over the period of observation along with sulfides. The theoretical quantity of sulfate expected in a liter of sludge after 20 days was calculated to be 45 millimoles; the observed quantity of sulfate was 20 millimoles and of sulfide, 2 millimoles (a loss of 23 millimoles).

After feeding and sampling had been discontinued for several days a quiescent sludge layer developed. On the surface of this sludge layer white specks appeared. It is believed that these specks were sulfur granules because the black ferrous sulfide color also decreased sharply. Previous sharp decreases in the black sulfide color had been observed, but without the appearance of the white specks.

The sludge dosed with sodium sulfate and sodium chloride showed a more rapid initial loss in gas production than the sample dosed with sulfate alone. From the midpoint of observation till the end of the experiment, the presence of salt made no difference in pH or gas production.

The data for study of sulfide toxicity both with and without the addition of sodium chloride are presented in Table III and Figure 6. These data show very little difference that can be assigned to the addition of sodium chloride. In each case there was a slow drop to pH 6.2 and then a period of pH equilibrium while the daily gas production continued to fall off slowly.

DISCUSSION

The observed reaction of sludge-digestion organisms to the hydrogen sulfide water system was not as expected after reading the literature. The

idea that sulfides would be toxic beyond a concentration of 100 mg per liter becomes increasingly difficult to accept because it now appears that hydrogen sulfide was a normal constituent of the primitive atmosphere when anaerobic organisms were the only biota. Certainly, if hydrogen sulfide were present in the atmosphere, it must have been present in solution in the aqueous environment. Thus, toxicity is probably a poor term for explaining the response of digesting sludges to sulfides. A better term or conceptualization involves an "altered metabolic pathway" or successful "competition" by bacteria other than methane producers, which oxidize hydrogen sulfide and produce little organic acid.

Apparently, even without a sulfide concentration high enough to develop a black-metal sulfide color (see Control, Figure 5), the bacteria can partially alter the competitive situation or use altered metabolic pathways such that there is temporary reduction in gas production. When higher concentrations of hydrogen sulfide are present there is a greater tendency for the use of altered pathways or greater competition. Elevation of temperature increases the pressure on the sensitive bacteria by either reducing the production of food for the methane bacteria or interfering with their function. From the fact that there is no increase over theoretical in gas production following a period of limited gas production, it would appear probable that there is an interference with the production of food which is readily available for the methane organisms. Thus, instead of producing acetic acid or butyric acid, the bacteria may produce larger molecules of organic matter which accumulate in solution and which are not available to the methane bacteria.

Now that concepts other than toxicity have been developed, the samples are no longer available for study. Analyses for unusual organic molecules in

solution or for completely different flora during the periods of reduced gas production should be attempted. These ideas may well be the subject of a later research proposal.

I would say that sulfides can depress specifically and directly the methane bacterial activity such that organic acids accumulate. The concentration at which sulfide interferes with the methane organisms is much greater than the 100 mg/l reported by Aulenbach and Heukelekian[1], when daily additions of both food and sulfides are used rather than single initial feedings with simultaneous sulfide dosing.

When sulfides were used by the bacteria, the sulfide concentration in the digester (according to our analytical procedures) did not occur in excess of 100 mg/l or the figure found by Aulenbach and Heukelekian (1). At this concentration, however, only a small proportion of the potential methane and carbon dioxide gas production was observed along with a constant pH. The reduction in carbon dioxide, as well as methane, would lend support to the idea of an unusual first stage reaction in the digester.

Because methane gas production is considered the only "normal" sludge digestion process for waste water treatment, the above discussion seems highly theoretical and non-productive. It does indicate, however, that other bacterial processes might be studied for use with certain industrial wastes, such as the Kraft pulp-mill waste which Aulenbach and Heukelekian were studying. The fact that samples of digesting sludge differ so much from one another in response to the same conditions, even when they are collected from the same source, makes the outlining of an experimental approach to such a process frightening. Several years ago, a study of the "toxicity" of chromates to sludge digestion was undertaken; the responses were so erratic that publication was denied.[5] At

that time, batch digestion experiments were used, and dosing with chromates was done initially only. No records were made of pH in the sludge when it was brought into the laboratory. Hence, the cause of variable responses to the chromates was not understood or even guessed. Apparently much more luck is involved, than generally conceded, in finding the "right" organisms in a mixed industrial and domestic waste-water sludge such that methane and carbon dioxide fermentation is established and maintained.

The question may be raised as to why the conclusion was reached that the response is "competition" or "altered metabolic pathways" rather than toxicity. It is generally known that glucose sugar is converted by yeast to ethanol and carbon dioxide. It is also possible, however, to alter conditions of pH and temperature, or to add sulfites, to obtain glycerin rather than ethanol. Altered metabolic pathways used by a wide variety of organisms and resulting in a number of end products are discussed by Casida.[2] Because of the mixed culture which is normal in sludge digestion, the alternative possibility is the growth of a new organism which can compete for sugar to yield a different end product. Possible such end products could be hydrocarbons or higher fatty acids which could be produced with the hydrogen available from hydrogen sulfide. Certain microorganisms produce terpenes and/or sterols (Kodicek[3] amd Albro and Huston[4]). These products could well be favored at times also, and contribute to a fall in methane gas production.

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SYNTHETIC SURFACTANT DEGRADATION

by

Robert S. Ingols and Ekkehart Gasper

Synthetic surfactants have been a tremendous boon to public health in many ways, but the problems in waste water treatment and the persistent foam on our rivers point out that more information is needed to improve condition of our rivers. A recent review (2) indicated that even high concentrations (200-400 mg/l surfactant) have very little oral toxicity for laboratory animals, but the review does not include the response of microorganisms to these concentrations of surfactants. This discussion will concern itself with the response of microorganisms to surfactant concentrations of 200 mg/l or more in a separate industrial waste water treatment facility.

While many studies have been made on synthetic surfactants at the low concentrations which are normal to domestic waste water, few publications have dealt with the high concentrations which the textile industry uses (1,2). Nonionic surfactants are used to aid dye absorption by synthetic fabrics in the carpet industry. The nonionic surfactant can be used effectively with a larger variety of dyes than would be possible with ionized surfactants of either charge. Because agitation is also needed for uniform color uptake, a low or non-foaming surfactant is preferred over a foam producer. The nonionic surfactants in this study have polyethylene oxide chains which are normally biostable (1) because of the frequently reoccurring ether linkages. The water insoluble hydrocarbon portion of the molecule must be linear for biodegradation, while the presence of a second polar group at the terminal carbon favors the alkyl chain oxidation and retards foaming.

This paper seeks to define the detention time and necessary conditions for the biodegradation in a separate waste water treatment facility. When extended aerobic treatment is used what concentration of surfactant can be present and still allow floc development? What extent of surfactant degradation can be expected under aerobic degradation or anaerobic conditions?

METHODS AND MATERIALS

Aerobic Digestion

Return activated sludge was collected from a sewage treatment facility in Atlanta, Georgia, and a 200 ml sludge layer measured into each of several one liter cylinders. After adding food and chemical (see legends) the volume in each cylinder was brought up to one liter with tap water. Vigorous aeration was then started. Foaming was prevented by spraying an antifoam agent into the aerating sludge.

After 22 hours of operation the air supply was shut off and sludge allowed to settle for 30 minutes. Samples were taken from the supernatant liquid for pH measurements and COD tests. The liquid was siphoned off to the 200 ml mark, after 2 hours settling. Any sludge that may have developed in excess of the original volume was also withdrawn. The feeding and chemical dosing procedure of the previous day was repeated. The experiments were performed at room temperature ($25^{\circ}C$).

Anaerobic Digestion

Fresh, anaerobic digester sludge was collected from the same Atlanta treatment facility, and 500 ml measured into one liter aspirator bottles. These were rubber stoppered with the provisions for two openings: one for

the escape of gases, and the other for the daily dosing of the digester with food and surfactants. Daily gas production was followed by the displacement of a saturated salt solution (150 g/l NaCl and 5 ml/l HCl) in one liter gasometers. The experiments were performed at room temperature (25°C).

RESULTS

Activated sludge was obtained from Atlanta's South River plant, which treats waste water from both domestic and industrial sources. Several 2.5 g samples were placed in liter cylinders and diluted to volume after adding food and surfactant. The activated sludge reduced the COD of one gram normal (0.5 g glucose, 0.5 g peptone) food from 1770 to 200 mg/l in 22 hours at room temperature as shown in Figure I. When more food was added as anionic surfactant (ORVUS AB Granules*) the effluent COD was increased in proportion to the added COD of the surfactant. There was no change in the COD removed up to the added amount of 250 mg/l (1460). With the highest concentration of surfactant there was an eight percent loss in COD reduction the first day, but thereafter, the incremental loss in the COD reduction can be accounted for by an accumulation of the surfactant residuel in the sludge layer.

Because of the very high total food concentration with the highest surfactant concentration (a 2000 mg/l COD) in Figure I, 300 mg/l food concentration was used in the control for Figure II. The data given in Figure II shows that a lower total food concentration does not reduce the toxicity or increase the utilization of 250 mg/l LAS. The highest total original COD in Figure II was only 770 mg/l. At the end of 24 hours the COD of the higher surfactant concentration mixture was reduced to the value of the control, but

*Obtained from Procter and Gamble - Cincinnati, Ohio

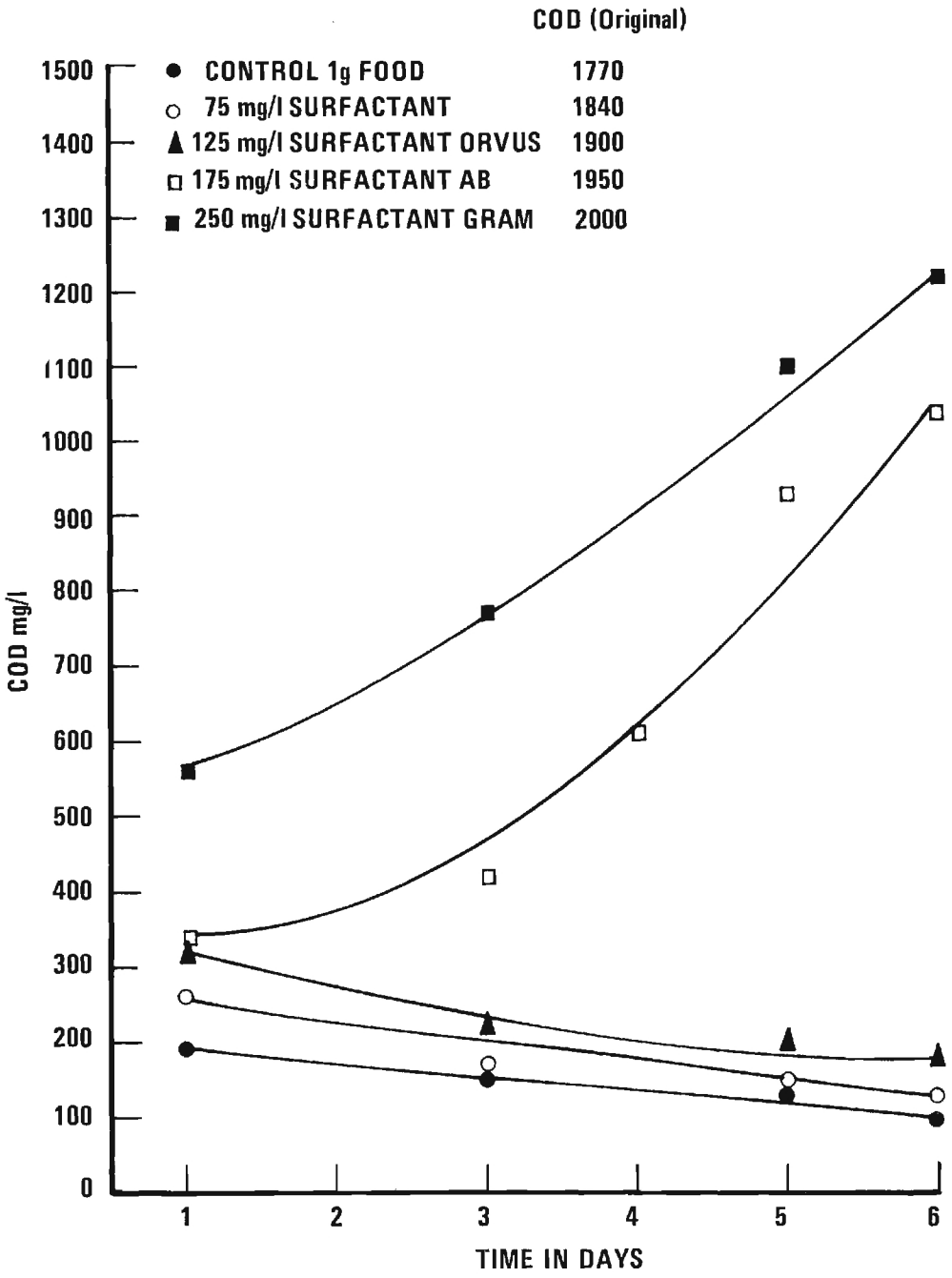


Figure 1. Effect of Various Concentration of Anionic Surfactant upon the ability of Two Grams of Activated Sludge to Reduce the Concentration of the Surfactant plus One Gram Normal Food with 22 Hours Seration.

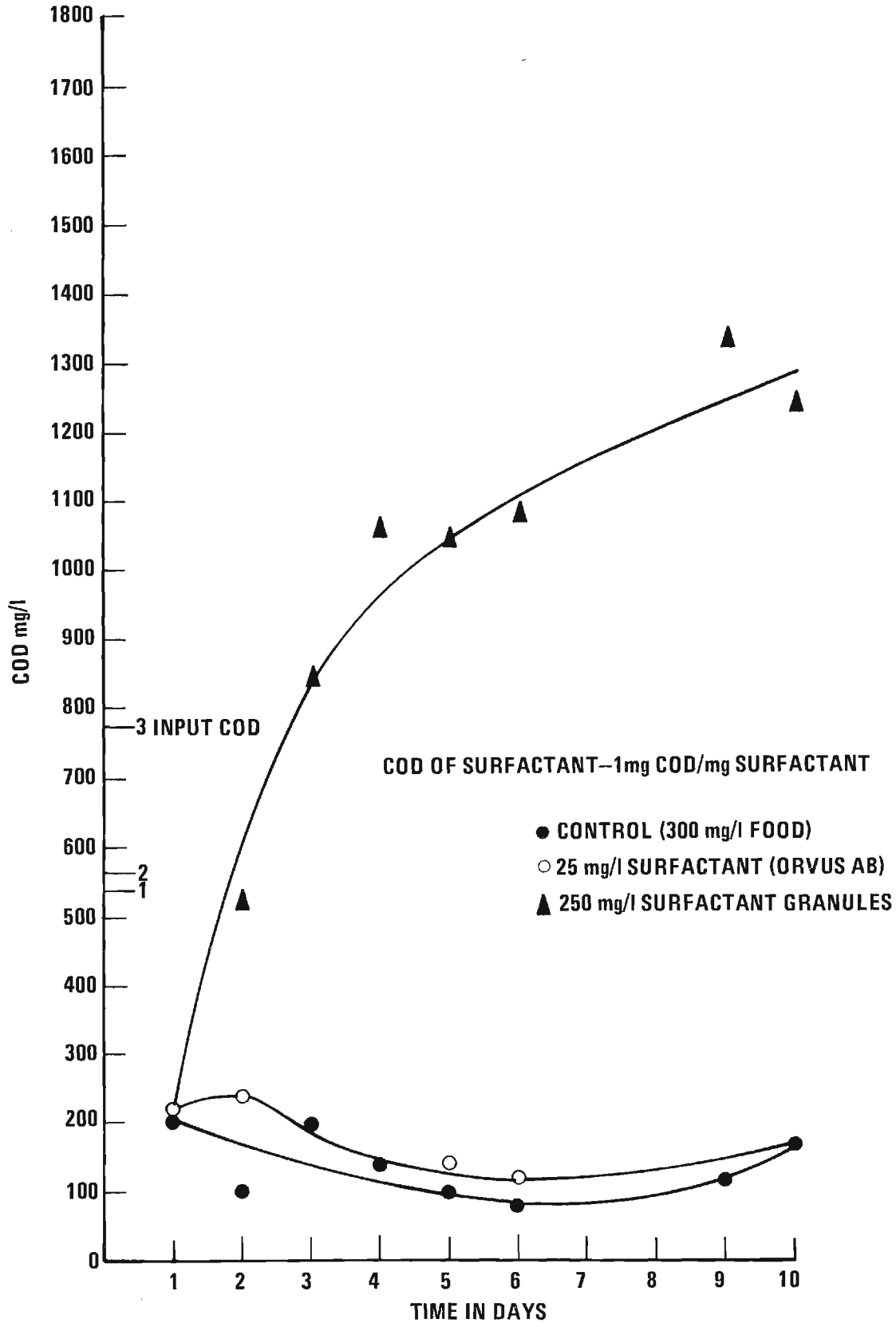


Figure 2. Effect of Various Concentrations of Anionic Surfactant upon the Ability of Two Grams Activated Sludge to Reduce the Concentration of Surfactant plus Less 0.3 g Normal Food with 22 Hours Aeration.

after 48 hours there was no apparent oxidation and even some sludge dispersion. Thus, even the "biodegradable" LAS is not readily oxidized when it is found in the high concentration of certain industrial waste waters. The 250 mg/l becomes increasingly toxic after 24 hours.

Because the textile industry uses nonionic-surfactants which are discharged in waste water at 200-400 mg per liter, only the high concentration of 175 mg Ekaline G Flakes (EGF) per liter was studied in obtaining part of the data of Figure III. Again, the increment in the effluent COD agrees with that of the control plus the COD of the surfactant for the EGF. The slight rise over the period of study would agree with the carry-over in the liquid volume of the sludge layer. These data indicate that the EGF are not degradable at this concentration in the presence of normal food. The data in Figure III for the Alkonal CN is not discussed in detail because its formula is not available.

A BOD of the EGF was determined at several low concentrations with the dilution technique using a seed sample from an aereation-tank treating waste water containing EGF. The curve of Figure IV for the lowest food concentration shows that the BOD develops as a two step function. Whether the second step is nitrification or breakdown of the less available polyethylene portion is not known. There is a marked lag in the oxygen demand at the concentrations of 11 mg/l and higher (the lag lasted for 4 days in some of the replicates as indicated in Table I). The 110 mg EGF per liter was not expected to have a BOD, but in the absence of normal food the bacteria were able to utilize the surfactant molecules.

The conclusion was reached that the EGF were biodegradable as shown by their BOD values but that aerobic biodegradation occurs only in the absence

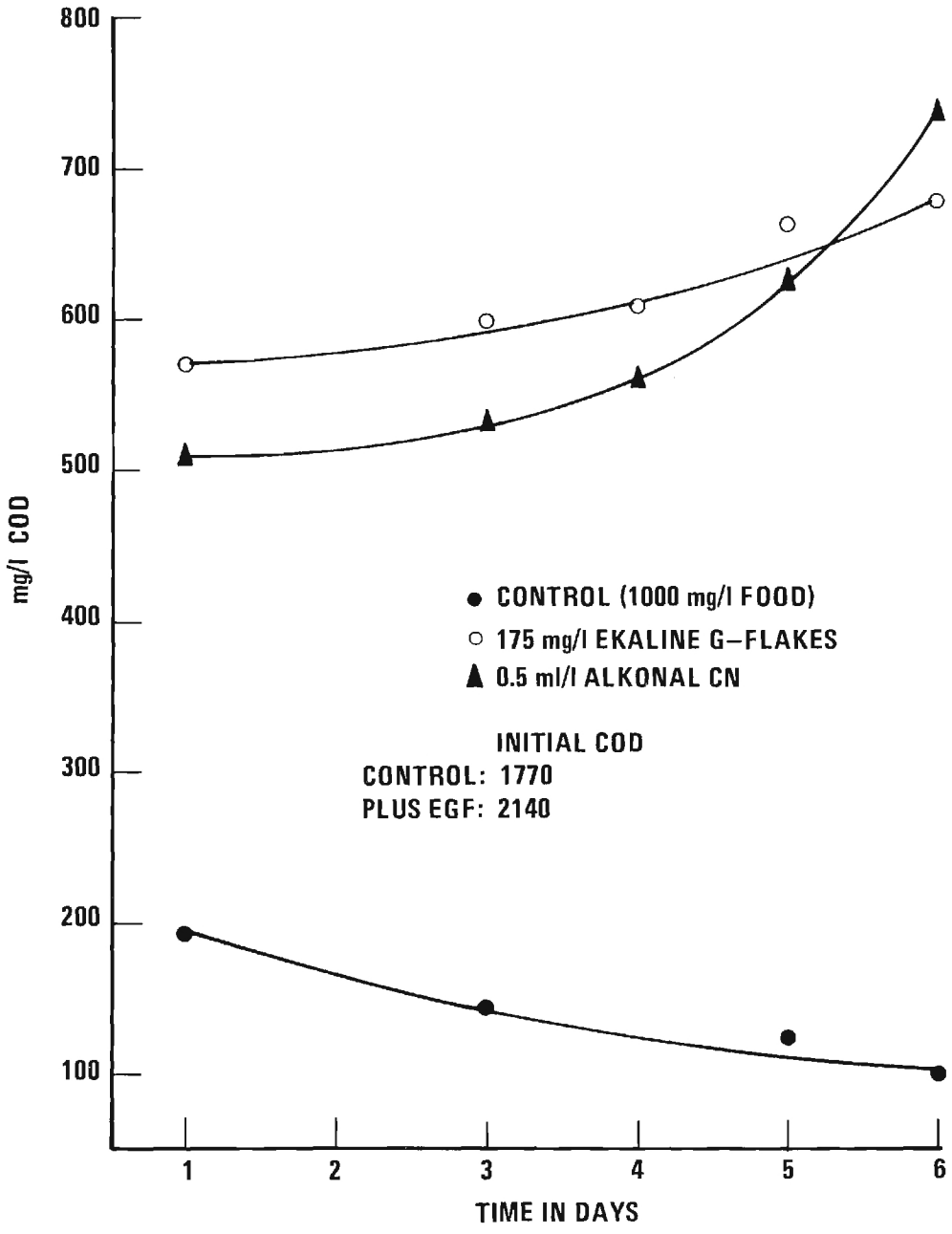


Figure 3. Effect of 175 mg of the Nonionic Surfactant, Ekline G Flakes, upon the Ability of Two Grams of Activated Sludge to Reduce the Concentration of Surfactant plus One Gram Normal Food.

Table I

Dilution BOD Studies with

Various Ekaline G. Flakes

Concentrations

Concentration	BOD after days				
Surfactant	1	2	3	4	5
mg. per liter	mg/l	mg/l	mg/l	mg/l	mg/l
1.1	0.7	1.1	1.9	2.8	3.8
3.3	1.1	3.3	(2.3)	3.5	4.4
11.0	1.9	4.4	(2.5)	(2.1)	7.9
110.0	2.4	>17.0	---	---	---

Circled numbers were not plotted in Figure IV.

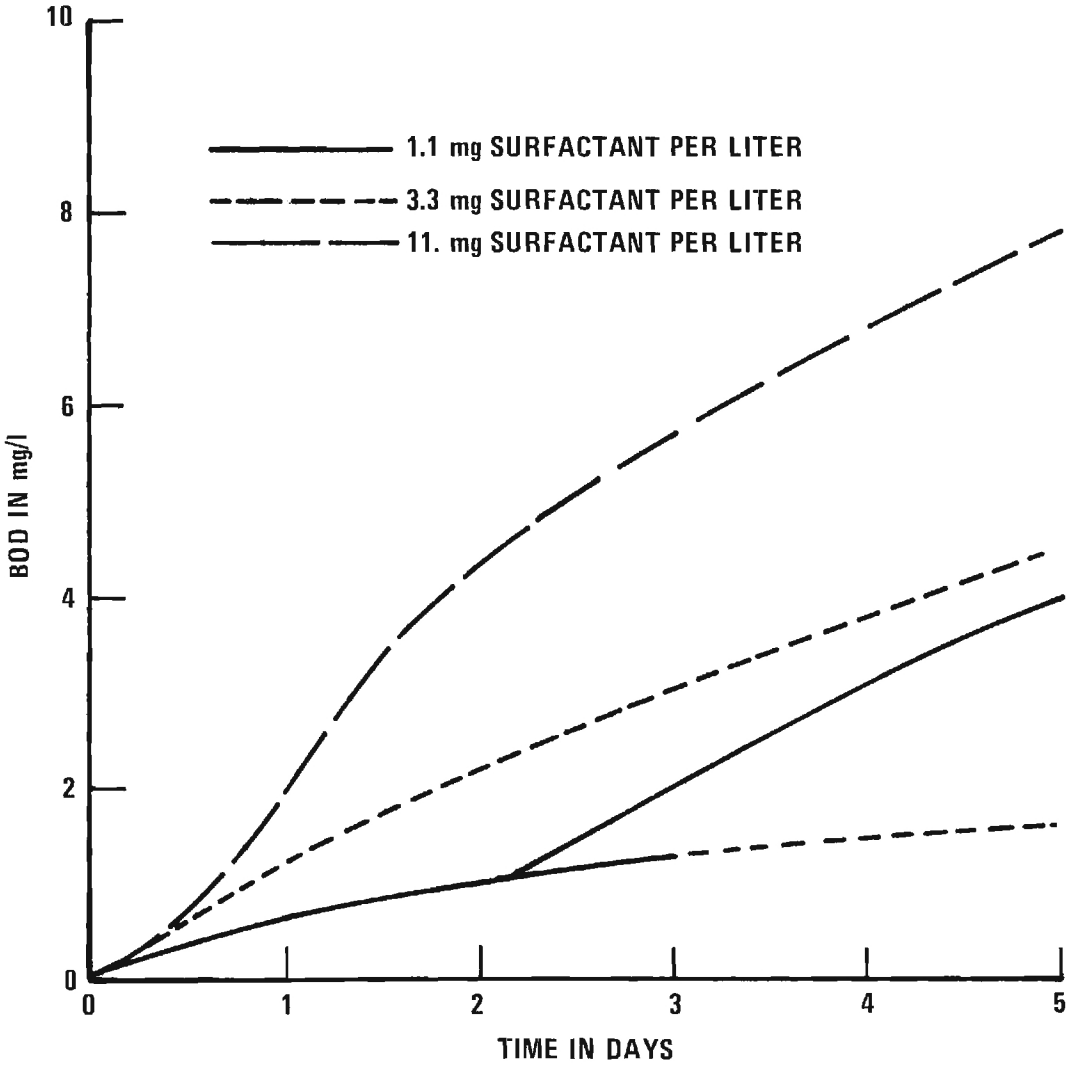


Figure 4. BOD Values of 3 Concentrations of Ekaline G Flakes Using an Acclimated Seed.

of other normal food. This brings us to the practical question as to whether the surfactant can be degraded under anaerobic conditions.

The fact that the surfactant did not decompose at high concentrations under aerobic conditions in the presence of other food, made it necessary to ask whether the same could be observed under anaerobic conditions. Anaerobic (digestion tank) sludge was obtained locally. It was fed daily a 2:1 glucose-peptone mixture. The bacteria in the control continued to produce gas daily for 36 days. When surfactant was added as shown in Figure V, no difference in gas volume was observed until all feeding was discontinued. With no added food there was enough food present that gas production was almost unchanged for several days. However, little gas was produced in the presence of surfactant during the next 15 days. A COD of the supernatant with surfactant (after centrifuging and filtration) accounted for all of the surfactant added.

While Alkonal CN is not used in large quantities, its effect on sludge digestion was also studied. From the data of Figure VI it can be seen that the Alkonal CN in the quantities studied interfered with gas production.

Samples of two dye becks were brought into the laboratories at five-day intervals. The first sample, as shown in the data of Table II and Figure 7, had a much higher content of organic matter than the second sample (2400 mg/1 COD vs 1600 mg/1 COD). Based on the COD and realizing that there was some dye present (each dye sample was taken from a spent solution just as it was discharged to the sewer), it was concluded that the first sample apparently contained 0.9 g per liter surfactant and the second 0.6 g per liter. This difference is caused by the differences in weight of carpet processed (carpet is processed in a beck in lengths of 500 yds., but varies in weight because of the weight of pile). The carpet is rinsed with a volume of water equal to

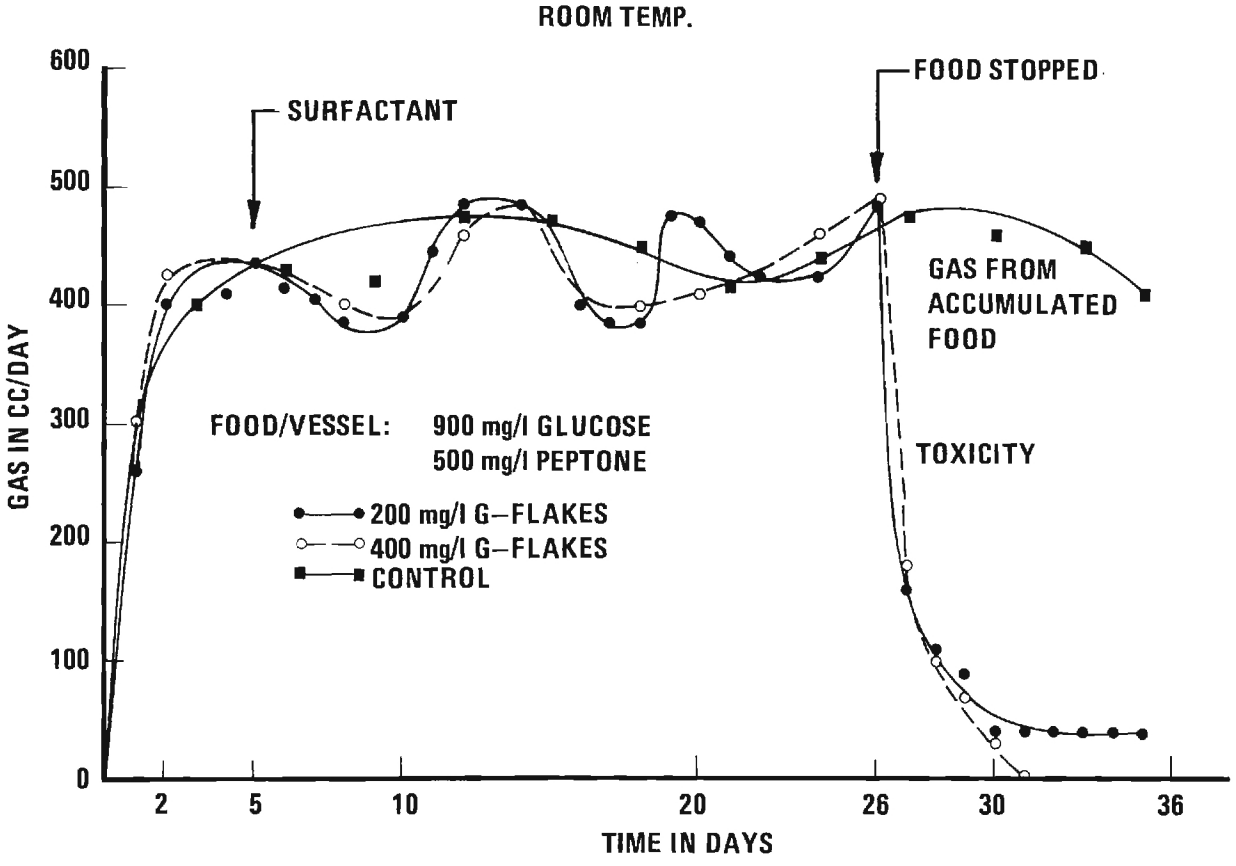


Figure 5. Effect of Two Concentrations of Ekaline G Flakes upon the Digestability of Normal Food.

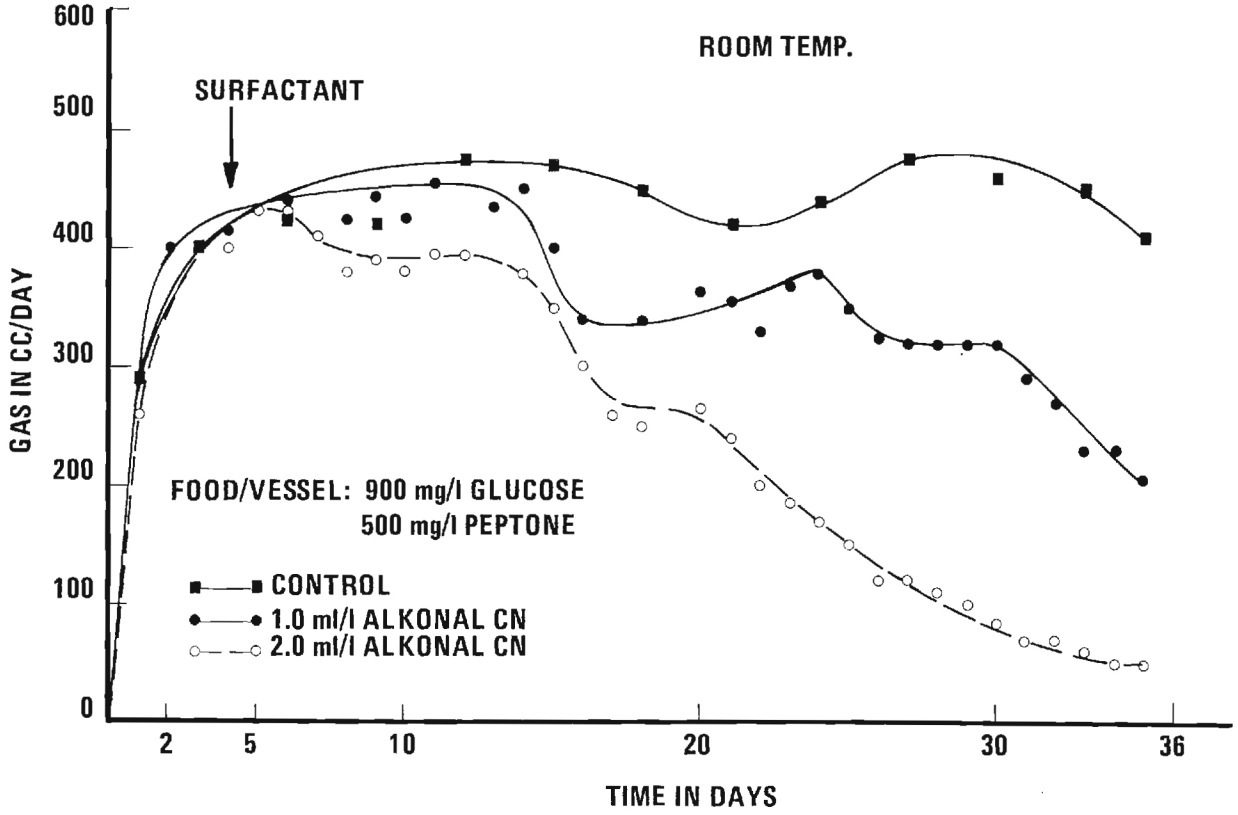


Figure 6. Effect of Alkonal CN upon the Digestability of Normal Food.

Table II

Aeration Time	Dye sample plus one volume of rinse water					Dye sample plus three volumes of rinse water				
	COD	Reduction				COD	Reduction			
		as decanted		with floc removal			as decanted		with floc removal bacentrifuge	
days	after 22 hours	mg/l	percent	mg/l	percent	after 22 hours	mg/l	percent	mg/l	percent
0	(1200)	-	-	-	-	(670)	-	-	-	-
1	1100	100	9	-	-	520	150	22	-	-
2	1160	40	3	-	-	600	70	11	-	-
3	1300	0	0	-	-	580	90	13	-	-
	1100	-	-	100	9	410	-	-	260	40
4	1340	0	0	-	-	600	70	11	-	-
	1070	-	-	130	11	320	-	-	350	53
5	890	310	25	-	-	520	150	22	-	-
	720	-	-	480	40	300	-	-	370	55
6	510	690	57	-	-	440	230	34	-	-
	25	-	-	950	79	350	-	-	320	48
0	800	-	-	-	-	420	-	-	-	-
1 (7)	610	190	24	-	-	350	70	17	-	-
	475	-	-	320	40	260	-	-	150	38
2	510	300	37	-	-	240	180	43	-	-
	270	-	-	530	68	160	-	-	260	60
3	420	380	48	-		280	140	33	-	-
	230	-	-	570	71	140	-	-	280	67
4	390	410	51	-	-	290	130	30	-	-
	210	-	-	590	74	140	-	-	280	67

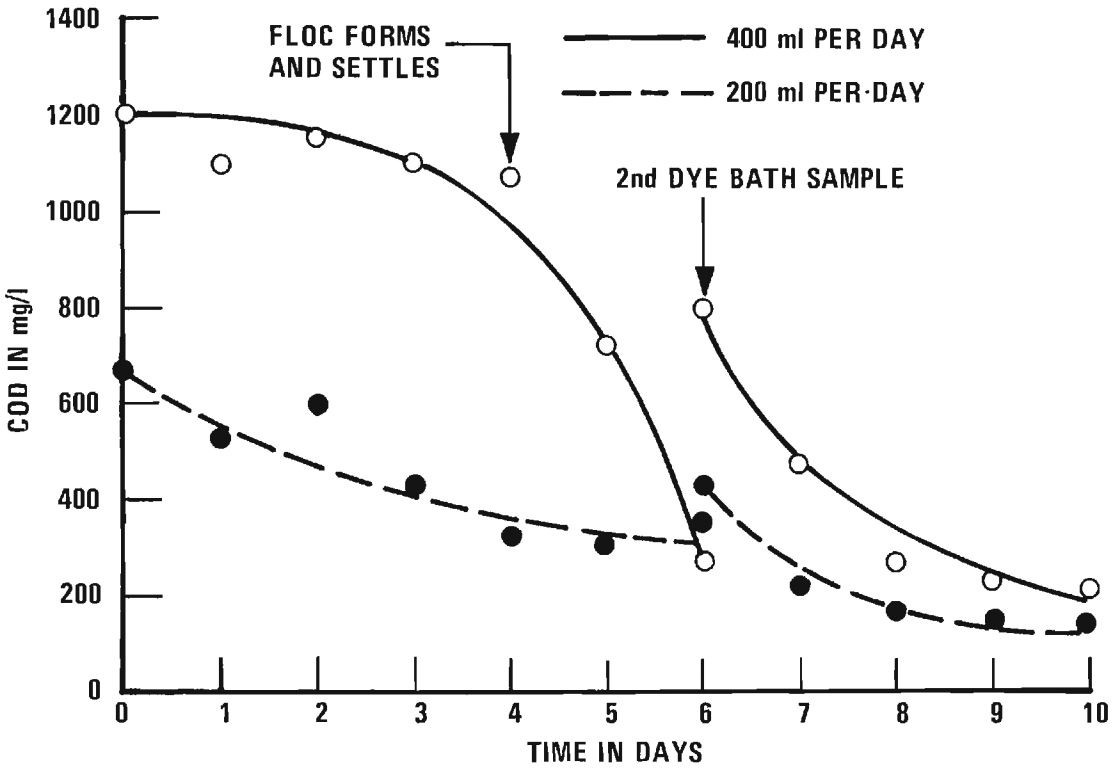


Figure 7. Ability of Acclimated Seed to Form Floc and Degrade Detergent at 2 Different Concentrations with Two Waste Dye Water Samples with 22 Hours Aeration.

the dye bath. A sample of the aeration pond from this mill was brought into the laboratory as seed. The 200 ml of seed was fed 400 ml of the dye solution daily for the left hand column of figures in Table II, whereas only 200 ml dye sample was fed daily for the numbers in the right hand columns. Atlanta tap water was used as the rinse water. There was an absence of a sludge layer initially. However, a very small sludge layer formed following several days aeration a constant volume of supernatant was decanted to leave all the settled sludge in 200 ml residue. It is obvious that much of the sludge settled poorly for centrifuging removed much more COD than settling alone. The data of Figure 7 give the maximum COD removed. When enough floc finally formed in the sample with the higher dye concentration, the COD reduction became significant. Because a large portion of the nonionic polyethylene surfactant molecule is not readily biodegradable, it would appear that most of the degradable portion had been oxidized when seventy percent of the COD had been removed.

THEORETICAL CONSIDERATIONS

The theoretical oxidation of the hydrocarbon of a polyethylene dodecanol may be shown as follows: (This is similar to, but is not necessarily the formula for EGF.)

$$(1)\quad H(C_2H_4O)_8(CH_2)_{11}CH_2OH + 18\ O_2 \rightarrow 12\ CO_2 + 13\ H_2O$$

m.w. 538 $\qquad$ 18x32= 576

Theoretical oxygen to surfactant ratio would be 1.1 to 1.0

If some of the polyethylene oxide chain is broken as shown by Frazee, Osburn and Crisler (1) then the oxygen requirement may be increased as

follows:

(2) $H(C_2H_4O)_8(CH_2)_{11}CH_2OH + 38\ O_2 \rightarrow 28\ CO_2 + 29\ H_2O$

m.w. 538 $38 \times 32 = 1216$

Theoretical oxygen to surfactant ratio is 2.25 to 1.0.

Thus, depending on the extent of surfactant molecule destroyed, the BOD per unit weight of surfactant may be expected to be anywhere from 0.75 for oxidation of the alkyl chain to 1.75 if the seed is starved and the polyethylene chain is also degraded (oxidized). The lowest surfactant concentration in Table I shows nitrification or breakdown of the polyethylene chain. The median concentration of 3.3 mg/l shows essentially complete oxidation of the hydrocarbon chain plus some nitrification or ethylene oxide breakdown. The highest concentration in Figure 4 shows the BOD which might be expected from the oxidation of the hydrocarbon chain with some protoplasm synthesis. Thus, the acclimated seed shows good surfactant oxidation at the low concentrations.

The theoretical COD of the surfactant molecule should be the same as that for the complete oxidation as given in equation number 2. The COD by analysis is only 2.1 mg/mg EGF while the theoretical value of a similar molecule should be 2.3 mg/mg surfactant. It appears that the actual COD is 93 percent of the model. The data from Figure 3 show that there is a first day increment of 380 mg COD with 175 mg EGF or that 100 percent of the added COD remains. Each day after that there is an increase in the COD difference between the control and the sample receiving normal food plus EGF. Some residual COD is left in the 200 ml of the residual seed layer. This explains the slow rise of daily increments in COD from 380 to 570 in six days.

DISCUSSION

It is interesting to develop concepts for the design of treatment facilities for treating waste water with Ekaline G. Flake as the principal organic constituent contributing to the BOD of the waste water. Even when acclimated bacteria are used, a long period of four days is required for the development of floc. The floc develops more readily when a lower concentration is given for oxidation.

Neither aerobic nor anaerobic conditions lead to appreciable destruction of the surfactant when other normal food is present and when the normal food is also renewed daily. In the absence of other food there tends to be a long lag period (even for acclimated bacteria) at surfactant concentrations greater than 3 mg/l.

Because high surfactant concentrations occur in some carpet mill effluents, and because it has been observed that no floc formed in two years operation in the aeration facility of one mill, the question arose as to whether floc can form, and if so, under what conditions. The presence of disperse dyes confuses the issue because they are somewhat toxic. In carpet manufacturing no sizing material is used so that there is very little normal food contributing to the BOD.

The mill has its separate treatment facility because of its location; thus, there is no other source of normal food except some toilet wastes from mill personnel. On the basis of the time required for floc formation under ideal conditions, it would appear that it is necessary to provide an equalizing tank (to reduce thermal and concentration shock), with 48 hours aeration and a separate sedimentation tank for producing return sludge. The present facilities have a final polishing tank as well.

SUMMARY

The destruction of nonionic surfactants from industrial waste water poses problems in design. In the presence of normal food, the synthetic molecules of Ekaline G. Flakes at 200 mg/l are not broken down within 24 hours aeration with ten times their weight of activated sludge. A very diffuse aerobic floc can be developed by allowing 48 hours detention for organisms which obtain most of their organic carbon from the EGF.

REFERENCES

1. Frazee, C. D., Osburn, Z. W., and Crisler, R. O., "Application of Infra-red Spectroscopy to Surfactant Degradation Studies," The Journal of the Oil Chemists' Society 41, 808 (1964).
2. Swisher, R. D., "Exposure Levels and Oral Toxicity of Surfactants," Archives of Environmental Health 17, 232-238 (1968).

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION

225 North Avenue, Northwest · Atlanta, Georgia 30332

September 23, 1969

Dr. Robert Bunch
Taft Sanitary Engineering Center
Federal Water Pollution Control Adm.
4600 Columbia Pkwy.
Cincinnati, Ohio

Re: Project B-338
Grant # WP-01375-01
Quarterly Report

Dear Bob:

The work on the grant for studying the effect of the salts of sodium chloride and sodium sulfate upon sludge digestion has preceeded slowly during the summer.

The preliminary draft of a manuscript describing the effect of detergents upon the aerobic treatment of textile mill waste water has been prepared. The activated sludge floc disintegrates in detergent concentrations in excess of 125 mg per liter when dosed daily. Carpet mills frequently have detergent concentration of 500 mg per liter in their dye becks which are emptied directly to the sewer. The concentration of surfactant drops with rinse water to 150 or 200 mg per liter in the waste water treatment facility. The absence of floc has been observed in actual field practices where the mill has its own aerobic facility. The detention time in an aerated facility that will allow development of floc which is required to concentrate bacterial action is therefore based on the need to reduce the detergent concentration to a value less than 100 mg per liter at all times. This has been shown to require 48 hours in studies in the laboratory.

The BOD of partially degradable non-ionic detergents is interesting. Attempts to get a BOD value per unit weight of detergent has been performed several times. The BOD is much higher for the lowest concentration (with dilution BOD techniques). Thus, at 1.1 mg per liter the BOD is 2.8 mg per liter or 2.5 mg BOD per mg surfactant; while at 11.0 mg surfactant per liter,

the BOD is 7.9 mg per liter or 0.7 mg BOD per mg surfactant. At much higher concentrations, of 100 mg surfactant per liter the first day BOD is small, but between the first and second day, all DO disappears. It would appear that there is a lag period before the right enzymes are produced to attack the surfactant molecule or to overcome the toxicity. The seed for these observations, however, was obtained from a waste water treatment facility which received this non-ionic surfactant in large quantities daily.

With higher concentration of surfactant, nitrification is retarded while all nitrification disappears at the highest surfactant concentrations studied where the floc still persists.

The newer dyes used with synthetic fibers (disperse dyes) dissolve in only three to five mg per liter concentration. They are completely refractive in some cases though non-toxic while some are toxic even though partially degradable.

Thus, the new pattern of waste water treatment with individual mills of the carpet or tufted textile industry demands extended aeration with sludge return. The development of floc is generally possible with separate sludge return facilities. The presence of floc does not always produce a color free effluent even though there may be a low BOD in the effluent.

Sincerely yours,

Robert S. Ingols
Project Director

GEORGIA INSTITUTE OF TECHNOLOGY
EXPERIMENT STATION 225 North Avenue, Northwest · Atlanta, Georgia 30332

January 7, 1970

Dr. Robert Bunch
Taft Sanitary Engineering Center
Federal Water Pollution Control Adm.
4600 Columbia Pkwy.
Cincinnati, Ohio

Re: Quarterly Report B-338

Dear Bob:

Enclosed is a copy of the manuscript prepared for submission to the program committee for the Water Pollution Control Federation conference in Boston for October this year.

Considerable time was spent in preparing the manuscript and no other work was done in part because of the problem in finding a research assistant. I thought that one had been hired, but his first employer was so impressed by my offer that he was offered a raise that I could not match. Thus, my search continues.

Sincerely yours,

Robert S. Ingols
Project Director

RSI/sc

ABSTRACT

SYNTHETIC SURFACTANT DEGRADATION
Robert S. Ingols

While some problems from synthetic organic molecules such as surfactants have developed from domestic waste water treatment, many more problems are possible with changing mixtures of synthetic materials in industrial waste water treatment.

In the textile industry synthetic surfactants are used in high concentrations (500 to 1000 mg/ℓ) as an aid in dying synthetic fibers. Rinse water and some other minor flow streams may reduce this concentration to 200 mg surfactant per liter waste water. When a specific mill is located outside of city limits near a small stream separate waste water treatment facilities have to be designed to treat the waste with this amount of surfactant.

The nonionic surfactant, "Ekaline G. Flakes," molecules have a high BOD per unit weight at concentrations less than 5 mg/ℓ as shown in Table I. The circled figures in Table I show that the bacteria do not always respond readily and these low values were not included in the curves of Figure I.

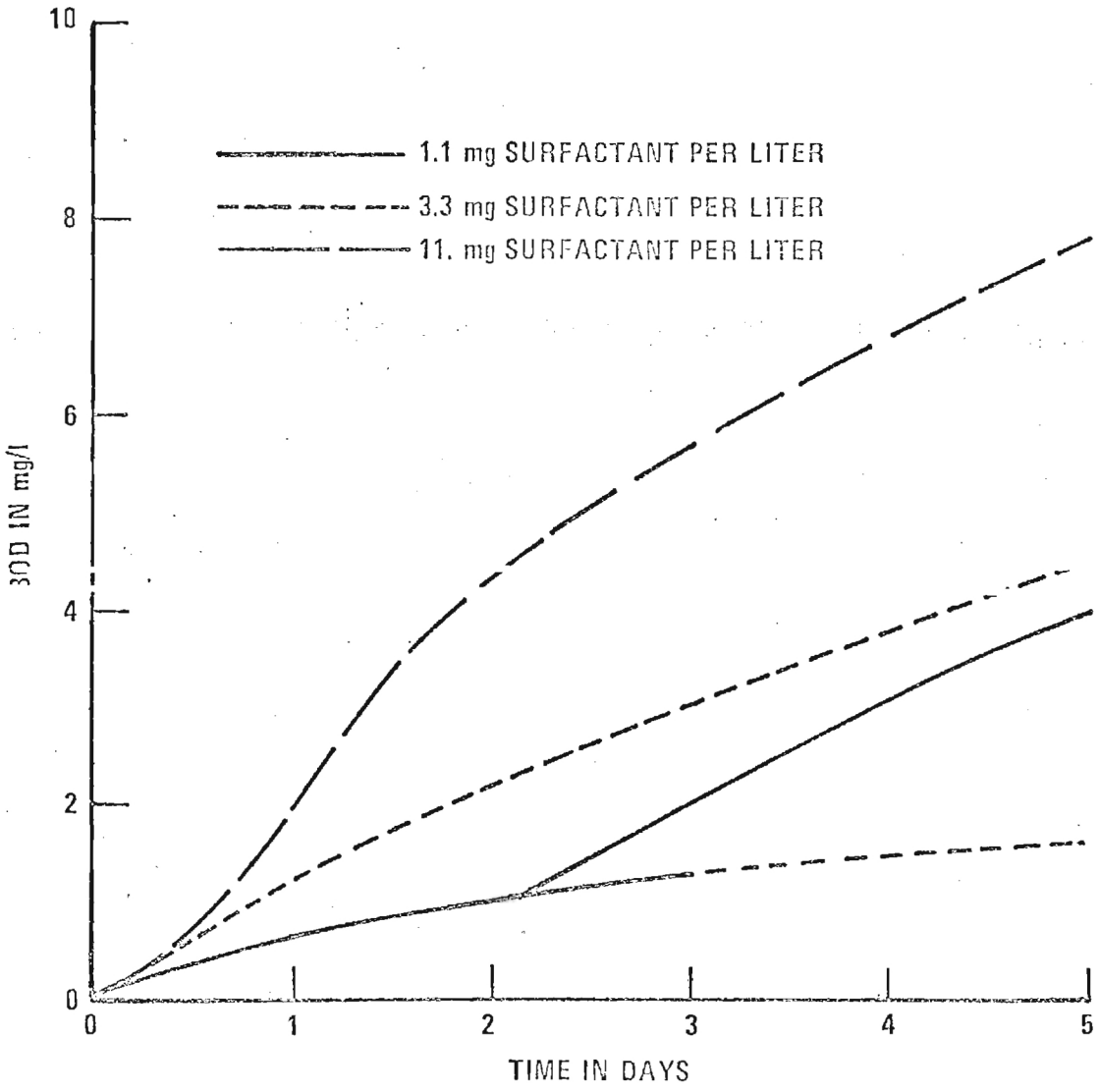
When this surfactant is fed to activated sludge at 175 mg per liter along with normal food of one gram per liter, there is very little indication of surfactant degradation as shown in Figure II. Thus, biodegradable synthetic surfactants are used as food only at low concentrations or in the absence of normal food when present in high concentrations.

Because of the lower relative cost of anaerobic conditions, it is necessary to study anaerobic action with the surfactant. The data of Figure III indicate that there is very little use of EGF during 30 days of feeding digester sludge which also receives normal food. When all feeding was stopped the

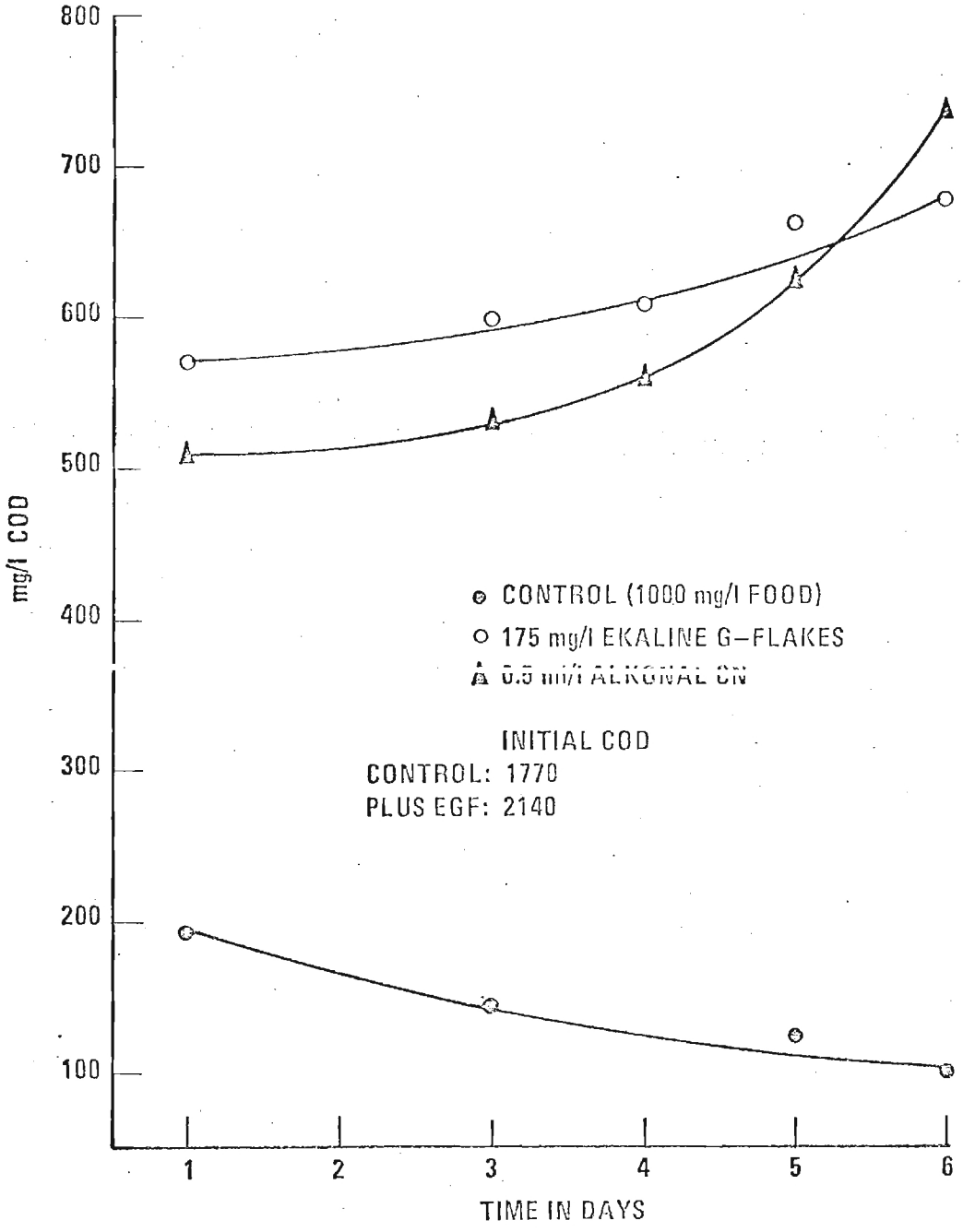
control continued to produce gas while very little gas was produced in the presence of surfactants while observed for another 15 days. When a sample of the waste water from a dye beck was observed, very little action or change in COD was observed.

The aerobic treatment of the waste water for 22 hours from a dye beck at 900 mg/ℓ surfactant did produce a sharp reduction in strength as shown in Figure IV after 3 days of dosing. Sludge finally developed which could degrade the organic matter. When the dye beck was used at half the concentration discussed above, the organisms were able to degrade the organic matter earlier and to show less difficulty with a second batch of waste water from another dye beck.

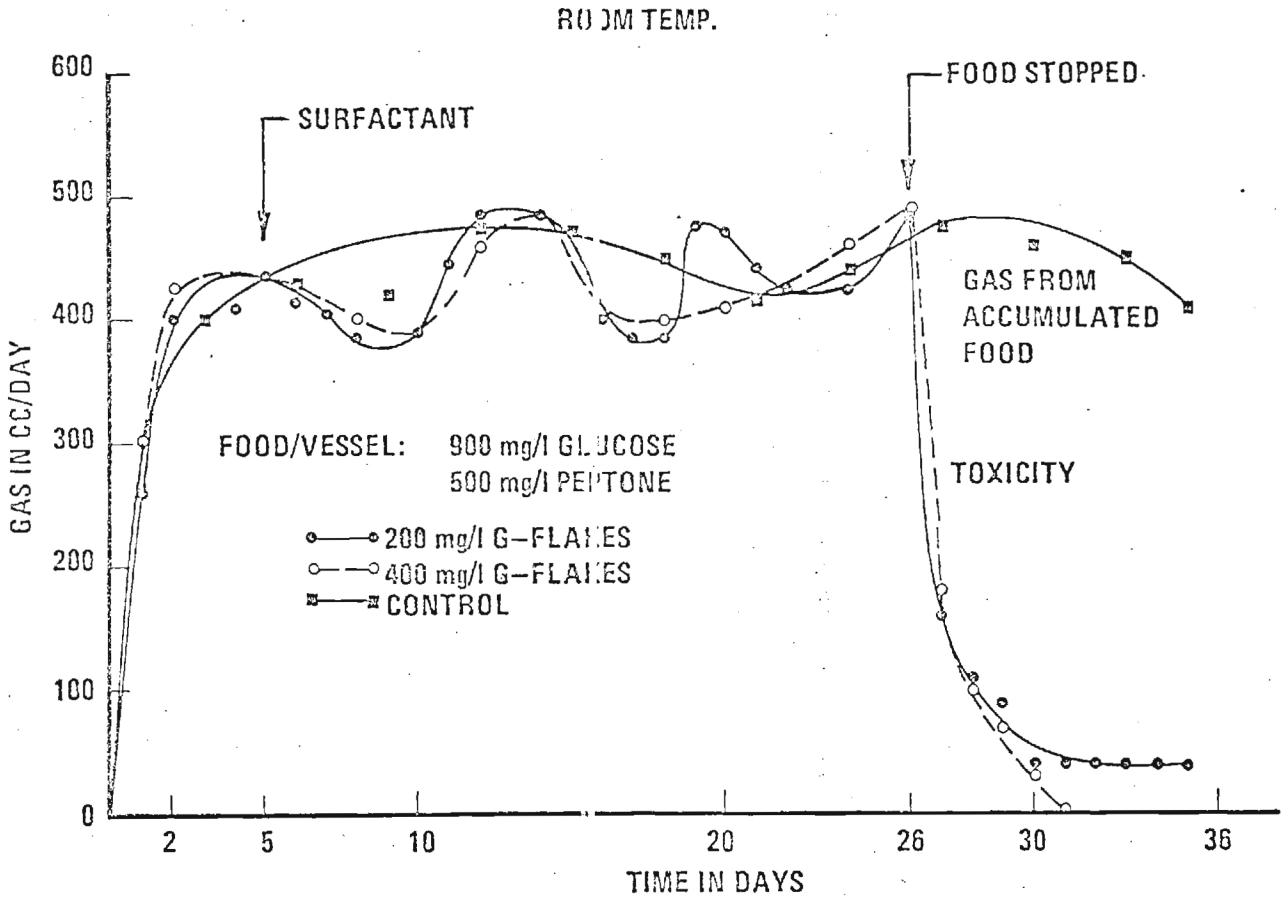
Thus, the non-ionic synthetic surfactants can be oxidized by bacteria with time at high concentrations in the absence of normal food molecules.



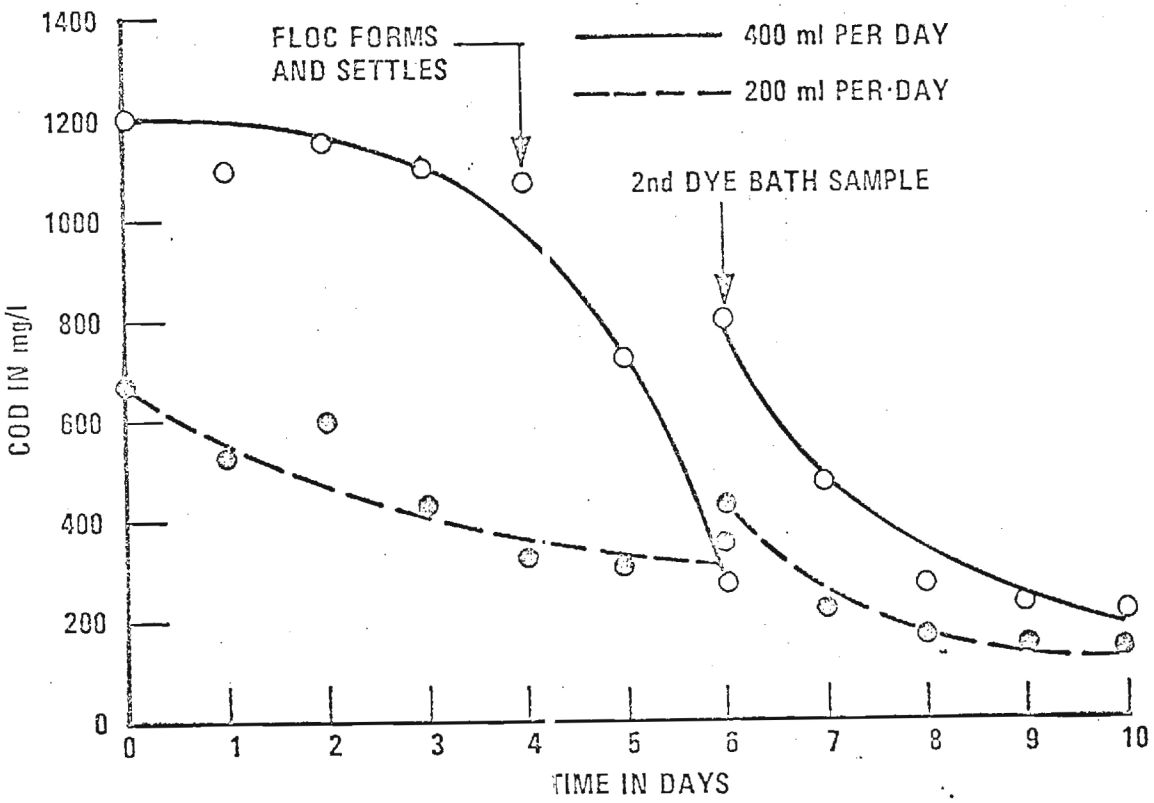
. BOD values of 3 concentrations of Ekaline G Flakes using an acclimated seed.



2. Effect of 175 mg of the nonionic surfactant, Ekline G Flakes, upon the ability of two grams of activated sludge to reduce the concentration of surfactant plus one gram normal food.



Effect of two concentrations of Ekaline G Flakes upon the digestability of normal food.



Ability of acclimated seed to form floc and degrade detergent at 2 different concentrations with two waste dye water samples with 22 hours aeration.

Synthetic Surfactant Degradation

Robert S. Ingols and Ekkehart Gasper

Synthetic surfactants have been a tremendous boon to public health in many ways, but the problems in waste water treatment and the persistent foam on our rivers point out that more information is needed to improve condition of our rivers. A recent review (2) indicated that even high concentrations (200-400 mg/l surfactant) have very little oral toxicity for laboratory animals, but the review does not include the response of microorganisms to these concentrations of surfactants. This discussion will concern itself with the response of microorganisms to surfactant concentrations of 200 mg/pl or more in a separate industrial waste water treatment facility.

While many studies have been made on synthetic surfactants at the low concentrations which are normal to domestic waste water, a few publications have dealt with the high concentrations which the textile industry uses (1,2). Nonionic surfactants are used to aid dye absorption by synthetic fabrics in the carpet industry. The nonionic surfactant can be used effectively with a larger variety of dyes than would be possible with ionized surfactants of either charge. Because agitation is also needed for uniform color uptake, a low or non-foaming surfactant is preferred over a foam producer. The nonionic surfactants in this study have polyethylene oxide chains which are normally biostable (1) because of the frequently reoccurring ether linkages. The water insoluble hydrocarbon portion of the molecule must be linear for biodegradation, while the presence of a second polar group at the terminal carbon favors the alkyl chain oxidation and retards foaming.

This paper seeks to define the detention time and necessary conditions for the biodegration in a separate waste water treatment facility. When

extended aerobic treatment is used what concentration of surfactant can be present and still allow floc development? What extent of surfactant degradation can be expected under aerobic degradation or anaerobic conditions?

Methods and Materials

Aerobic Digestion

Return activated sludge was collected from a sewage treatment facility in Atlanta, Georgia, and a 200 ml sludge layer measured into each of several one liter cylinders. After adding food and chemical (see legends) the volume in each cylinder was brought up to one liter with tap water. Vigorous aeration was then started. Foaming was prevented by spraying an antifoam agent into the aerating sludge.

After 22 hours of operation the air supply was shut off and sludge allowed to settle for 30 minutes. Samples were taken from the supernatant liquid for pH measurements and COD tests. The liquid was siphoned off to the 200 ml mark, after 2 hours settling. Any sludge that may have developed in excess of the original volume was also withdrawn. The feeding and chemical dosing procedure of the previous day was repeated. The experiments were performed at room temperature (25°C).

Anaerobic Digestion

Fresh, anerobic digester sludge was collected from the same Atlanta treatment facility, and 500 ml measured into one liter aspirator bottles. These were rubber stoppered with the provisions for two openings: one for the escape of gases, and the other for the daily dosing of the digester with food and surfactants. Daily gas production was followed by the displacement of a saturated salt solution (150 g/l NaCl and 5 ml/l HCl) in one liter gasometers. The experiments were performed at room temperature (25°C).

Results

Activated sludge was obtained from Atlanta's South River plant, which treats waste water from both domestic and industrial sources. Several 2.5 g samples were placed in liter cylinders and diluted to volume after adding food and surfactant. The activated sludge reduced the COD of one gram normal (0.5 g glucose -0.5 g peptone) food from 1770 to 200 (1580) in 22 hours at room temperature as shown in Figure I. When more food was added as anoinic surfactant (ORVUS AB Granules*) the effluent COD was increased in proportion to the added COD of the surfactant. There was no change in the COD removed up the added amount of 250 mg/l (1460). With the highest concentration of surfactant, there was an eight percent loss in COD reduction the first day, but thereafter, the incremental loss in the COD reduction can be accounted for by an accumulation of the surfactant residual in sludge layer.

Because of the very high total food concentration with the highest surfactant concentration (a 2000 mg/l COD) in Figure I, 300 mg/l food concentration was used in the control for Figure II. The data given in Figure II shows that a lower total food concentration does not reduce the toxicity or increase the utilization of 250 mg/l LAS. The highest total original COD in Figure II was only 770 mg/l. At the end of 24 hours the COD of the higher surfactant concentration mixture was reduced to the value of the control, but after 48 hours there was no apparent oxidation and even some sludge dispersion. Thus, even the "biodegradable" (LAS) is not readily oxidized when it is found in the high concentration of certain industrial waste waters. The 250 mg/l becomes increasingly toxic after 24 hours.

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*Obtained from Procter and Gamble-Cincinnati, Ohio

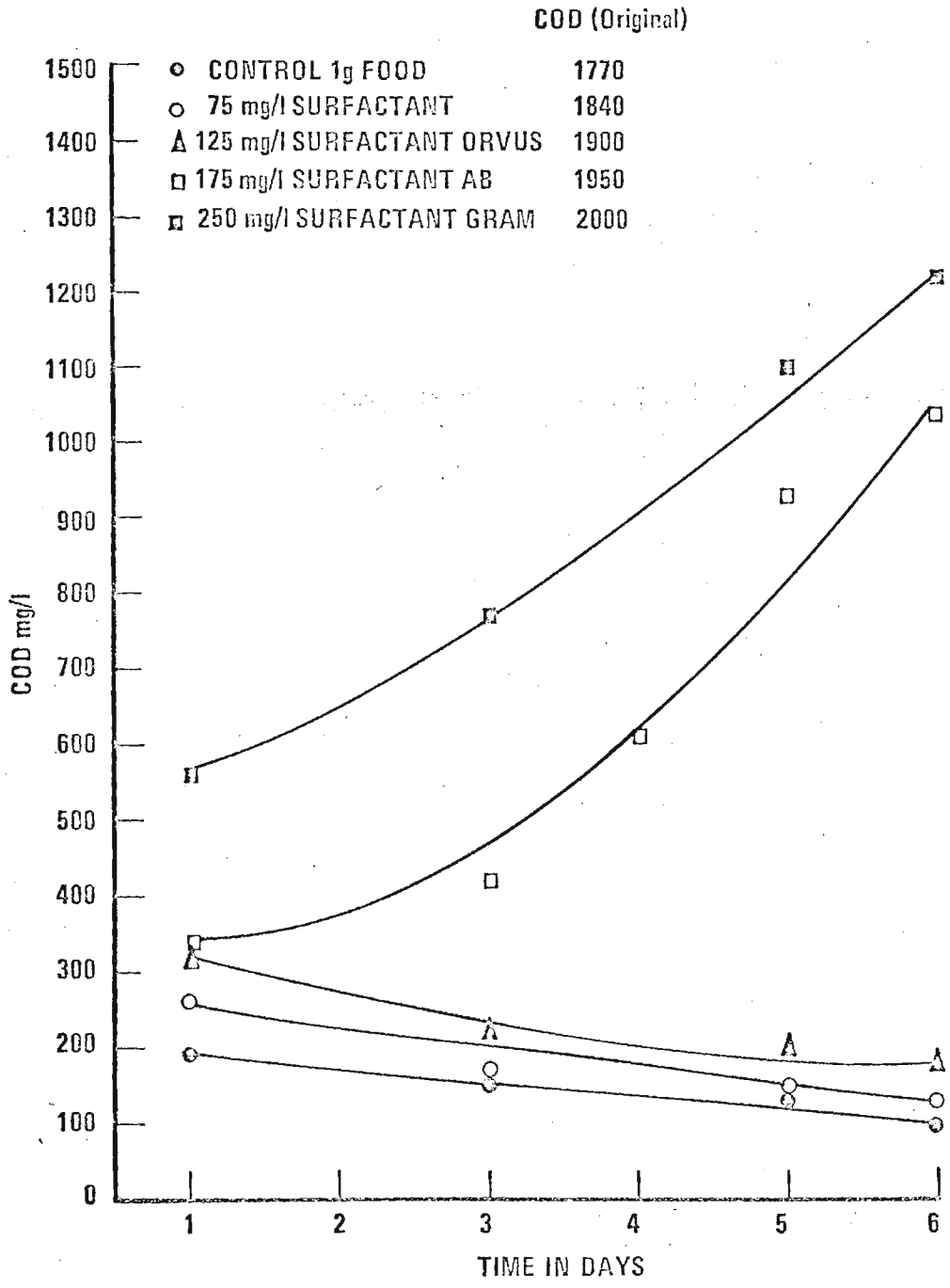
COD (Original)
CONTROL 1g FOOD 1770
75 mg/l SURFACTANT 1840
125 mg/l SURFACTANT ORVUS 1900
175 mg/l SURFACTANT AB 1950
250 mg/l SURFACTANT GRAM 2000
COD mg/l
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
1
2
3
4
5
6
TIME IN DAYS

Figure I

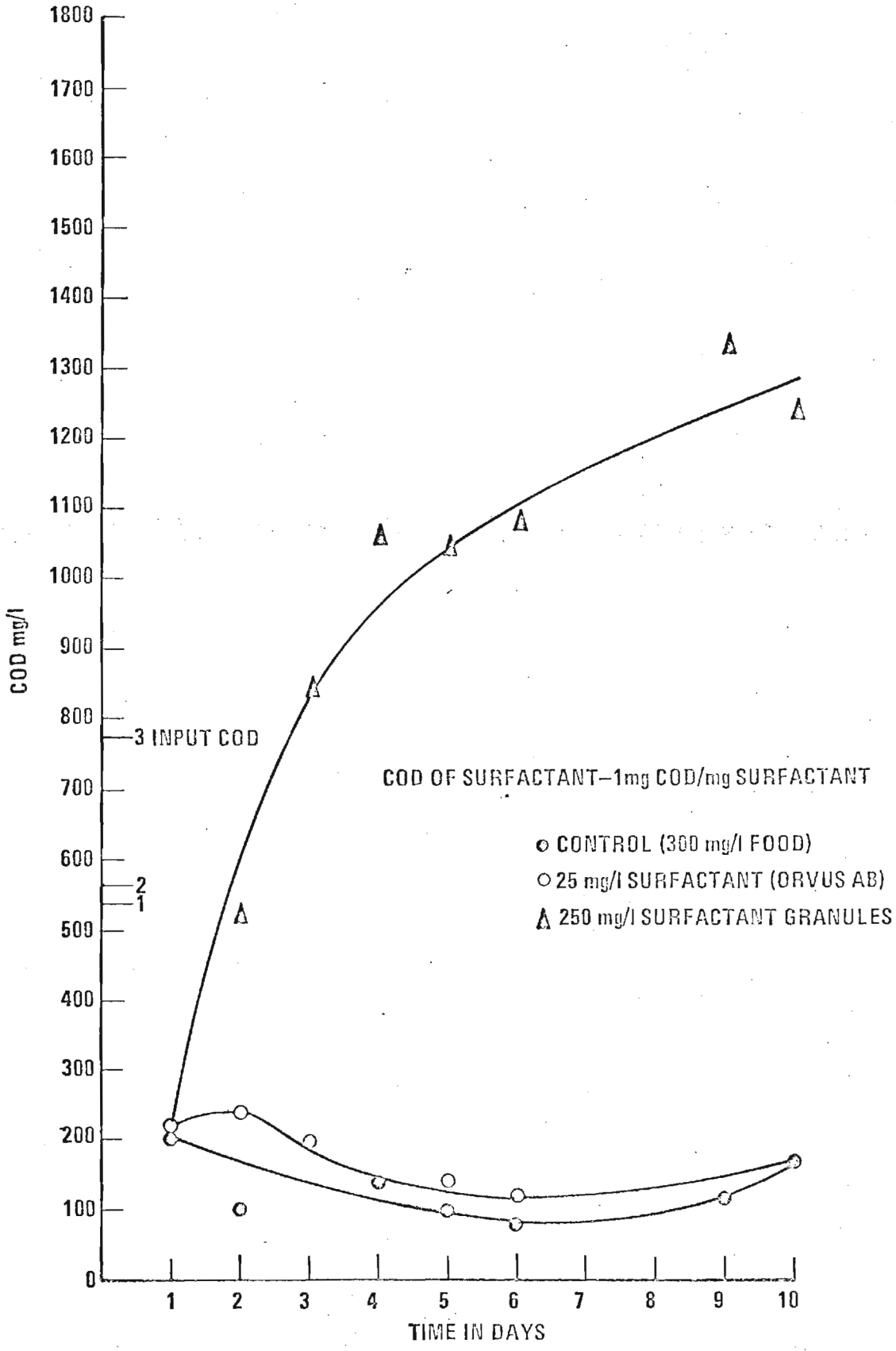
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
COD mg/l
3 INPUT COD
2
1
COD OF SURFACTANT–1mg COD/mg SURFACTANT
CONTROL (300 mg/l FOOD)
25 mg/l SURFACTANT (ORVUS AB)
250 mg/l SURFACTANT GRANULES
1
2
3
4
5
6
7
8
9
10
TIME IN DAYS

Figure II

Because the textile industry uses nonionic-surfactants which are discharged in waste water at 200-400 mg per liter only the high concentration of 175 mg Ekaline G Flakes (EGF) per liter was studied in obtaining part of the data of Figure III. Again, the increment in the effluent COD agrees with that of the control plus the COD of the surfactant for the EGF. The slight rise over the period of study would agree with the carry over in the liquid volume of the sludge layer. These data indicate that the EGF are not degradable at this concentration in the presence of normal food. The data in Figure III for the Alkonal CN is not discussed in detail because its formula is not available.

A BOD of the EGF was determined at several low concentrations with the dilution technique using a seed sample from an aeration tank treating waste water containing. The curve for the lowest food concentration shows that the BOD develops in a two step function. Whether the second step is nitrification or breakdown of the less available polyethylene portion is not known. There is a marked lag in the oxygen demand at the concentrations of 11 mg/l and higher (the lag lasted for 4 days in some of the replicates as indicated in Table I). The 110 mg EGF per liter was not expected to have a BOD, but in the absence of normal food the bacteria are able to utilize the surfactant molecules.

The conclusion was reached that the EGF were biodegradable as shown by their BOD values but that aerobic biodegradation occurs only in the absence of other, normal food This brings us to the practical question as to whether the surfactant can be degraded under anaerobic conditions.

The fact that the surfactant did not decompose at high concentrations under aerobic conditions in the presence of other food, made it necessary to

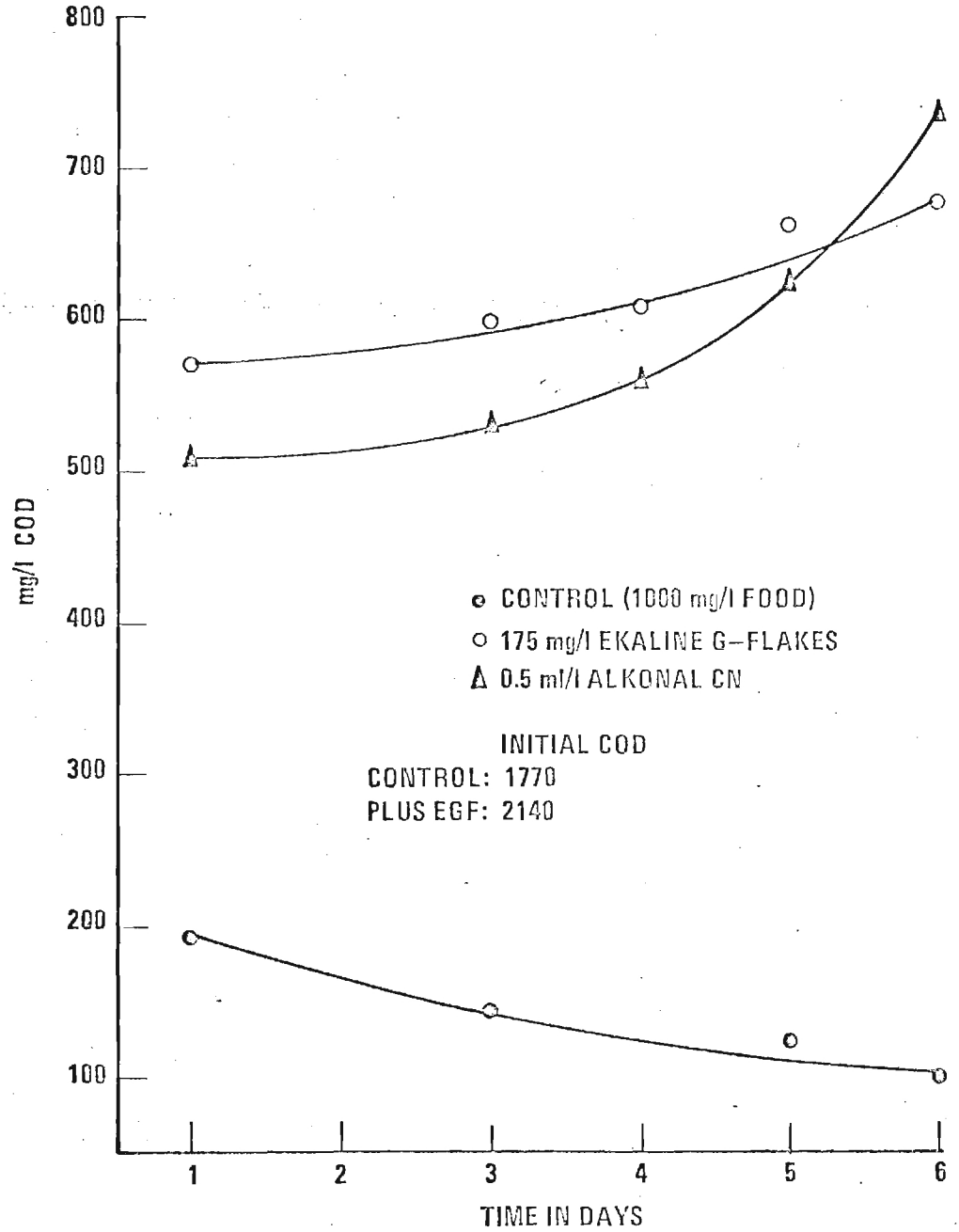
800
700
600
500
400
300
200
100
mg/l COD
o CONTROL (1000 mg/l FOOD)
o 175 mg/l EKALINE G–FLAKES
Δ 0.5 ml/l ALKONAL CN
INITIAL COD
CONTROL: 1770
PLUS EGF: 2140
1
2
3
4
5
6
TIME IN DAYS

Figure III

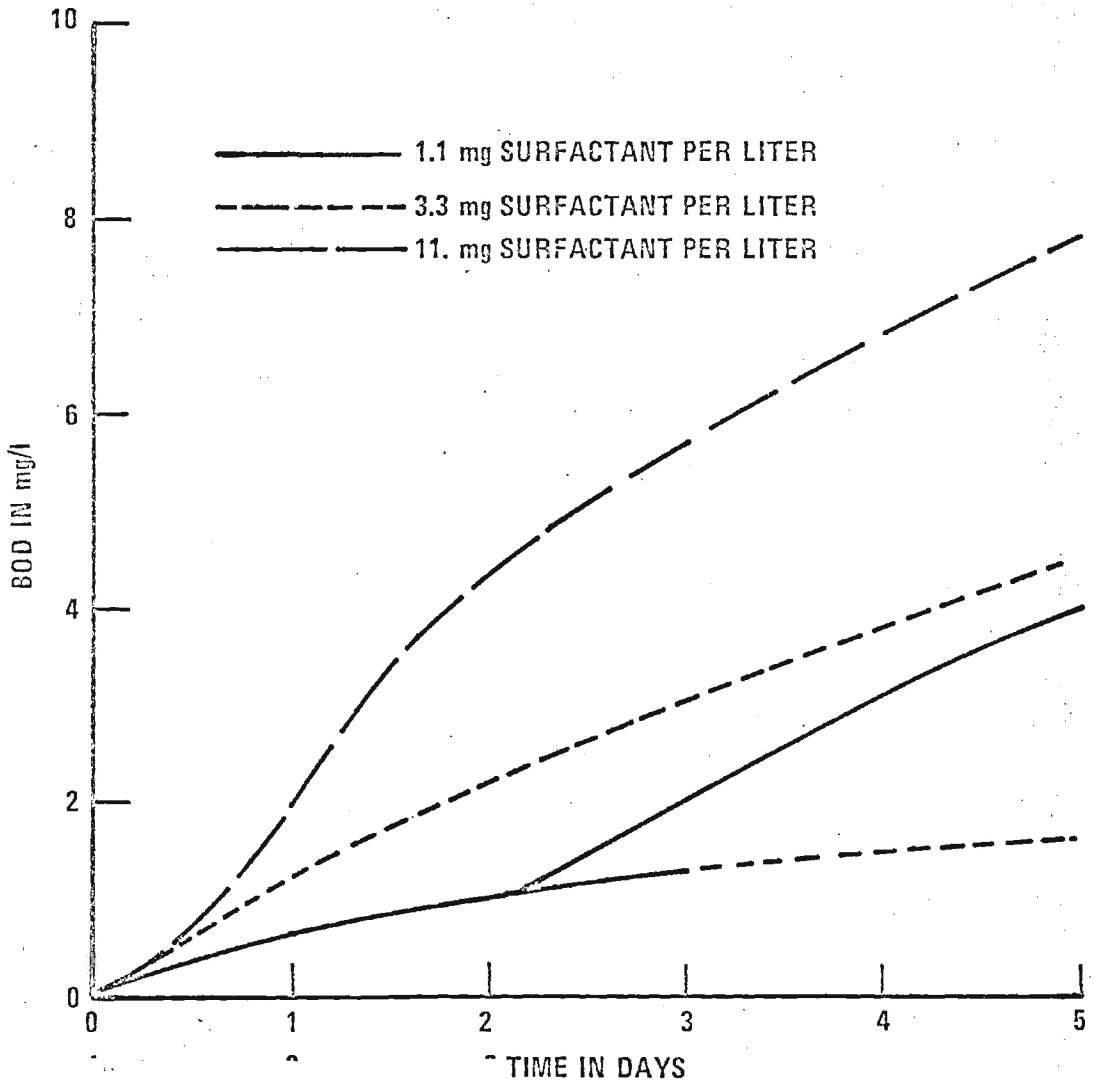
1.1 mg SURFACTANT PER LITER
3.3 mg SURFACTANT PER LITER
11. mg SURFACTANT PER LITER
BOD IN mg/l
TIME IN DAYS
0
2
4
6
8
10
0
1
2
3
4
5

Figure IV

Table I

Dilution BOD studies with

various Ekaline G. Flakes

concentrations

Concentration	BOD after days				
surfactant	1	2	3	4	5
mg. per liter	mg/1	mg/1	mg/1	mg/1	mg/1
1.1	0.7	1.1	1.9	2.8	3.8
3.3	1.1	3.3	(2.3)	3.5	4.4
11.0	1.9	4.4	(2.5)	(2.1)	7.9
110.0	2.4	>17.0	---	---	---

Circled numbers were not plotted in Figure IV.

ask whether the same could be observed under anaerobic conditions. Anaerobic (digestion tank) sludge was obtained locally. It was fed daily a 2-1 glucose-peptone mixture. The bacteria in the control continued to produce gas daily for 36 days. When surfactant was added as shown in Figure V, no difference in gas volume was observed until all feeding was discontinued. With no added food, there was enough food present that gas production was almost unchanged for several days while very little gas was produced in the presence of surfactant during the next 15 days. A COD of the supernatant with surfactant (after centrifuging and filtration) accounted for all of the surfactant added.

While Alkonal CN is not used in large quantities, its effect on sludge digestion was also studied. From the data of Figure VI it can be seen that the Akonal CN in the quantitites studied interfered with gas production.

Samples of two dye becks were brought into the laboratories at five-day intervals. The first sample, as shown in the data of Table II and Figure 7, had a much higher content of organic matter than the second sample (2400 mg/l COD vs 1600 mg/l COD). Based on the COD and realizing that there was some dye present (each dye sample was taken from a spent solution just as it was discharged to the sewer), it was concluded that the first sample apparently contained 0.9 g per liter surfactant and the second 0.6 g per liter This difference is caused by the differences in weight of carpet processed (carpet is processed in a beck in lengths of 500 yds, but varies in weight because of the weight of pile). The carpet is rinsed with a volume of water equal to the dye bath. A sample of the aeration pond from this mill was brought into the laboratory as seed. The 200 ml of seed was fed 400 ml of the dye solution daily for the left hand column of figures in Table II whereas only 200 ml dye sample was fed daily for the numbers in the right hand columns. Atlanta tap

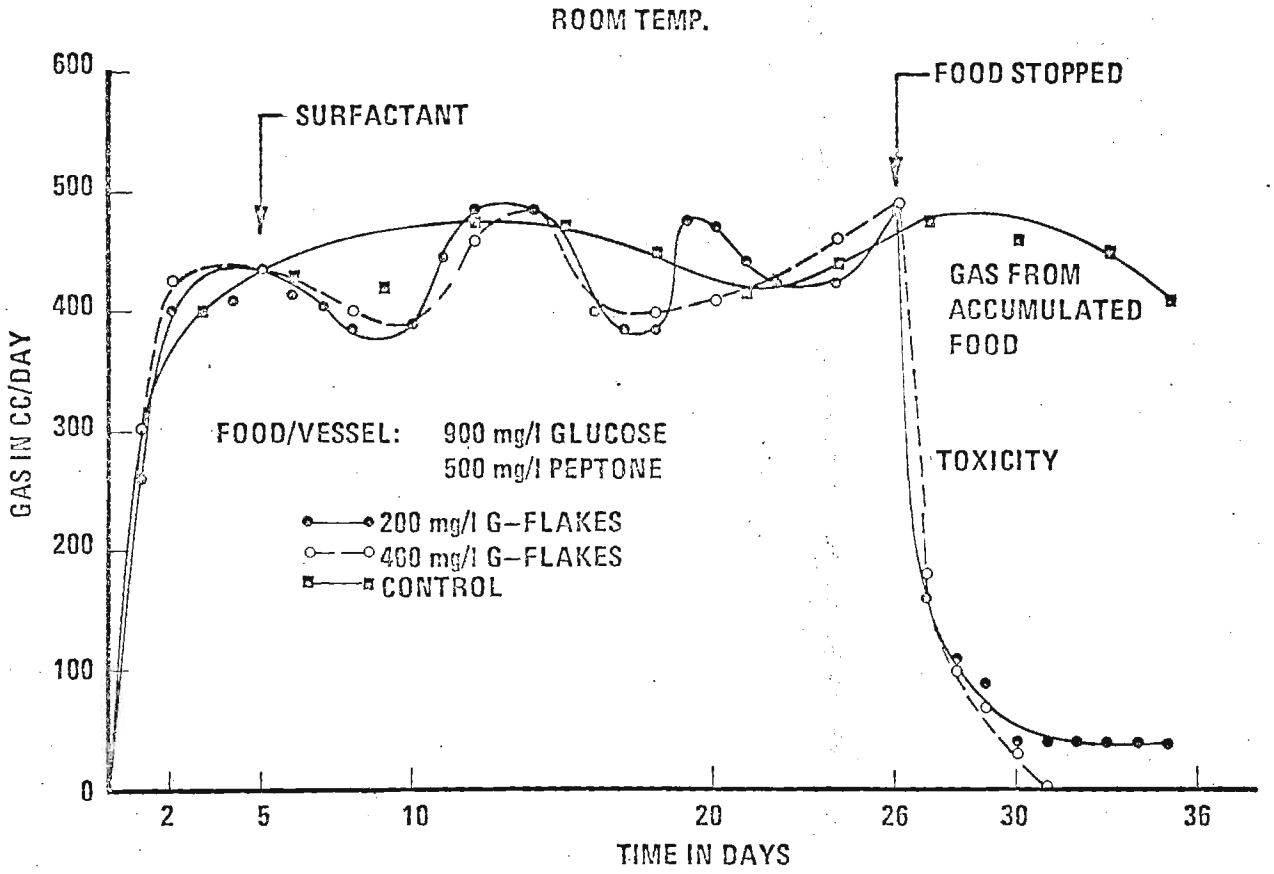
ROOM TEMP.
FOOD STOPPED
SURFACTANT
GAS FROM ACCUMULATED FOOD
FOOD/VESSEL: 900 mg/l GLUCOSE
500 mg/l PEPTONE
TOXICITY
200 mg/l G–FLAKES
400 mg/l G–FLAKES
CONTROL
GAS IN CC/DAY
600
500
400
300
200
100
0
2
5
10
20
26
30
36
TIME IN DAYS

Figure V

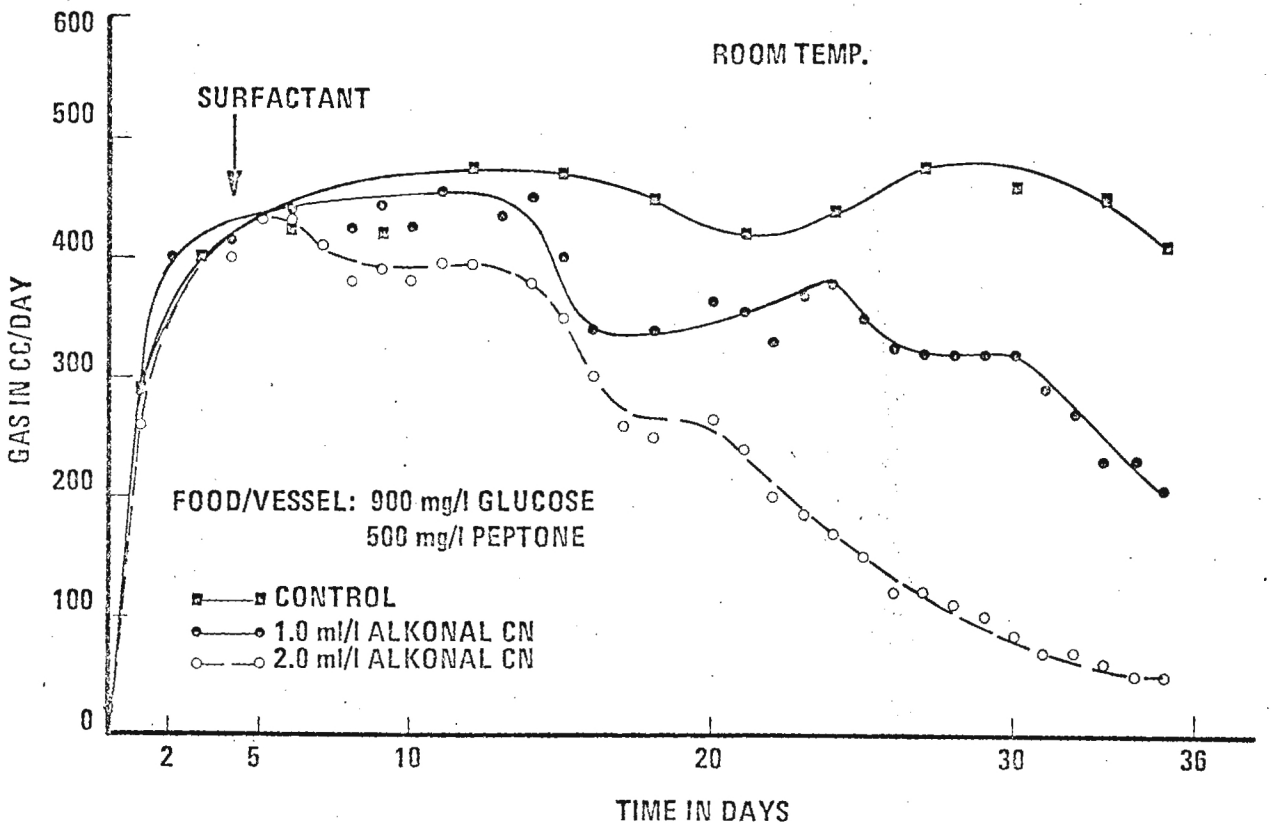
ROOM TEMP.
SURFACTANT
GAS IN CC/DAY
600
500
400
300
200
100
0
FOOD/VESSEL: 900 mg/l GLUCOSE
500 mg/l PEPTONE
CONTROL
1.0 ml/l ALKONAL CN
2.0 ml/l ALKONAL CN
2
5
10
20
30
36
TIME IN DAYS

Figure VI

Table II

Aeration Time	Dye sample plus one volume of rinse water					Dye sample plus three volumes of rinse water				
	COD	Reduction				COD	Reduction			
		as decanted		with floc removal			as decanted		with floc removal bacentrifuge	
days	after 22 hours	mg/l	percent	mg/l	percent	after 22 hours	mg/l	percent	mg/l	percent
0	(1200)	-	-	-	-	(670)	-	-	-	-
1	1100	100	9	-	-	520	150	22	-	-
2	1160	40	3	-	-	600	70	11	-	-
3	1300	0	0	-	-	580	90	13	-	-
	1100	-	-	100	9	410	-	-	260	40
4	1340	0	0	-	-	600	70	11	-	-
	1070	-	-	130	11	320	-	-	350	53
5	890	310	25	-	-	520	150	22	-	-
	720	-	-	480	40	300	-	-	370	55
6	510	690	57	-	-	440	230	34	-	-
	25	-	-	950	79	350	-	-	320	48
0	800	-	-	-	-	420	-	-	-	-
1 (7)	610	190	24	-	-	350	70	17	-	-
	475	-	-	320	40	260	-	-	150	38
2	510	300	37	-	-	240	180	43	-	-
	270	-	-	530	68	160	-	-	260	60
3	420	380	48	-		280	140	33	-	-
	230	-	-	570	71	140	-	-	280	67
4	390	410	51	-	-	290	130	30	-	-
	210	-	-	590	74	140	-	-	280	67

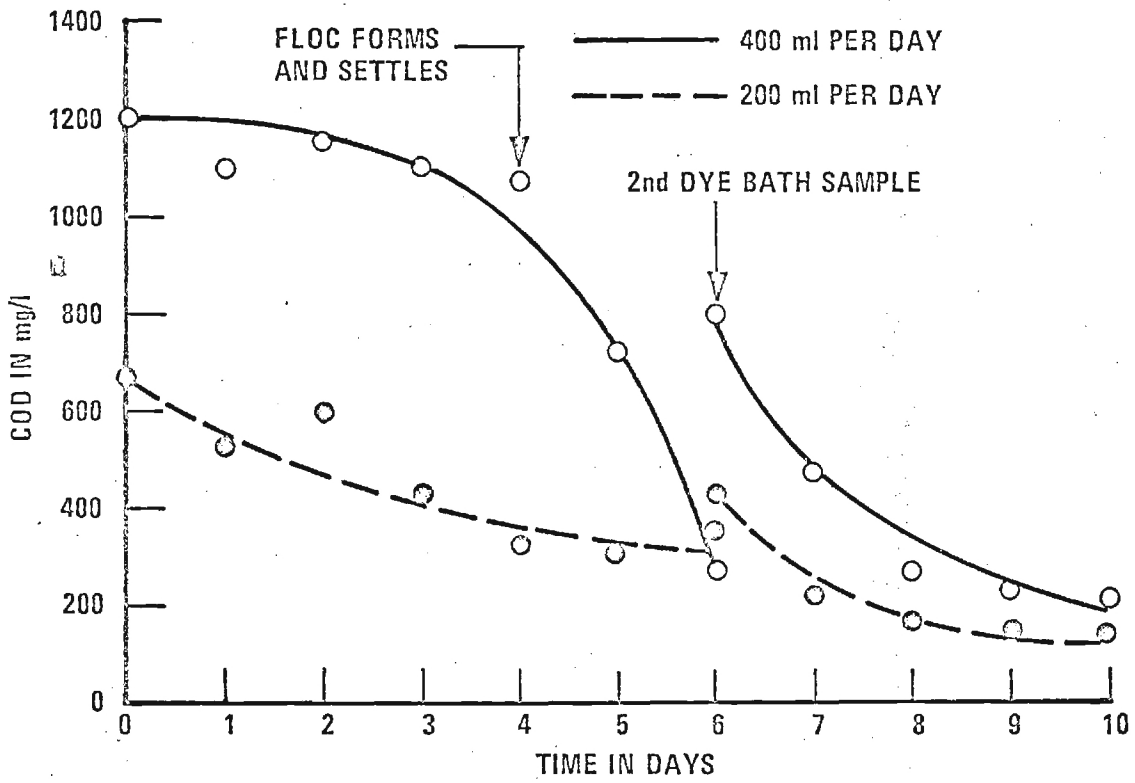
FLOC FORMS
AND SETTLES
400 ml PER DAY
200 ml PER DAY
2nd DYE BATH SAMPLE
COD IN mg/l
1400
1200
1000
800
600
400
200
0
0
1
2
3
4
5
6
7
8
9
10
TIME IN DAYS

Figure VII

water was used as the rinse water. In the absence of a sludge layer at first and after a very small sludge layer formed following several days aeration, a constant volume of supernatant was decanted to leave all the settled sludge in 200 ml residue. It is obvious that much of the sludge settled poorly for centrifuging removed much more COD than plain settling. The data of Figure 7 gives the maximum COD removed. When enough floc finally formed in the sample with the higher dye concentration the COD reduction became significant. Because a large portion of the nonionic polyethylene surfactant molecule is not readily biodegradable, it would appear that most of the degradable portion has been oxidized when seventy percent of the COD has been removed.

THEORETICAL CONSIDERATIONS

The theoretical oxidation of the hydrocarbon of a polyethylene dodecanol may be shown as follows: (This is not similar to but not necessarily the formula for EGF.)

(1) $H(C_2H_4O)_8(CH_2)_{11}CH_2OH + 18\ O_2 \rightarrow 12\ CO_2 + 13\ H_2O$

538 molecular weight

Theoretical oxygen to surfactant quotient would be 1.1 to 1.0

If some of the polyethylene oxide chain is broken as shown by Frazee, Osborn and Crisler (1) then the oxygen requirement may be increased as follows:

(2) $H(C_2H_4O)_8(CH_2)_{11}CH_2OH + 38\ O_2 \rightarrow 28\ CO_2 + 29\ H_2O$

538 molecular weight 1216

Theoretical oxygen to surfactant quotient is 2.25 to 1.0

Thus, depending on the extent of surfactant molecule destroyed the BOD per unit weight of surfactant may be expected to be anywhere from .75 for

oxidation of the alkyl chain to 1.75 if the seed is starved and the polyethylene chain is also degraded (oxidized). The lowest surfactant concentration in Table I shows nitrification or breakdown of the polyethylene chain. The median concentration of 3.3 mg/l shows essentially complete oxidation of the hydrocarbon chain plus some nitrification or ethylene oxide breakdown, while the highest concentration in Figure 4 shows the BOD which might be expected from the oxidation of the hydrocarbon chain with some protoplasm synthesis. Thus, the acclimated seed shows good surfactant oxidation at the low concentrations.

The theoretical COD of the surfactant molecule should be the same as that for the complete oxidation as given in equation number 2. The COD by analysis is only 2.1 mg/mg EGF while the theoretical value of a similar molecule should be 2.3 mg/mg. surfactant. It appears that the actual COD is 93 percent of the theoretical. The data from Figure 3 shows that there is a first day increment of 380 mg COD with 175 mg EGF or that 100 percent of the added COD remains. Each day after that there is an increase in the COD difference between the control and the sample receiving normal food plus EGF. Some residual COD is left in the 200 ml of the residual seed layer. This explains the slow daily increment in COD from 380 to 570 in six days.

Discussion

It is interesting to develop concepts for the design of treatment facilities for treating waste water with Ekaline G. Flake as the principal organic constituent contributing to the BOD of the waste water. Even when acclimated bacteria are used a long period of four days is required for the development of floc. The floc developes more readily when a lower concentration is given

for oxidation.

Neither aerobic nor anaerobic conditions lead to appreciable destruction of the surfactant when other normal food is present and when the normal food is also renewed daily. In the absence of other food there tends to be a long lag period even for acclimated bacteria at surfactant concentrations greater than 3 mg/l.

Because high surfactant concentrations occur in some carpet mill effluents and floc because it has been observed that no floc formed in two years operation in the aeration facility of one mill, the question arose as to whether floc can form and if so under what conditions. The presence of disperse dyes confuses the issue because they are present and are also somewhat toxic. In carpet manufacturing no sizing material is used so that there is very little normal food contributing to the BOD.

The mill has its separate treatment facility because of its location; thus, there is no other source of normal food except some toilet wastes from mill personnel. On the basis of the time required for floc formation under ideal conditions it would appear that it is necessary to provide an equalizing tank (to reduce thermal and concentration shock), with 48 hours aeration and a separate sedimentation tank for producing return sludge. The present facilities have a final polishing tank.

Summary

The destruction of nonionic surfactants from industrial waste water poses problems in design. In the presence of normal food, the synthetic molecules of Ekaline G. Flakes at 200 mg/l are not broken down within 24 hours aeration with ten times their weight of activated sludge. A very diffuse aerobic floc

can be developed by allowing 48 hours detention for organisms which obtain most of their organic carbon from the EGF.

References

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