Combined Treatment of High Sulfate Water and Sewage Sludge

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INTRODUCTION

This study was prompted by the high sulfate concentration in the waters of western Oklahoma. At the present time, there is a project under way to treat the water by reverse osmosis or a similar method. If this method proves to be feasible, there will be a large amount of highly concentrated brine for disposal. One method of disposal might be to mix the brine with domestic sludge in an anaerobic digester. If an active population of sulfate-reducing bacteria is maintained in the digester, these bacteria would utilize the sludge as a carbon source and the sulfates as oxygen donors, reducing the sulfates to sulfides. The hydrogen sulfide gas evolved could be used to produce elemental sulfur or sulfuric acid for commercial purposes.

The object of the experiment was to determine the feasibility of using sulfate-reducing bacteria in the anaerobic decomposition of waste-water sludge. In the conventional anaerobic digestion process, bacteria, commonly called acid-formers, decompose organic matter into organic acids and carbon dioxide. These organic acids are then decomposed by another group of bacteria commonly called methane-formers, into methane, carbon dioxide and water. It has been shown that sulfate-reducing bacteria are theoretically more efficient than the methane-formers and may be used to advantage in this process (Pipes, 1960). There are a number of reasons why this has not been a widespread practice, however:

1—The gas produced by the bacteria contains a high concentration of hydrogen sulfide, an odorous, corrosive, not readily flammable gas. The disposal of the gas may cause operational problems.

2—The hydrogen sulfide is inhibitory to the bacteria in the digester, so it must be removed as quickly as possible for optimum results.

3—The sulfate-reducing bacteria use the oxygen from the SO_4 radical to oxidize the organic matter, and therefore large concentrations of sulfate must be available for complete oxidation. High concentrations of sulfates are not found in most water supplies and are not wanted in any water supply, so sulfate must be added to the sewage after it reaches the sewage treatment plant.

The availability of high-sulfate waters in western Oklahoma reduce the magnitude of some of these disadvantages. Package plants (Grekel, Kunkel, and McGalliard, 1965) for the recovery of sulfur from H_2S gas are now available commercially. These package plants have a capacity of as little as 50 long tons/day with 80-90% recovery of the sulfur. The hydrogen sulfide can be removed from the sludge by recirculating the digester gas after the hydrogen sulfide is removed from the gas in the package plants. The waste water from a reverse-osmosis unit will provide an inexpensive source of sulfates.

LITERATURE SURVEY

Many investigators have conducted research on both anaerobic digestion and on sulfate-reducing bacteria but very little research has been

done on a combination of the two. Most textbooks covering the subject of sewage treatment have a discussion of anaerobic digestion. Information on sulfate-reducing bacteria, however, is not so well documented. The most comprehensive and up-to-date review of literature on sulfate-reducing bacteria was presented by Postgate (1965), who included a bibliography of 203 references. Despite the fact that much research has been done on sulfate-reducing bacteria, it has been done by people in many different fields with a number of diverse objectives. Postgate (1965) stated: "Despite their anaerobic habit, representatives of the group tolerate some of the most extreme terrestrial conditions of heat, cold, salinity, and pressure, so that in an era when science may be poised on the discovery of a true exobiology, knowledge of bacteria so firmly independent of the common terrestrial environment assumes renewed interest. In more mundane terms, the ubiquity of these bacteria and their proneness to generate large quantities of H_2S lead to a variety of impressive industrial, economic, and ecological effects, and for this reason papers relevant to them tend to be scattered over journals ranging from purely academic to those devoted to detailed technology."

To illustrate the controversy surrounding these bacteria we might notice that it is still a moot question whether the bacteria are autotrophic or heterotrophic. Butlin, Adams, and Thomas (1949) claimed they are facultative autotrophs while Postgate (1965) disputed this. The optimum temperature for growth is near 37 C as it is with many bacteria, but the maximum and minimum temperatures for growth vary widely. The first thermophilic sulfate-reducing bacterium to be isolated was found in the mud of a frozen ditch. Zobell (1947), however, cultivated a strain of the bacteria at 80 C. Butlin, Adams, and Thomas (1949) claimed that despite these bacteria being obligate anaerobes, "practically every type of soil and natural water contains them."

Some characteristics of these bacteria have been firmly established, however. Most of the sulfate reducers form spores; most are motile; all require iron as a micronutrient; and they are able to reduce sulfates, sulfites, and thiosulphates to sulfides.

In a laboratory study, Abd-el-Malek and Rizk (1963), using an artificial medium, found that the alkalinity of the medium increased with an increase in sulfate reduction. This is caused by the indirect production of calcium carbonate in the reduction of calcium sulfate and organic material. It was also reported in this study that cultures with an initial concentration of 2% (*w/v*) sodium sulfate showed faster reduction of sulfate as well as larger increases in alkalinity and a greater sulfide production than initial concentrations of 0.2, 3, 4, 6, 12 or 16%. In fact, concentrations greater than 6% semed to be inhibitory. In this same study, cultures of 2% sodium sulfate were adjusted to various pH values from 3.0 to 9.5. After inoculation with sulfate-reducing bacteria, all cultures between pH 3.5 and 8.0 showed black coloration, indicating growth, within 16 davs. The final pH in all cultures showing growth was between 8.6 and 8.8.

The rate of growth of these bacteria and their sulfate reduction depends upon a number of factors. Cultures normally show linear growth rates, but by using "a weak-base sulfate, together with a continuously renewed atmosphere containing CO_2 to buffer the medium and remove the sulfide, permits exponential growth in a defined medium at a minimum doubling time of about 3 hr to produce cell yields in the region of 0.75 mg (dry weight) of organisms/ml." (Postgate, 1965). Sulfide yields also depend upon the carbon source, chelating agents, oxidation-reduction potential of the medium and the cation concentration.

The economic usefulness of sulfate-reducing bacteria has not been thoroughly researched as yet. It was shown that the population of sul-

fate-reducing bacteria in a river increased markedly downstream from a paper mill in Canada (Desrocher and Fredette, 1960). This suggests that sulfate-reducing bacteria may be used to treat some paper-mill wastes. Sulfate-reducing bacteria have been used in India and Czechoslovakia to treat distillery wastes (Ghose and Basu, 1961; Barta, 1962). There have been two studies using sulfate-reducing bacteria to oxidize domestic sewage sludge. The first and most extensive was carried out in England under the direction of K. R. Butlin (Butlin, Selwyn, and Wakerly, 1956, 1960). It was discontinued after it had reached the stage of economic feasibility and had shown the economic bonus of improved sludge dewatering by this method. Another study was conducted by Pipes (1960) in the U.S. One object of this study was to determine if sulfate-reducing bacteria could degrade such things as grease, hair, feathers, skin and other keratins. It too, was successful.

Description of Experiment

The apparatus used in this experiment is shown diagrammatically in Fig. 1. The digester was a 2000-ml Erlenmeyer vacuum flask with a gas inlet tube at the bottom. A small diaphragm pump, operating for 5 out of every 20 min, recirculated the gas trapped above the sludge. The recirculated gas was bubbled through a 1% solution of zinc acetate to remove the hydrogen sulfide (Pomeroy, 1964) and allow the methane and carbon dioxide mixture to strip more hydrogen sulfide from the digester. The excess gas produced by digestion was collected over an acidified brine solution in calibrated bottles. The digester temperature was maintained at 32± 1C with an external heater.

The experiment was conducted in three parts. The successful completion of each part was necessary before beginning the next one. The first part was actually a batch-digestion process to determine if an active sulfate-reducing bacterial population was present in the sludge. A sample of 1000 ml of digested sludge from the Norman, Oklahoma, sewage-treatment plant was placed in the digester along with 500 ml of raw sludge. After a steady gas production of about 0.1 l/day was established, 300 ml of sludge was withdrawn from the digester. This was replaced with 50 ml of 6,000 mg/l sulfate solution plus 250 ml of raw sludge. The contents of the digester were well mixed and a 150-ml sample was withdrawn. Two

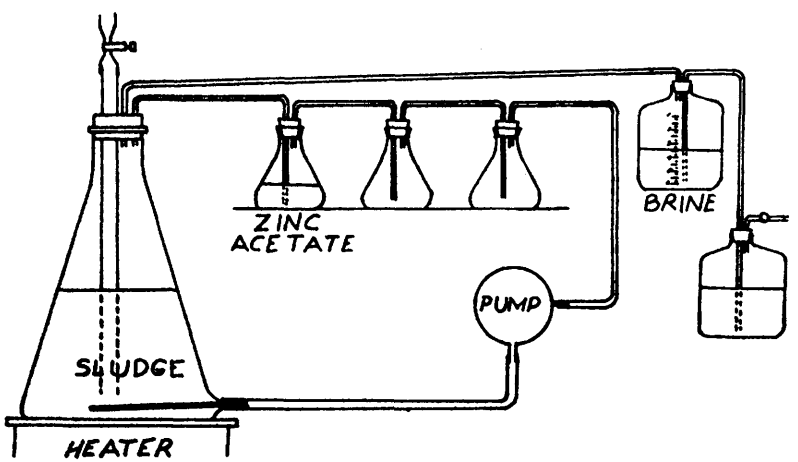

Figure 1. Experimental Apparatus.

weeks later, a 150-ml sample was withdrawn and analyzed. In this experiment, the H_2S was not absorbed in zinc acetate but was collected with the other gases.

In the second part of the experiment, a known amount of sulfate was added to the digester and the time necessary to decrease the sulfate concentration to near zero was determined. This was accomplished by operating the digester on a semicontinuous basis of daily sampling and feeding 150-ml portions. This gave a theoretical detention time of 10 days in the digester. The sludge was analyzed daily for pH, alkalinity, volatile acids, sulfate concentration (turbidimetric method and gravimetric method), total and volatile solids, COD, and total gas production.

Actually this part of the experiment was performed twice—once without H_2S removal and once with H_2S absorption in zinc acetate. In the former case, the H_2S production was estimated by absorbing measured volumes of the gas produced in acidified zinc acetate solution in an Orsat apparatus. In the latter case, the hydrogen sulfide absorbed was determined iodometrically.

In the third part of the experiment, an excess of calcium sulfate was added to the digester. This was to determine if high concentrations of sulfate would inhibit the bacterial growth and also to determine the rate of reduction of sulfate at this concentration.

Discussion of Results

The analysis of sludge, using contemporary methods and tools, does not yield reliable, reproducible, and accurate data. Most of the methods of analysis used in this experiment are described in *Standard Methods for the Analysis of Water and Wastewater, 12th Edition*. The other tests used are described in the Appendix. The trouble with these tests, however, is that most of them were developed for homogeneous, dilute samples. The sludge from a digester is certainly neither dilute nor homogeneous. The problems associated with nonhomogeneity were compounded by the small sample size in this experiment.

The results of the first part of the experiment are shown in Table I. In terms of the primary objectives of this part, it was successful because the sulfates were reduced. This demonstrated that the sulfate-reducing bacteria did not need to be cultured before addition to the digester, but a viable population of sulfate-reducing bacteria exists in a conventional anaerobic digester. This test indicated some problems with the analysis of the system. The gas production could be measured only to the nearest

Table I. Summary of Results: Part 1

	Initial	Final
pH	8.4	7.9
Alkalinity, mg/l $CaCO_3$	1880	2620
Vol. Acids, mg/l Acetic Acid	792	456
Sulfates, mg/l SO_4	310	0
Total Solids, mg/l	30,700	30,300
Vol. Solids, mg/l	14,000	14,900
COD, mg/l	32,720	25,120

Theoretical Sulfide Production = 155 mg S

Sulfide Recovered as H_2S = 0.043 l = 22.1 mg S = 14.2% theoretical

Theoretical Oxygen Demand Reduction due to Sulfate Reduction = 310 mg/l

Total COD Reduction = 7,600 mg/l

Gas Production = 2.15 l

CO_2 = 17% = .366 l

H_2S = 2% = 0.043 l

Others = 81% = 1.731 l

0.1 l and estimated to the nearest 0.05 l. A volume of 0.05 l H_2S represents about 26 mg sulfide, so the precision was limited. The H_2S content of the gas produced was measured by absorption in 1% zinc acetate solution in an Orsat apparatus. Here the precision was limited because other gases were also absorbed in the zinc acetate, and the results were often erratic.

The results of the second part of the experiment are shown in Tables II and III and the sulfide generation and sulfate removal relationships are shown in Figures 2 and 3. There are some significant differences and similarities between these two tables. Part (a) used the same gas-collection method as used in the first part. Shortly after the experiment, gas production ceased due to the build-up of an inhibitory concentration of soluble sulfides in the digester. The digester contents were then changed, the gas production was allowed to stabilize, and a flask containing zinc acetate placed in the gas-recirculation line to absorb the H_2S. Part (b) was then performed exactly as part (a) except that the H_2S was absorbed in zinc acetate. There was a greater COD reduction in less time in part (a), but this was probably due to the different bacterial population. The percent sulfide recovered for part (b), however, was much larger than that measured in part (a). The erratic results of the COD and solids tests illustrate the problems of nonhomogeneity mentioned earlier.

The results of part 3 are shown in Table IV. The gas collected contained a higher percentage of carbon dioxide than in any of the other tests because there were more sulfates present as oxygen donors. Since there was a high (saturation) concentration of sulfates available for several days, the rate of reduction was much greater than for part 2. The methods of analysis used for sulfates measure only the dissolved sulfates. Even though 5,000 mg/l of sulfates had been added to the digester, the analysis showed only a maximum of 2,020 mg/l sulfates.

The plateau on the curve in Fig. 4 demonstrates that a driving force was created between the maximum solubility of sulfates (about 2,000 mg/l) and the sulfates in solution (about 1450 mg/l). This driving force caused the particular sulfates to dissolve as the bacteria utilized the soluble sulfates. On the third day, all of the sulfates were in solution and their concentration began to drop.

The sulfide recovered was less than expected in all tests. Probably this was due to the precipitation of insoluble metal sulfides such as iron sulfide and the conversion of some hydrogen sulfide to elemental sulfur. There was no known way to measure these quantities, however.

TABLE II. SUMMARY OF RESULTS: PART 2a

	Start	Day 1	2	3	4
pH	8.2	8.1	8.0	8.2	8.0
Alkalinity, mg/l $CaCO_3$	1840	1980	2200	2400	2540
Vol. Acids, mg/l Acetic Acid	360	720	1340	1510	1780
Sulfates, mg/l SO_4	2020	1350	570	160	50
Total Solids, mg/l	49,100	55,100	55,400	40,200	52,800
Vol. Solids, mg/l	24,400	23,600	24,300	20,400	24,900
COD, mg/l	39,200	44,800	38,000	34,400	38,800
Gas Production, l	0.0	0.3	0.6	0.1	0.1

Theoretical Sulfide Production = 1010 mg S

Sulfide Recovered as H_2S = 0.02 l = 10.3 mg S = 1.02% theoretical

Theoretical Oxygen Demand Reduction due to Sulfate Reduction = 2020 mg/l

Total COD Reduction = 9,560 mg/l

Total Gas Production = 1.1 l

CO_2 = 18.0% = 0.20 l

H_2S = 1.8% = 0.02 l

Others = 80.2% = 0.88 l

Overall Rate of Reduction of Sulfate = 9,300 mg/l/day/ft³

TABLE III. SUMMARY OF RESULTS: PART 2b

	Start	Day 1	2	3	4	5
pH	7.0	6.7	6.6	6.7	6.6	6.9
Alkalinity, mg/l $CaCO_3$	2740	2560	2400	2700	2840	2680
Vol. Acids, mg/l Acetic Acid	3360	3340	3310	3600	3720	3530
Sulfates, mg/l SO_4	2020	1100	605	380	125	80
Total Solids, mg/l	46,500	46,800	51,600	48,600	47,400	50,400
Vol. Solids, mg/l	24,100	22,900	24,800	24,700	24,100	23,900
COD, mg/l	40,800	45,600	45,600	44,000	42,400	41,600
Gas production, l	0.0	0	0.1	0.2	0.2	0.2
Sulfide Collection, mg S	0.0	32.3	68.3	82.2	85.2	77.9

Theoretical Sulfide Produced = 1010 mg S

Sulfide Collected = 345.9 mg S = 34.3% theoretical

Theoretical Oxygen Demand Reduction due to Sulfate Reduction = 2020 mg/l

Total COD Reduction = 8,360 mg/l

Total Gas Production = 0.7 l

CO_2 = 21.5% = 0.15 l

H_2S = 0

Others = 78.5% = 0.55 l

Overall Rate of Reduction of Sulfate = 7,300 mg/l/day/ft³

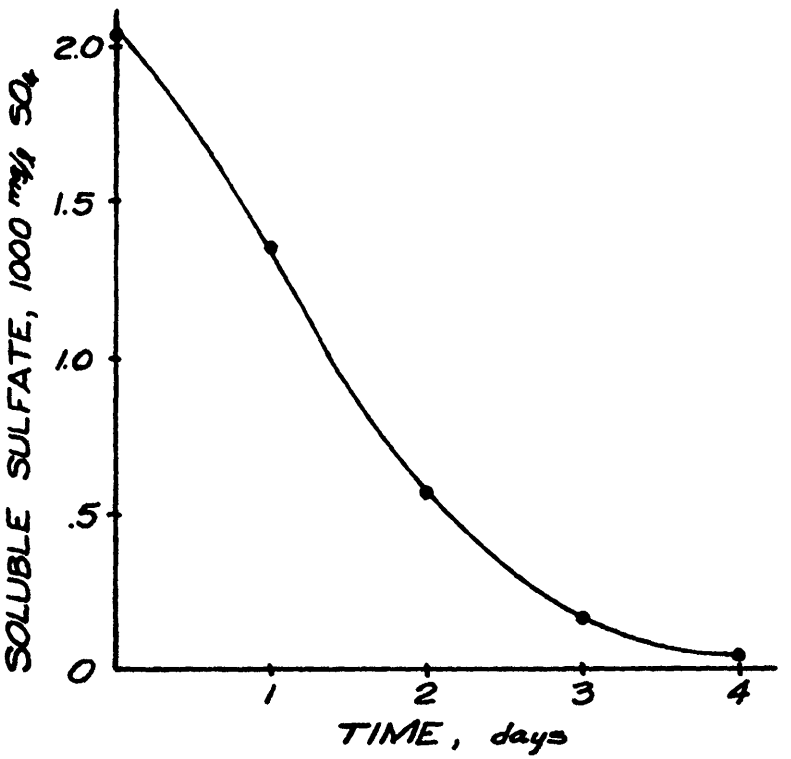

Figure 2. Sulfate Removal.

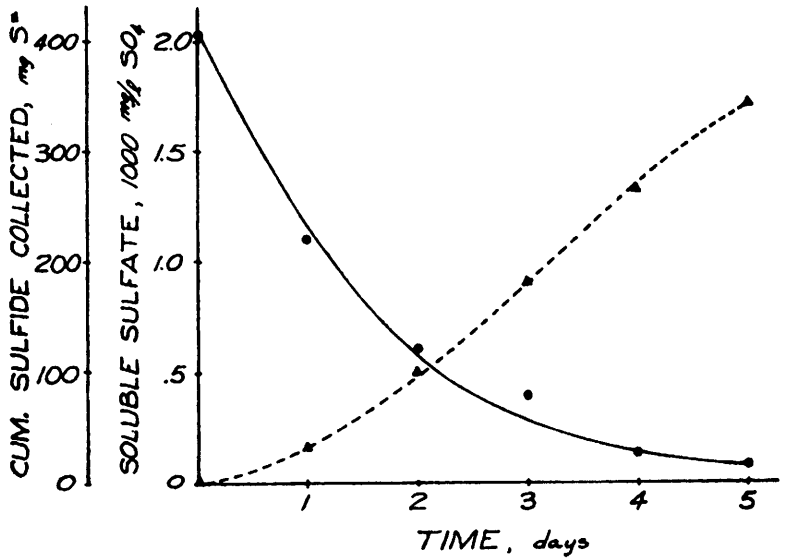

Figure 3. Sulfate Removal and Sulfide Generation.
---- Sulfide collected, ——— soluble sulfates

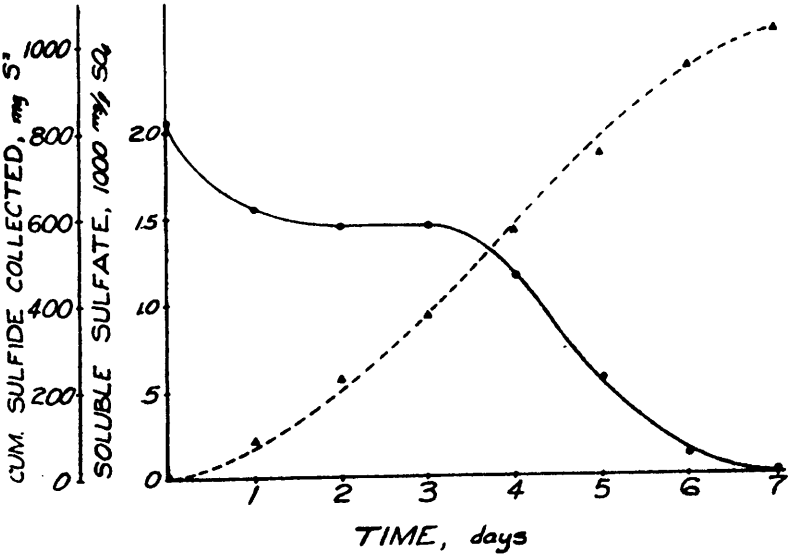

Figure 4. Sulfate Removal and Sulfide Generation.
---- Sulfide collected, ——— soluble sulfates.

TABLE IV. SUMMARY OF RESULTS: PART 3

	Start	Day 1	2	3	4	5	6	7
pH	6.9	6.8	6.9	7.0	7.3	7.5	7.4	7.3
Alkalinity, mg/l $CaCO_3$	2,680	2,400	2,980	2,480	2,840	3,180	3,400	3,300
Vol. Acids, mg/l Acetic Acid	3,530	3,000	3,220	3,120	3,580	3,120	2,760	2,930
Sulfates, mg/l SO_4	5,080 / 2,020	1,550	1,450	1,450	1,150	560	123	14
Total Solids, mg/l	50,400	44,500	37,500	52,600	54,400	50,500	53,200	56,001
Vol. Solids, mg/l	23,900	20,610	19,600	25,900	26,500	26,900	26,700	27,000
COD, mg/l	41,600	32,700	35,000	43,400	43,400	46,400	47,100	46,400
Gas Production, l	0.0	0.15	0.25	0.3	0.4	0.8	0.9	0.6
Sulfide Collected, mg S	0.0	82.5	141	147	193	177	202	88

Theoretical Sulfide Production = 2450 mg S

Total Sulfide Collected = 1030 mg S = 40.5% theoretical

Theoretical Oxygen Demand Reduction due to Sulfate Reduction = 5,080 mg/l

Total COD Reduction = 18,320

Total Gas Production = 3.4 l

CO_2 = 33.6% = 1.14 l

H_2S = 0

Others = 66.4% = 2.26 l

Overall Rate of Reduction of Sulfate = 13,700 mg/l/day/ft³

CONCLUSIONS

The conclusion from this study is that it would be feasible to treat high-sulfate waters in combination with domestic sludge. The optimum rate of sulfate addition to domestic sludge for the best reduction will be determined in a later study. Further studies should be carried out with a larger digester in order to give more reproducible and representative samples. In order to do an accurate and detailed study of this process, however, new techniques and new tools need to be developed for the analysis of anaerobic sludge.

The sulfates added to the digester need not be in solution because the particular sulfates will dissolve as the soluble sulfate concentration decreases.

The methane bacteria can co-exist in the digester with sulfate-reducing bacteria. This was shown by a greater COD reduction than could be expected by sulfate reduction alone and also by the low (20-30%) CO_2 content in the gas produced.

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