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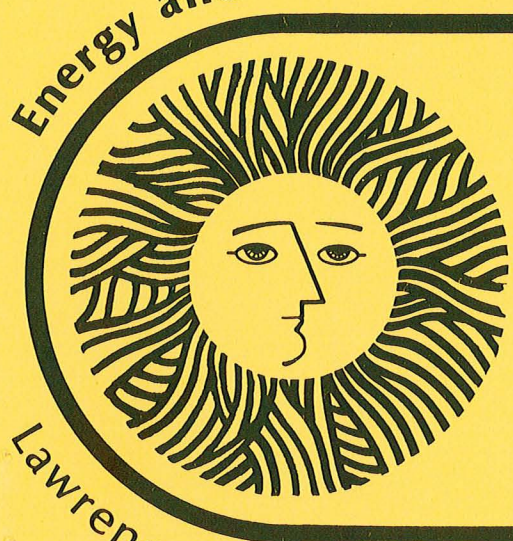
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and R.E. Poulson*

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ANAEROBIC FERMENTATION OF SIMULATED IN-SITU OIL SHALE RETORT WATER*

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INTRODUCTION

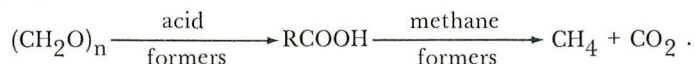
Water coproduced with shale oil and decanted from it is referred to as retort water. This water originates primarily from the combustion of organics and from the release of free and bound water present in the oil shale matrix. When retorting occurs in the presence of oxygen, the retort water to oil volume ratio is ~1. This is equivalent to 2.1 MGD for a 50,000 barrel per day oil shale plant and is comparable to the volume of wastewater produced by a town with a population of 14,000. The composition of retort water is characterized by a pH range from 8.5 - 9.6 and high levels of a number of inorganic and organic constituents. The principal inorganic constituents are ammonia, ammonium, and bicarbonate. The organic constituents are primarily polar, and carboxylic acids are often a major component.

Water management will be complex for the oil shale industry due to the scarcity of water in the region, the uncertain regulatory climate and the complex nature of retort water. Retort water will be required to meet the water needs of an oil shale complex and will be upgraded for on-site use. Potential uses, arranged in order of requisite quality, are spent shale compaction (poor quality water is suitable), dust control, mining, prerefining, agriculture and cooling tower makeup (good quality water is required). Any excess water will be stored for future use, evaporated or discharged to surface or ground waters. Stringent water quality regulations combined with the shortage of water in the region will limit direct discharge to surface or ground waters, and promote reuse combined with evaporation of residuals.

Each potential use of retort water will likely require the removal of some or all of the organic material which may be achieved by biological, physical or chemical processes. The purpose of this work was to investigate the removal of soluble organics from a retort water by anaerobic fermentation. Suspended solids, oils and grease, and ammonia removal were investigated as requisite pretreatment for anaerobic fermentation. Biological processes are typically more economical than physical or chemical processes for the removal of organics. The anaerobic fermentation process was chosen because the level of soluble organics in retort water is too high for direct treatment by an aerobic process and methane gas, a good fuel, is produced. Relative to aerobic processes, anaerobic fermentation stabilizes a larger portion of the organic material; has lower nutrient requirements; produces less sludge; handles toxic substances better; and is more suitable for seasonal loading.

PROCESS FUNDAMENTALS

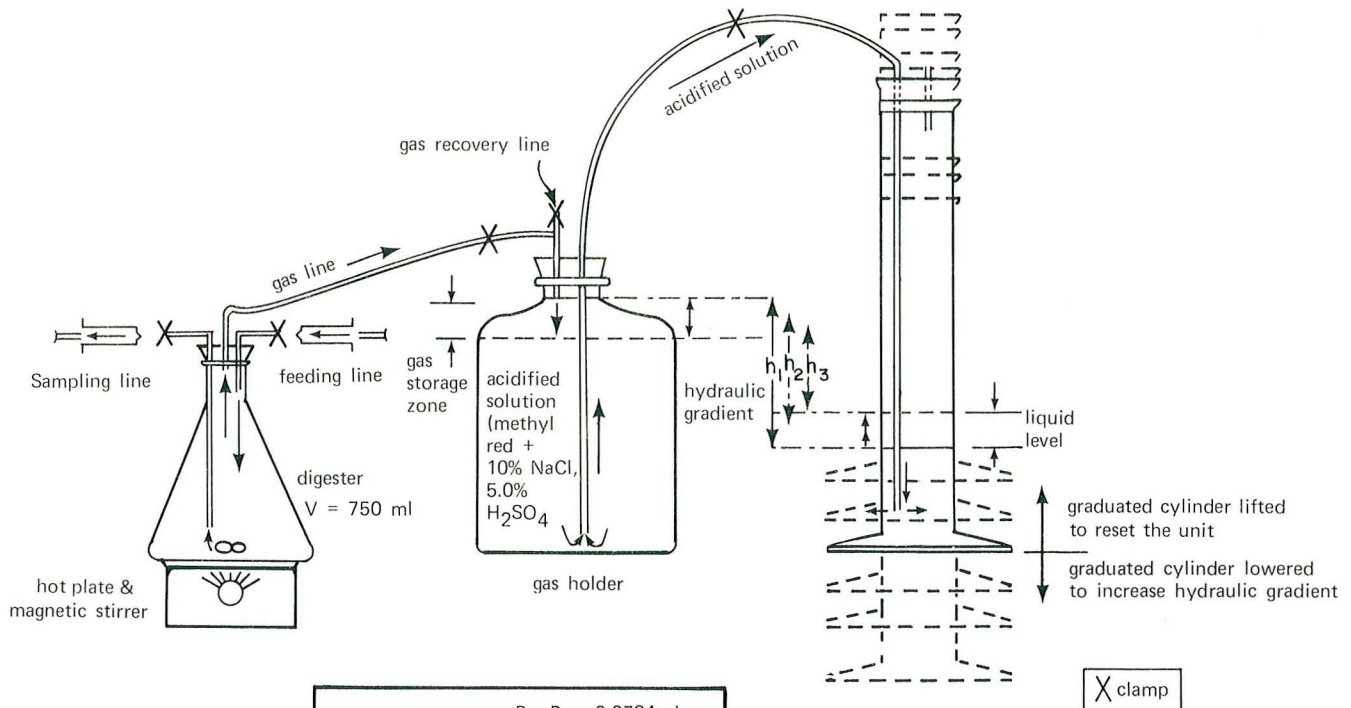
Anaerobic fermentation is a biological treatment process conventionally employed for the treatment of municipal sludges and other concentrated wastes.(1) A schematic of the conventional process is shown in Fig. 1. The process consists of a heated digestion tank containing waste and bacteria. Raw waste is introduced either periodically or continuously and is preferably mixed with the digester contents. A two-stage biochemical process occurs within the digester. This process has been described in Refs. (1,2) and is summarized by the following equation:



The waste, represented by $(\text{CH}_2\text{O})_n$, is stabilized by conversion to CH_4 and CO_2 , gases which are removed from the system and which may be collected and used. In the first stage, complex organics are converted largely to fatty acids by a group of facultative and anaerobic bacteria commonly called the "acid formers." No waste stabilization occurs during this stage. The waste stabilization occurs during the second stage of treatment. In this stage, the fatty acids are converted into CO_2 and CH_4 by a group of bacteria called the "methane formers." These bacteria are strictly anaerobic.

Successful use of the process depends on the proper maintenance of these two groups of organisms. Optimum conditions for anaerobic treatment include a pH range from 6.6 - 7.6, absence of certain toxic

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$$V_G = V_L \frac{273}{760} \frac{P - P_v - 0.0734 \rho h}{T(^{\circ}K)}$$

V_G = Volume (liters) of fermentation gas at standard temperature & pressure
 V_L = Volume (liters) of liquid displaced by fermentation gases
 P = Atmospheric pressure, mm Hg
 P_v = Vapor pressure (mm Hg) of water over the container liquid at temperature T
 ρ = Density of container liquid
 h = Height of the column of liquid suspended above the liquid outlet

XBL 7710-2163

Fig. 2. Schematic of anaerobic acclimation system. (a) Digester's contents are mixed and kept at constant temperature ($35 \pm 1^{\circ}C$) by means of a hotplate-magnetic stirrer. (b) Fermented gas is introduced into a gas holder unit by means of a slight negative pressure created by the water column differential (h). The gas holder unit contains an acidified solution to prevent the dissolution of CO_2 . The gas, on entering the gas holder, displaces some of the acidified solution which is collected in the graduated cylinder. This volume of acidified solution is used to calculate the volume of gas produced using the formula for V_G . (c) The fermentation gas is recovered and the acidified solution level reset by lifting the graduated cylinder and properly operating the valves.

materials, sufficient nutrients, anaerobic conditions and a temperature range from 29 - 38°C. (3) Frequent causes for failure of the process are nutrient deficiencies and toxicity. Optimum and toxic levels for a number of constituents for the process are summarized in Table 1. These values should not be considered absolute because of the possibility of synergistic and antagonistic effects.

Table 1. Optimum and toxic levels for anaerobic fermentation. (4)

Parameter	Optimum Level (a) (mg/l)	Toxic Level (b) (mg/l)
Sodium	230	>4600
Potassium	390	>3900
Ammonium (as NH ₄)	180	>1350
Calcium	200	>2000
Magnesium	120	>1200
Soluble sulfide (as S)	(c)	> 200
Nitrogen	(d)	-
Phosphorus	(d)	-

- (a) Maximum efficiency from an anaerobic treatment system can be obtained by maintaining the major ions as close to their optimum values as possible.
- (b) Toxic levels may vary considerably from the values shown due to synergistic or antagonistic effects of other ions.
- (c) At levels lower than 200 mg-S/l, sulfides can have a beneficial effect by precipitating certain toxic heavy metals, e.g., Cu, Zn, Ni, Fe.
- (d) Optimum levels of nitrogen and phosphorus have been demonstrated to depend on the growth rate and concentration of organisms present in the system. They are ~11% of cell volatile solids weight for N and 2% of cell volatile solids weight for P. (3)

LITERATURE REVIEW

In preliminary experiments, Yen (5) seeded (10%) a 4.5-liter batch anaerobic digester with municipal sludge. Retort water from LERC's 10-ton oil shale retort was buffered at pH 7 with 1.0 g/l KH₂PO₄, and the digester was loaded with 50 lb BOD₅/1000 ft³. The COD in the influent was reduced from 3050 - 2500 mg/l in 30 days and CH₄ was detected. Subsequently, Yen (6) loaded one digester with retort water and another with glucose. The nutrient solutions KH₂PO₄ and NH₄Cl were added to the glucose digester and KH₂PO₄ to the retort water digester. The COD in the glucose digester decreased from 550 - 350 mg/l in 25 days while the COD of the retort water digester decreased from 550 - 400 mg/l in 55 days and CH₄ production steadily dropped. In another experiment (7), acclimation was accomplished by adding 75 mg/ml COD and a phosphate buffer solution incrementally to a digester containing a glucose substrate. The COD decreased from an initial value of around 600 - 300 mg/l by the 42nd day of operation and thereafter, increased to a final value of 750 after 90 days. The CH₄:CO₂ ratio steadily decreased; no pH change was noted. Yen concluded that digester failure in the latter two experiments was due to the accumulation of a toxicant within the digester.

EXPERIMENTAL METHODS

Four Experiments (I - IV) were conducted to assess the treatability of a retort water by the anaerobic fermentation process and to identify toxic and deficient constituents in the water. These experiments are summarized in Table 2. In each experiment, a raw retort water was pretreated to remove oil and grease, suspended solids and ammonia, to adjust the pH and to alter any toxic or deficient constituents. An attempt was then made to acclimate a microbial population to the pretreated water. The raw, pretreated, and anaerobically treated waters and digester mixed liquor were chemically characterized to determine the cause for digester failure and/or the efficiency of organic removal.

The four experiments summarized in Table 2 resulted in the development of a method to successfully

Table 2. Summary of Experiments I-IV.

EXPERIMENT	PURPOSE	PRETREATMENT	DIGESTER	Acclimation Step		INFLUENT				MIXED LIQUOR		RESULTS			
				% Organic Load		Total Ammonia (mg/l)	Organic Loading (lb Vm/ft ³ -day)	Hydraulic Residence Time (days)	Mean Cell Residence Time (days)	NH ₄ ⁺ -N (mg/l)	S ⁼ (mg/l)	BOD ₅ Removal (%)	Failure Caused By		
				Retort Water	Artificial Substrate										
I	Assess affect of ammonia on digester performance	<u>Retort Water A</u> pH elevation to 11 with 1N NaOH; 24 hr aeration; skimming; pH adjustment to 7.3 with 1N H ₂ SO ₄ <u>Retort Water B</u> pH adjustment to 7.3 with 1N H ₂ SO ₄	A	0%	100%	125	0.065	25	25			84%	<u>Digester A</u> Sulfide toxicity		
						B	125	0.065	25					25	84%
			A	25%	75%	125	0.013	58	58					38%	<u>Digester B</u> Ammonia toxicity
						B	0.020	58	58						
			A	50%	50%	125	0.013	38	38					11%	
						B	0.026	38	38						
			A	66%	34%	125	0.014	30.5	30.5					122	
						B	1813	0.036	25						
II	Resolve sulfide toxicity problem	pH elevation to 11 with Ca(OH) ₂ ; skimming; pH adjustmnet to 7.3 with CO ₂	C	8%	92%	125	0.065	25	25	1565			Ammonia toxicity & nutrient deficient conditions		
						B	1813	0.036	25					25	
III	Residue ammonia toxicity problem and operate digester as cell recycle unit	pH evaluation to 11 with Ca(OH) ₂ ; extensive aeration; skimming pH adjustment to 7.0 with CO ₂	D	0%	100%	125	0.035	50	∞				Nutrient deficient conditions		
						B	357	0.0087	15					∞	
IV	Solve nutrient deficient condition Control	Same as III; Ca, Mg and P added None; 100% artificial substrate used	D	100%	0%	357	0.0026	50	∞			78%	No failure occurred		
						E	357	0.0026	50			50	80%	No failure occurred	
						F	357	0.034	50			50	84%	No failure occurred	

pretreat retort water, acclimate a microbial population to it and stabilize the organics present in the pretreated water. This methodology is presented in the "Results" section. The following sections discuss, in general terms, the experimental procedures used in Experiments I - IV.

Experimental Apparatus. A schematic of the batch laboratory-scale anaerobic digesters used in this study is shown in Fig. 2. These digesters were seeded with 750 ml of digested sludge from the City of Richmond Water Pollution Control Plant, Richmond, California. The characteristics of the digested sludge are summarized in the first column in Table 3. Retort water was added to the seeded digesters. On start up, the system was flushed with nitrogen gas to produce anaerobic conditions.

Retort Water. The retort water used in this study was from run 13 of LERC's 150-ton simulated in-situ oil shale retort. Retort operating conditions and shale characteristics for this run are summarized in Table 4.

Table 3. Characterization of Richmond's anaerobic digested sludge and artificial substrate used in acclimation procedure.

	Anaerobic Digested Sludge ^(a)	Artificial Substrate ^(b)
Total solids	29,000 mg/l	29,500 mg/l
Volatile matter	16,000 mg/l	26,300 mg/l
Percent volatile matter	—	89%
Suspended solids	—	nil
pH	7.0	7.05
Alkalinity as CaCO ₃	3,600 mg/l	1,710 mg/l
Volatile acids as CH ₃ COOH	77 mg/l	550 mg/l
Organic nitrogen	—	3,960 mg/l
NH ₃ -N	—	125 mg/l
Total phosphate as PO ₄ [≡]	—	1,020 mg/l
Reactive (inorganic) phosphate as PO ₄ [≡]	—	540 mg/l
COD (dichromate)	—	38,340 mg/l
BOD ₅ (5 day, 20°C)	—	29,000 mg/l
DNA	—	nil

(a) Source of Sludge — City of Richmond Water Pollution Control Plant, Richmond, California.

(b) Prepared from 20 gm/l tryptone, 10 gm/l dextrose and 6 gm/l beef extract. (8)

Table 4. Retort operating conditions and shale characteristics for Run 13, LERC 150-ton simulated in-situ oil shale retort.

<u>Shale Characteristics</u>	
Shale Source	Anvil Points, Colorado
Shale Size	Mine run (fines - 72 in.)
Fischer Assay	24.6 gal/ton
Void Volume	37.8%
<u>Operating Conditions</u>	
Length of run	10.82 days
Atmosphere	21% O ₂ ; recycle not used
Maximum Bed Temperature	1500°F
Retort Advance Rate	1.94 in./hr
Air Injection Rate	138.9 scf/min

The composition of a retort water depends on the process, retort operating conditions and the type of oil shale used. Wide variations in retort water composition occur due to these factors. Therefore, it is important to consider the results of this work in the framework of both of the process, the oil shale used and the retort operating conditions that produced the water.

Pretreatment. The raw retort water was pretreated using several different procedures. Each method used is briefly summarized in Table 2 in the pretreatment column. Pretreatment methods were designed to solve nutrient deficient or toxic conditions encountered during the acclimation procedure.

Acclimation. The microbial population in the digested sludge was acclimated to pretreated retort water by incremental additions of retort water to an artificial substrate. The composition of the artificial substrate is shown in the second column on Table 3. The incremental additions used in each experiment are summarized in Table 2 in the column entitled "step" in terms of percent organic load applied. After initiation of each step of the acclimation procedure, each digester was monitored until steady-state conditions were attained. The parameters used as indicators of steady state were volatile suspended solids, volatile acids, and volume and composition of digester gas. Digester performance was evaluated by monitoring BOD₅ and COD in the influent and effluent.

Analytical Procedures. Two types of parameters were measured in this work. They were those used to assess the operational behavior of the system (COD, BOD₅, volatile acids, volatile suspended solids, volume and composition of digester gas) and those used to identify toxic or deficient constituents (NH₃, S, Ca, Mg, P and others). The analytical methods used to measure these parameters are summarized in Table 5.

Table 5. Analytical methods for chemical characterization.

<u>Parameter</u>	<u>Method</u>
Al, Br, Cl,* Cu, Pb, Mn, Na,* V, Zn	Neutron activation analysis
As, Ba, B, Ca,* Cr, Co, F, I, Fe, Mg,* Ni, P,* K,* Se, Si,* S*	Spark source mass spectrometry
Ca,* Mg,* K,* Na,* Si,* P,* Cl,* S*	X-ray fluorescence spectrometry on freeze-dried sample (9)
COD; BOD ₅ , Total Alkalinity, Solids, Volatile Acids, Hardness, pH, Kjeldahl N, oil & grease	<u>Standard Methods</u> , 13th Edition (10)
Sulfides	<u>Standard Methods</u> , 12th Edition (11)
Inorganic & Organic Carbon	Beckman Model 915 Total Carbon Analyzer with a Model 215A Infrared Detector. Organic carbon determined according to <u>Standard Methods</u> , 14th Edition (12)
Gas Analysis	Varian Aerograph Model 90-P gas chromatography unit with He carrier gas
Ammonia	<u>Standard Methods</u> , 13th Edition (10) modified to accommodate small sample size

The asterisked () parameters were determined by neutron activation analysis or spark source mass spectrometry in the raw retort water and by x-ray fluorescence in the pretreated retort water.

RESULTS

Effluent Characterization. The characterization of the raw retort water used in this study is presented in Table 6. The water is well buffered at a pH of 8.6 by the ammonia and carbonate system. The most significant inorganic constituents (greater than 500 mg/l) are ammonium, ammonia, bicarbonate, sodium and sulfate. Minor inorganic constituents include most trace elements, calcium, magnesium and phosphorus. Soluble organics, as measured by BOD₅ and COD, are considerably greater than found in conventional municipal wastes. Volatile acids are a major organic component and constitute 40% of the measured TOC. [This is an operational parameter (Ref. 10) for certain fatty acids. The volatile acids determination

Table 6. Characterization of raw, pretreated and anaerobically treated retort water.

	Raw Retort Water	Pretreated Retort Water (Digester Influent)	Anaerobically Treated Retort Water (Digester Effluent)
Alkalinity, Total (mg/l CaCO ₃)	38,000	1,800	—
Aluminum	16.6	—	—
Arsenic	1.4	—	—
Barium	0.17	—	—
Biochemical Oxygen Demand, 5-day (BOD ₅)	5,325	2,695	580
Boron	3.4	—	—
Bromine	1.5	—	—
Calcium	3.3	67	—
Carbon, Inorganic	5,850	310	—
Carbon, Total Organic (TOC)	4,980	2,260	—
Chemical Oxygen Demand (COD)	8,800	9,440	2,250
Chlorine	57	21	—
Chromium	0.018	—	—
Cobalt	0.31	—	—
Copper	15.6	—	—
Fluorine	26	—	—
Hardness (as CaCO ₃)	86	—	—
Iodine	0.11	—	—
Iron	4.7	—	—
Lead	0.3	—	—
Magnesium	24	—	—
Manganese	0.22	—	—
Nickel	0.014	—	—
Nitrogen, Total NH ₃ (as NH ₃)	10,150	357	—
Nitrogen, Kjeldahl (as N)	11,000	—	—
pH	8.6	7.0	—
Phosphorus (as P)	8.5	42	—
Potassium	37	24	—
Selenium	0.24	—	—
Silicon	25	28	—
Sodium	655	—	—
Solids, Total Dissolved	4,210	—	—
Solids, Total	—	780	—
Solids, Volatile	—	2,100	—
Solids, Suspended	—	nil	—
Sulfate (as SO ₄)	1,100	—	—
Sulfur, Total (as S)	406	860	—
Vanadium	1.8	—	—
Volatile Acids (as CH ₃ COOH)	3,300	900	350
Zinc	6.4	—	—

measures water-soluble fatty acids that can be distilled at atmospheric pressure (up to six carbon atoms). When an analysis is referred to, the term volatile acids is used. Otherwise, the term fatty acids is used.] Wen (13), Yen (14) and Cook (15) found high levels of fatty acids in other retort waters.

Experiments I - IV. The four Experiments (I - IV) summarized in Table 2 led to the development of a method to pretreat and acclimate a microbial population to retort water and to stabilize 76 - 80% of the organics present in the pretreated retort water.

In Experiments I - III, gas production dropped to very low levels before the end of the acclimation procedure, indicating process failure. Typically, the onset of failure was indicated by a reduction in gas

production and an increase in volatile acids and COD concentrations. This is most likely due to improper functioning of the methane formers. The cause of the failures, based on chemical analyses of the pretreated influent and digester mixed liquor, was determined successively to be sulfide and ammonia toxicity and Ca, Mg and P deficiencies. Sulfide toxicity resulted from the use of H_2SO_4 for pH adjustment and not from the water itself. Pretreatment schemes were devised to resolve each problem as it was identified. Ultimately, in Experiment IV, all problems were resolved and the anaerobic fermentation process was used successfully to stabilize organics in pretreated retort water. The reproducibility of the results was verified by setting up a second digester, E (see Table 2 for designation in D, E), for which similar results were obtained. Digester performance was equivalent to that observed with more conventional wastes such as municipal sludge.

During these experiments, it was observed that a toxicity and a nutrient deficiency problem could be differentiated by comparing total gas production and gas composition. When toxicity was the cause of failure, the gas composition changed significantly; CH_4 decreased and CO_2 and trace gases increased. When the system was nutrient limited, total gas production decreased while gas composition remained constant and comparable to that observed in a properly operating digester.

Pretreatment and acclimation procedures developed to stabilize organics in pretreated retort water are summarized in the sections on pretreatment and acclimation. The results presented correspond to those obtained during Experiment IV which was summarized in Table 2.

Pretreatment. The purpose of pretreatment was to make the raw retort water compatible with the anaerobic fermentation process. Each pretreatment step used would likely be required irrespective of whether biological treatment was part of the overall treatment system.

The pretreatment procedure was designed to reduce ammonia below the reported toxicity threshold of 1350 mg/l NH_4^+ , to reduce suspended solids, oils and grease and to adjust the pH to 7. This was achieved in the laboratory as follows:

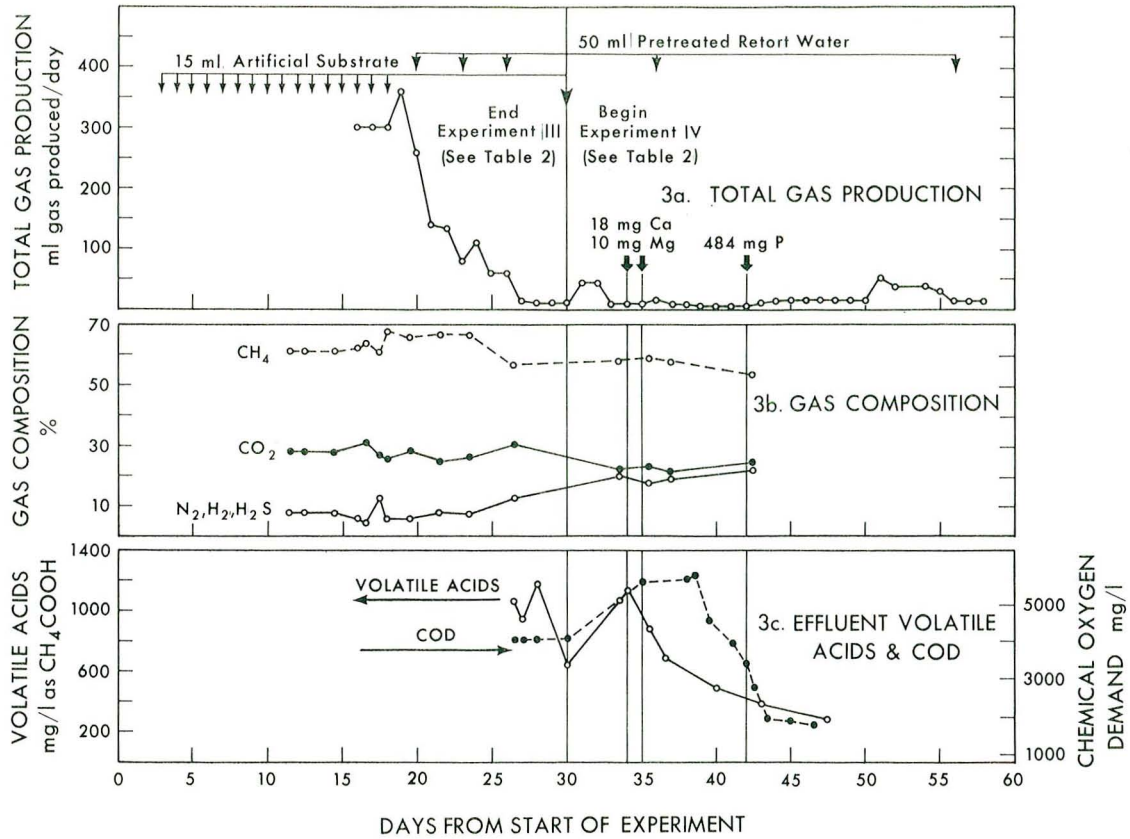
- (1) The pH was raised to 11 using $Ca(OH)_2$. This converts NH_4^+ to NH_3 gas which can then be stripped from solution by aerating.
- (2) The pH 11 water was injected into an aeration basin with compressed air. Spraying the retort water with compressed air enhanced liquid-air contact, thereby improving stripping of the NH_3 from the water. The resulting mixture was aerated for 24 hr with a sparger.
- (3) Floatables (suspended solids plus oils and grease) were removed by skimming, following aeration.
- (4) The pH of the retort water was adjusted to a final pH of 7.0 using compressed CO_2 .
- (5) Nutrients were added directly to the digester. Nutrient addition is discussed subsequently.

This precise pretreatment sequence would not be used in a full-scale treatment system due to economic considerations. It was used for this bench-scale work because it is easy to carry out on a small scale with inexpensive, readily available laboratory equipment, and it produces a water with the necessary pH and ammonia concentrations.

In practice, dissolved solids and oil and grease would be removed by sedimentation and/or dissolved air flotation. Ammonia might be reduced by steam stripping. Nutrient addition might be achieved, in part, by blending retort water with other waste streams at an oil shale plant that are enriched in the required nutrients, e.g., municipal sludge.

Additional pretreatment may be required to reduce the volume of water to be treated. Table 2 indicates that the hydraulic residence times used in these studies ranged from 15 to 50 days. These large residence times would require a large volume digester to accommodate 2.1 MGD per 50,000 barrels/day of oil production capacity and would not be used in a full-scale plant. In practice, cell recycle, which increases the cell residence time and allows a reduction in hydraulic residence time, would be used. Kinetic studies are presently under way to determine if hydraulic residence times on the order of 2 to 3 days or less can be used with no significant reduction in organic removal.

The effect of pretreatment on the chemical composition of the retort water is shown in Table 6. By comparing the first column, raw retort water, and the second column, pretreated retort water, the effect of pretreatment on the measured parameters can be quantified. This comparison shows that BOD_5 is reduced by 49%, volatile acids by 73%, TOC by 55%, total NH_3 by 96%, Cl by 63% and alkalinity by 95%. The decrease in BOD_5 , TOC and volatile acids is due to the conversion and removal of fatty acids during



XBL 7710-2162

Fig. 3. Time variation of total gas production, gas composition, volatile acids and chemical oxygen demand for Experiments III and IV.

pH adjustment. The BOD₅, TOC and volatile acids decreases are probably due to the reduction in solubility of high molecular weight fatty acids. At pH 7 many of these could drop out of solution. This is supported by visual observation of a white precipitate. The NH₃ alkalinity (CO₂, NH₃) and Cl are removed by stripping during aeration. In addition to these reductions, the Ca concentration was increased by a factor of 20 and the COD by a factor of 1.07. The increase in Ca was caused by the addition of Ca(OH)₂ for pH adjustment to 11. The cause of the increase in COD is not clear. Analytical error is not the source as results were checked by a second analyst. The reductions in TOC, BOD₅ and volatile acids are consistent and suggest that the increase in COD is due to an inorganic constituent and not an organic one. No significant change is noted in K or Si. The significant increase in total sulfur and phosphorus is believed to be due to analytical problems since the S and P levels were determined by different analytical methods in the raw and pretreated water. Significant discrepancies in the analysis of retort water by different methods have been noted (16) and is due to the complex and unusual nature of retort water. This problem is presently being studied by LERC and others. (16)

Acclimation. In Experiment IV, the system was operated with cell recycle to increase the cell residence time in the digester. This was achieved by removing a sample of the mixed liquor, centrifuging it at 2500 rpm for 3 min and returning the centrate (biological mass) to the digester with a volume of pretreated retort water such that the total volume removed was equal to the total volume added. This resulted in an infinitely large cell residence time and hydraulic residence time of 50 days.

The system was acclimated by first adding 100% artificial substrate described in Table 3 to the digester and operating it until steady-state conditions were reached. After steady state, 100% retort water, pretreated as indicated, was added in 50 ml increments. Results of Experiments I - III indicated intermediate additions of different mixtures of retort water and artificial substrate were not necessary. Immediately preceding or following the addition of retort water, nutrients were added directly to the digester. In this work, the nutrients Ca, Mg and P were used. The optimum combination and quantity of nutrients were not determined and are presently being studied experimentally. The nutrients were added as a calcium/magnesium versenate solution and as phosphate buffer. These solutions were prepared as follows:

phosphate buffer

8.5 g KH₂PO₄, 21.75 g K₂HPO₄, 33.4 g Na₂HPO₄ and 1.7 g NH₄Cl were dissolved in 500 ml distilled water and diluted to 1 liter.

calcium/magnesium versenate solution

10 ml versine (EDTA) were added to a solution of 0.1 g each of CaCl₂ and MgSO₄ and 2 ml distilled water. The amount of versine required to complex the Ca and Mg added was determined titrimetrically on three separate aliquots according to the hardness determination, Standard Methods, 13th Edition. (10)

The effect of nutrient addition on system performance is summarized in Fig. 3. This figure shows the time variation of total gas production in ml gas/day, gas composition, COD and volatile acids. Figure 3a indicates that each time nutrients were added, the total gas production increased. Figures 3a and 3c indicate that before the addition of nutrients on the 34th day of the experiment, volatile acids and COD concentrations were increasing and the total gas production was decreasing. This suggests that the methane formers, which are responsible for waste stabilization, and which convert fatty acids into CH₄ and CO₂, were not functioning properly. The increase in volatile acids indicates the acid formers were functioning. After the addition of 18 mg Ca and 10 mg Mg on the 34th day, the volatile acid concentration dropped, indicating the nutrients had a favorable effect on the methane formers. After five days, waste stabilization commenced. Approximately ten days after the first addition of nutrients, the system reached steady state. Gas volumes at steady state were approximately 11 ft³ gas/lb volatile matter added. This is 92% of the theoretical possible production. (17) Gas composition was 55% CH₄, 25% CO₂ and 20% trace gases (N₂ was the predominant trace specie). The gas production and composition at steady state are comparable to those obtained with conventional waste types.

Treatability. The results presented in Fig. 3 were reproduced using a second digester, E. In addition, a control digester, F, was fed 15 ml/day artificial substrate during the duration of the study. The organic removal efficiencies of these three digesters as measured by BOD₅ and COD are summarized in Table 7 together with similar data for the pretreatment process and the total system consisting of pretreatment plus anaerobic fermentation. This table shows that the anaerobic fermentation process reduces both the BOD₅ and COD of pretreated retort water by 76 - 80%.

Table 7. Summary of retort water BOD₅ and COD removal efficiencies.

	Digester D (100% retort water)	Digester E (100% retort water)	Digester F (100% artificial substrate)
<u>Pretreatment</u>			
Influent COD	8,800	8,800	—
Effluent COD	9,440(a)	9,400(a)	—
Percent Removal	0%	0%	—
Influent BOD ₅	5,325	5,325	—
Effluent BOD ₅	2,695(a)	2,695(a)	—
Percent Removal	49%	49%	—
<u>Anaerobic treatment</u>			
Influent COD	9,440	9,440	38,340
Effluent COD	2,250	1,995	6,134
Percent Removal	76%	79%	84%
Influent BOD ₅	2,695	2,695	29,000
Effluent BOD ₅	580	530	5,220
Percent Removal	78%	80%	82%
<u>Total system</u>			
Influent COD	8,800	8,800	—
Effluent COD	2,250	1,995	—
Percent Removal	74%	77%	—
Influent BOD ₅	5,325	5,325	—
Effluent BOD ₅	580	530	—
Percent Removal	89%	90%	—

(a) Before nutrient addition

These removal efficiencies indicate that 76 - 80% of the soluble organics in the pretreated retort water are stabilized by the anaerobic fermentation process. The volatile acids data presented in Table 6 suggest that fatty acids are one of the components of retort water that are stabilized during anaerobic fermentation. Additional work is required to identify other organic components that are stabilized during the anaerobic fermentation process.

CONCLUSIONS

Based on the results of the four experiments summarized in Table 2, the following are concluded:

- 1) The retort water studied had to be pretreated to remove toxic and add deficient constituents before it could be successfully treated with the anaerobic fermentation process. Pretreatment included pH adjustment to 7, ammonia reduction and nutrient addition.
- 2) A digested sludge from a conventional municipal sewage treatment plant was successfully acclimated to the retort water studied.
- 3) A major fraction of the organics in the retort water studied was stabilized by conversion to CH₄ and CO₂ using the anaerobic fermentation process. BOD₅ and COD removal efficiencies were 76 - 80%. Within the limits of experimental error, the same removal rate was obtained for both BOD₅ and COD.
- 4) The effluent from anaerobic fermentation of the retort water studied (BOD₅: 530 - 580 mg/l) may be suitable for treatment by conventional aerobic processes. This process is presently being demonstrated experimentally.
- 5) The growth of the methane formers, which stabilize the organics, is nutrient limited in the retort water studied.

6) The pretreatment of the retort water studied removed 49% of the BOD₅. This was probably due to the reduction in solubility of high molecular weight fatty acids at neutral pHs; they drop out of solution and do not exert a BOD.

7) A major component removed from the retort water studied during anaerobic fermentation was fatty acids.

8) The long hydraulic residence time used in this study would not be used in practice. Cell recycle, which increases the cell residence and decreases the hydraulic residence time, would be exploited to achieve hydraulic residence times on the order of 2 - 3 days.

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