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ANAEROBIC BIOLOGICAL TREATMENT OF IN-SITU RETORT WATER

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DISCLAIMER

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INTRODUCTION

Oil shale retorting produces from 0.10 to 22 barrels of water per barrel of oil. For a 500,000 barrel per day plant, which represents about 6 percent of the 1977 crude oil production, this represents about 2 million to 500 million gallons of water, depending on the type of process and the plant location. Water production for surface processes is at the lower end of this range (0.10), while it is at the upper end for in-situ processes (0.5-22).

This water, referred to as retort water, originates from mineral dehydration, combustion of organics, groundwater seepage, and from process steam and moisture in the input gas. Retort waters are produced within a retort as a vapor which is condensed out at several points within the system. The majority of the oil and water (process condensate) is condensed in an underground sump at the bottom of the retort. Entrained oil mist and water vapor are also removed at the ground surface in a condenser train (gas condensate). The relative proportions and composition of each type of water depend on the exit gas temperature and the product collection system design and operation. The process condensate has traveled down the packed bed of shale in an emulsion with the oil and thus has leached constituents from the shale matrix and from the oil itself. Therefore, this water is expected to contain high concentrations of some elements. The gas condensate, on the other hand, exits from the retort as steam and is removed from the gas stream in a condenser train designed to remove entrained oil mist. This water will contain gaseous species not removed at the sump such as NH_3, CO_2, H_2S, Hg, and some organics.

In a commercial in-situ operation, the gas and process condensate may be collected and treated separately due to their different compositions. However, the design and operation of a commercial product collection system has not been investigated, and the effect of such a system on water production and composition has not been studied. In simulated in-situ retorts, such as those used in this study, these two types of waters have not been distinguished; they have generally been combined into a single fraction or only the process condensate has been considered. The reader is therefore cautioned that the results presented here may not be representative of a commercial in-situ oil shale industry. In this work, the term "retort water" is applied to the aqueous fraction collected from the Laramie Energy Technology Center's (LETC) 150-ton simulated in-situ retort.

Retort waters are brown to yellow in color, they have a pH that ranges from 8 to 9, and they contain very high levels of many organic

and inorganic constituents. They typically have high concentrations (<1000 ppm) of NH_3, NH_4, HCO_3, CO_3, SO_4, oil and grease, and soluble organic carbon. The concentration of many elements--with the exception of N, C, S, H, Na, Cl, Fe, K, Ca, As, and Ni--is less than 1 ppm. The organic constituents are primarily polar and include the normal carboxylic acids and organonitrogen compounds.

The disposal of retort water can be achieved by either land disposal, that is, ponding, deep well injection, or discharge to a receiving water. Retort water can also be reused on site, which may be an economically attractive alternative to disposal.

Land disposal, although requiring little or no treatment of the water prior to its disposal, may prove to be economically, environmentally, or technologically infeasible in many potential areas of in-situ oil shale development. In areas where land disposal of retort water is feasible, the treatment of retort water will be of little concern.

Deep well injection would likely prove to be an economically feasible disposal scheme. However, it is anticipated that existing and future regulatory policy may prohibit deep well injection of untreated retort water. Under present EPA policy groundwater with a TDS less than 10,000 mg/l is considered to be a potential source of drinking water. EPA policy may prohibit injection of wastes into a deep aquifer in which groundwater has a TDS concentration of less than 10,000 mg/l.

In contrast to land disposal, which requires little or no treatment, the discharge of retort water to a receiving water, or the on-site reuse of retort water, will require that the quality of the retort water be upgraded substantially. In order to discharge retort water to a receiving water, it must first be upgraded to a level that will conform with existing water quality objectives and with future EPA effluent limitations. Likewise, in order to reuse retort water on site, it must be upgraded to a level of quality dictated by its potential use. Treatment sequences required to upgrade retort water for a number of on-site uses are discussed elsewhere in this report.

In order to renovate retort water for disposal or reuse, treatment will be required to remove the following categories of contaminants:

- Suspended material
- Soluble organic material amenable to biodegradation
- Soluble organic material resistant to biodegradation
- Soluble inorganic material

With respect to these contaminant categories, colloidal material is included in the category of soluble material.

The removal of suspended material can be accomplished by flotation, filtration, or sedimentation processes. The removal of biodegradable soluble organics is commonly achieved by biological treatment and the removal of nonbiodegradable soluble organics can be achieved by adsorption, chemical oxidation, or electro-oxidation. Finally, soluble inorganics can be removed by ion exchange, distillation, electrodialysis, reverse osmosis, or various chemical precipitation processes.

PURPOSE

The purpose of the work described here is to investigate experimentally the removal of biodegradable soluble organics from retort water, using the anaerobic fermentation process. This specific process was chosen for investigation for the following reasons:

1. Any disposal option selected for retort water will require the removal of soluble organics.

2. Biological treatment is typically more economic than other processes that may be used to remove soluble organics.

3. There are only two broad classes of biological processes--aerobic and anaerobic. The level of soluble organics in retort water may be too high to be economically treated directly by an aerobic process.

4. Anaerobic fermentation has lower nutrient requirements and stabilizes a larger portion of the organic material than aerobic processes; it has minimal land requirements; and it produces methane gas, a good source of fuel energy.

NOTATION LIST

Abbreviations, acronyms, and chemical symbols used in the text are as follows:

BOD_5	5-day biochemical oxygen demand
CH_4	methane
COD	chemical oxygen demand
CO_2	carbon dioxide
DNA	deoxyribonucleic acid
HAc	acetic acid; CH_3COOH
Mixed liquor	digester contents
NH_3	ammonia gas
NH_4+	ammonium ion
TOC	total organic carbon

TDS	total dissolved solids
Total NH_3	total ammonia gas and ammonium ion present at pH 13
Vm	volatile matter
VSS	volatile suspended solids

LITERATURE SURVEY

Two sets of literature are applicable to the treatment of retort water. The first consists of the body of experimental work performed using retort water. The second includes literature on treatability of related effluents, such as refinery wastes, coking wastes, and the wastes produced by some of the synthetic fuel processes such as coal gasification. Only the first body of literature is included here. Related work completed in other countries is not presented. Pertinent results from related industries have been summarized by others (Refs. 2,3).

Hubbard (Ref. 1) studied a physical/chemical treatment system that included lime addition, carbon adsorption, and ion exchange. Hubbard pretreated samples of raw retort water by filtration through filter paper to remove suspended material. Lime was added to remove ammonia and some of the soluble organics, carbon adsorption was employed to remove the remaining soluble organics, and ion exchange was used to remove soluble inorganics. Using this physical/chemical system, Hubbard succeeded in reducing the ammonia concentration from 4800 mg/l to 120 mg/l and the TDS concentration from about 45,000 mg/l to about 1900 mg/l. Removal of organics was not reported.

Harding et al. (Ref. 2) conducted preliminary treatability studies on 150-ton retort water which indicated that several processes hold promise for application to this water. Thermal stripping demonstrated capability for reducing the concentrations of both NH_3 and CO_2. A weak-acid cation exchange system was also effective in removing these two constituents. Activated carbon showed reasonably good potential for removing the organic components and reduced the COD by 74 percent at a theoretical detention time of 57.5 minutes. Adsorbent resins XAD-2, XAD-4, XAD-7, and XAD-8 were effective in removing some of the COD.

Harding et al. (Ref. 4) investigated the suitability of three weak-acid cation exchange resins for the removal of ammonia and alkalinity from retort water. Results indicate that essentially complete removal of NH_4 and HCO_3 can be obtained at practical rates. Economic studies indicated that regeneration with CO_2, rather than a strong acid, was more economically attractive.

Yen has studied the use of biological processes for the treatment of retort water (Refs. 5-11). Much of Yen's research on biological processes was devoted to attempts to isolate specific strains of bacteria that are able to biodegrade the soluble organics present in

retort water. Yen noted that some components of retort water were inhibitory to bacterial growth. Inhibition was significant when the COD of diluted retort water was equal to or greater than 400 mg/l.

Yen assessed the activated sludge process for the treatment of retort water. In laboratory studies using two different seeds, the COD of diluted retort water was decreased by about 50 percent. However, Yen was unable to achieve a greater COD removal, presumably due to the presence of organic components that are resistant to biodegradation.

Yen also investigated the anaerobic fermentation of retort water. In laboratory studies using a digested sludge seed from a municipal treatment plant, the COD of diluted retort water was reduced from 3000 mg/l to 2500 mg/l over a 30-day period. In subsequent experiments, the COD of diluted retort water was reduced from 550 mg/l to 400 mg/l over a 55-day period.

In addition to conventional biological processes, Yen evaluated electro-oxidation for the reduction of soluble organics. In electro-oxidation, organic material is oxidized by oxygen produced at the anode of an electrochemical cell containing retort water. The reason for using this process was to determine if long-chain organic components in retort water could be broken down into smaller fragments that could be more readily biodegraded in a subsequent biological treatment process.

Yen's experiments with electrolytic oxidation (Ref. 12) have indicated that over 40 percent of the total solid residue and 80 percent of the benzene-soluble compounds present in retort water are removed. In addition, a 65 percent reduction in COD and 92 percent reduction in color intensity were obtained. Recovery of ammonia and carbon dioxide for use in the synthesis of other products may provide an economic basis for the process.

Mercer (Ref. 13) and others at Battelle are conducting studies of steam stripping, anaerobic and aerobic biological treatment, and carbon adsorption. These studies, to date, have indicated that steam stripping is viable and that biological treatment of some waters may be feasible if powdered activated carbon is added to the reactor and if long cell residence times are used.

Steam stripping of Geokinetics retort water (initial NH_3 = 3,000 mg/l) removed 90 percent of the ammonia with recycle of condensate at a boiloff rate of 4.5 percent and over 99 percent of the ammonia without recycle at a boiloff rate of 5.3 percent. Some fouling of the packing was observed. Anaerobic fermentation was used to successfully treat retort water by adding 2000 mg/l of powdered activated carbon. Batch activated sludge treatment removed 45 percent and 65 percent of the TOC and COD, respectively, from a mixture of activated-carbon-treated retort water and untreated-steam-stripped retort water.

Addition of 300 mg/l activated carbon increased these removals to 55 percent and 75 percent, respectively. COD reduction by activated carbon columns was relatively poor due to high concentrations of thiosulfate which is not adsorbed by activated carbon; results were favorable when biologically treated retort water was passed through the columns.

THE ANAEROBIC FERMENTATION PROCESS

Municipal wastewater and certain industrial wastewaters contain significant amounts of organic matter in dissolved, suspended, and colloidal form. A portion of this organic matter can be removed from a wastestream by anaerobic waste treatment (i.e., biological waste treatment in the absence of oxygen). In anaerobic waste treatment, certain organic compounds are stabilized or broken down during a microbial process known as anaerobic fermentation. The anaerobic fermentation of organic matter involves anaerobic and facultative microorganisms which biodegrade organic compounds to obtain energy for cell synthesis. This biodegradation of organic matter is often not complete because many wastestreams contain refractory organics that are resistant to biological degradation. During anaerobic fermentation, compounds such as carbohydrates and short-chain acids are broken down more easily than compounds such as fats and oils.

In anaerobic fermentation, two groups of microorganisms function concurrently. One group, commonly known as the "acid-formers," converts various organic compounds to volatile organic acids (mainly acetic, propionic, and butyric acid). The other group, commonly known as the "methane-fermenters," breaks down the volatile acids produced by the acid-formers to methane and carbon dioxide. The methane-fermenters operate within a narrow pH range and, therefore, are sensitive to significant changes in pH. The two microbial steps involved in anaerobic fermentation are summarized below.

$$(CH_2O)_x \xrightarrow[\text{formers}]{\text{acid}} RCOOH \xrightarrow[\text{fermenters}]{\text{methane}} CO_2 + CH_4$$

In order to maintain an anaerobic waste treatment system that will effectively stabilize an organic waste, the acid-formers and the methane fermenters must be in a state of dynamic equilibrium. Furthermore, the environmental conditions within an anaerobic fermentation unit must approach optimum conditions for both sets of microorganisms involved. Optimum conditions for an anaerobic fermentation unit are summarized in Table 1.

A variety of parameters is employed to assess the operational "health" of anaerobic fermentation units. At steady state conditions, the following operational parameters will remain constant: (1) the volatile acid concentration within the anaerobic fermentation unit,

Table 1. Optimum conditions for anaerobic waste treatment (Ref. 16).

Optimum temperatures: 29° to 58°C
Anaerobic environment
Sufficient biological nutrients:
Nitrogen
Phosphorus
Others
Optimum pH: 6.8 to 7.6
Absence of toxic material

(2) the gas production rate, (3) the gas composition (i.e., percent CO_2, percent CH_4, etc.); and (4) volatile suspended solids. If the above parameters remain constant during operation, it is indicative of a healthy anaerobic fermentation unit operating under steady-state conditions.

The successful treatment of a wastestream by anaerobic fermentation first requires a specific community of anaerobic and facultative microorganisms capable of breaking down the wastestream organics into simple end products. Such a specific population of microorganisms is seldom readily available; usually, it is necessary to develop one in the laboratory. This development process is called acclimation. In this process, a mixed population of microorganisms is kept under optimum environmental conditions and fed an artificial substrate that satisfies their nutritional requirements. When steady-state conditions are attained, wastewater is gradually substituted for the artificial substrate until 100 percent of the artificial substrate is replaced with wastewater. Steady-state conditions must be attained between each incremental change in artificial substrate/wastewater. Acclimation is accomplished when steady-state conditions are attained using 100 percent wastewater. The acclimation procedure employed in this research is described in detail in a subsequent section of this report.

Two of the most common problems encountered in the acclimation of an anaerobic seed or in the anaerobic treatment of an industrial wastestream are: (1) the presence of toxic ions/compounds which inhibit anaerobic fermentation, and (2) the absence of certain nutrients required by the microorganisms involved in anaerobic fermentation. The inhibitory concentration of various toxic ions/compounds and the required concentration of various nutrients are summarized in Table 2. The problem of toxicity can be overcome by removing or chelating toxic ions/compounds, and the problem of inadequate nutrients can be corrected by adding supplemental amounts of various nutrients.

Table 2. Optimum and toxic levels for anaerobic fermentation (Ref. 15).

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 percent of cell volatile solids weight for N and ~2 percent of cell volatile solids weight for P (Ref. 16).

An anaerobic fermentation unit can be modeled as a continuous-flow stirred tank reactor (CSTR). A schematic of an anaerobic fermentation unit, modeled as a CSTR without recycle, is presented in Figure 1. A wastestream with a flow rate of F is introduced into a reactor of volume V. The influent substrate concentration is S_o and the effluent and reactor substrate concentration is S_1. In this work, the substrate is the retort water. The concentration of cells (microorganisms) within the reactor and in the effluent is X_1. The influent cell concentration is X_o and is normally assumed to be equal to zero when a soluble substrate is used. The substrate concentration (S_o and S_1) is often approximated by measuring the 5-day biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), or total organic carbon (TOC). BOD_5 and COD are most frequently used because they provide a measure of the oxidation state of the effluent. The cell concentration (X_o and X_1) is usually approximated by measuring volatile suspended solids (VSS).

Two important parameters are often employed in describing the operational characteristics of a CSTR. These are hydraulic residence time θ and mean cell-residence time θ_c. For a CSTR without recycle, similar to that shown in Figure 1, the hydraulic residence time represents the average time that a parcel of water resides within the CSTR; it is defined by:

$$\theta = V/F$$

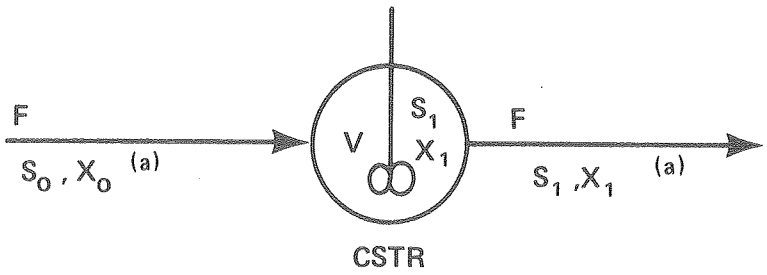
The mean cell-residence time θ_c represents the average time that a cell resides within the CSTR and, for a CSTR without recycle, is equivalent to the hydraulic residence time:

$$\theta_c = \frac{\text{mass of cells within reactor}}{\text{mass of cells leaving reactor per day}} = \frac{X_1 V}{FX} = \frac{V}{F} = \theta$$

EXPERIMENTAL

Waste Characterization

The characterization of the retort water used in this study is presented in Table 3. This retort water was from run 13 of LETC's 150-ton simulated in-situ retort. The operating conditions and shale characteristics for this run are summarized in Table 4. This water contains significant concentrations of both inorganic and organic constituents. Total solids and electrical conductivity are both high. The water is well-buffered at a pH of 8.6 by the carbonate system. The most significant inorganic constituents are ammonium, ammonia, carbonate, biocarbonate, chloride, sodium, and sulfate. Minor inorganic constituents include most trace elements, calcium, magnesium, and phosphorus. This is consistent with analyses of other retort waters presented elsewhere (Ref. 17). Although not analyzed for in this work, the most significant organic constituents are typically carboxylic acids, phenols, normal alkanes, and amides (Ref. 18).



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Legend:

F = influent flow, l/min

V = reactor volume, l

S_o = influent substrate concentrations mg/l

S_1 = effluent substrate concentration, mg/l

$X_0^{(a)}$ = influent cell concentration, mg/l, = 0

$X_1^{(a)}$ = effluent cell concentration, mg/l

[a] The influent cell concentration, X_o, is typically zero in a reactor without recycle. However, the parameter used to measure the cell concentration, VSS, may not be zero as the measurement includes volatile substances that are not cells. Therefore, theoretically, X_o and X_1 are cell concentrations; however, in practice, cell concentration is operationally defined by volatile suspended solids.

Figure 1. Schematic of continuous-flow stirred tank reactor without recycle.

Table 3. Characterization of retort water from run 13 of LETC's 150-ton retort.

	LETC Data[a]		
	Spark Source Mass Spectrometry mg/l	Other mg/l	University of California Data mg/l
Alkalinity, total (as $CaCO_3$)	-	-	38,000
Aluminum	0.68	-	16.6
Ammonium (as N)	-	10,000	9,100
Arsenic	1.4	-	-
Barium	0.17	-	-
Biochemical oxygen demand (BOD_5)	-	-	5,325
Boron	3.4	1.2	-
Bicarbonate (as HCO_3^-)	-	30,000	-
Bromine	0.13	-	1.52
Calcium	3.3	4.0	-
Carbon, Inorganic	-	-	5,850
Carbon, Organic	-	-	4,980
Chemical oxygen demand (COD)	-	8,800	8,800
Chlorine	-	-	56.9
Chromium	0.018	-	-
Cobalt	0.31	-	-
Conductance (μmhos/cm)	-	15,100	-
Copper	0.018	-	15.6
Fluorine	26[b]	31[b]	-
Hardness (as $CaCO_3$)	-	86	-
Iodine	0.11	-	-
Iron	4.7	-	-
Lead	0.057	-	0.29
Magnesium	24	19	13.8
Manganese	0.24	-	0.22
Nickel	0.014	-	-
Nitrogen, total NH_3 (as N)	-	9,900	10,150
Nitrogen, Kjeldahl (as N)	-	11,000	-
pH	-	8.7	8.62
Phosphorus (as P)	3.5	-	-
Potassium	37	37	-
Selenium	0.24	-	-
Silicon	25	32	-
Sodium	500	570	655
Solids, total dissolved	-	4,210	-
Sulfate	1,100	-	-
Sulfur, total (as S)	406	-	-
Vanadium	1.4	-	1.8
Volatile acids (as HAc)	-	-	3,300
Zinc	2.1	-	6.35

[a]Analyses provided by R. E. Poulson of Laramie Energy Technology Center.

[b]Ionic form, e.g., chloride, fluoride.

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

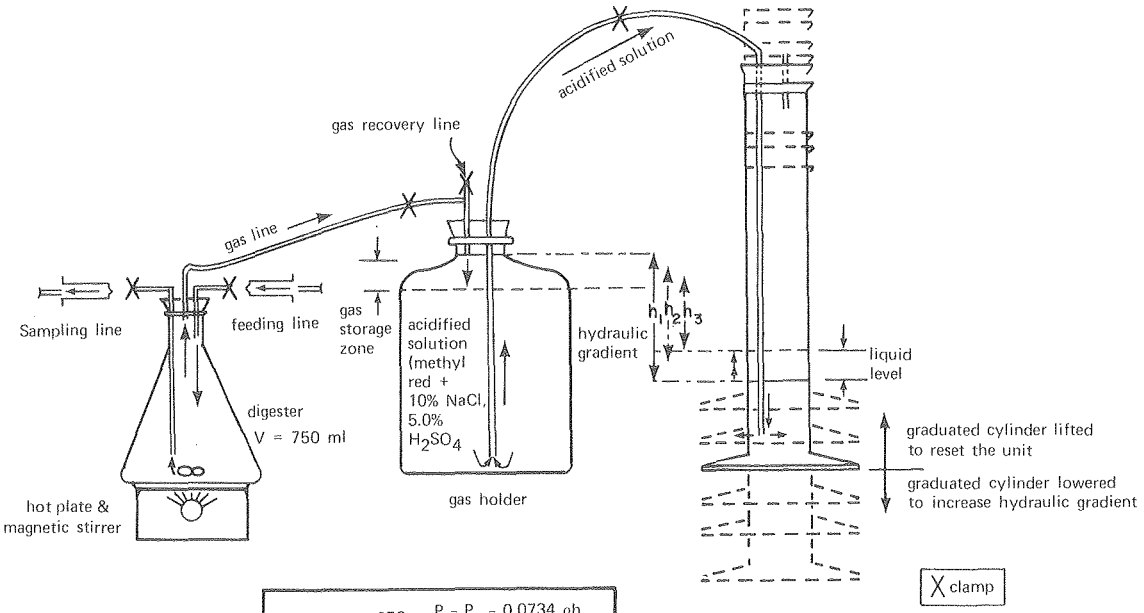
Shale Characteristics	
Shale Source	Anvil Points, Colorado
Shale Size	Mine run (fines-72 in.)
Fischer Assay	24.6 gal/ton
Void Volume	37.8%
Operating Conditions	
Length of Run	10.82 days
Atmosphere	21% O_2; recycle not used
Maximum Bed Temperature	1500°F
Retort Advance Rate	1.94 in/hr
Air Injection Rate	138.9 scf/min

Experimental Apparatus

A schematic of the laboratory-scale anaerobic digester used is shown in Figure 2. Components of the laboratory-scale digester shown in Figure 2 are described below. The hot plate and magnetic stirrer upon which the digester is situated provide (1) mixing to insure intimate contact between substrate and microorganisms; (2) uniform distribution of feed; (3) uniform temperature in the digesting mass; and (4) heat to enhance anaerobic fermentation. A temperature of 36°C ± 1°C was maintained throughout the experiments.

There are three basic input/output lines associated with the digester shown in Figure 2. The feeding line is used to introduce substrate into the digester. This is carefully accomplished with a syringe in order to maintain anaerobic conditions and not introduce air into the system. The sampling line is used to periodically remove an effluent sample from the digester for analysis, usually immediately before substrate is introduced. The gas line exists to allow produced gas to be captured in the gas holder.

The produced gas travels through the gas line and enters the gas holder. The gas holder contains an aqueous solution designed to minimize the dissolution of gases produced during fermentation. This solution is prepared by adding to a 10 percent w/w NaCl, 5 percent w/w H_2SO_4 solution, 3 ml of methyl red stock solution. The methyl red stock solution is prepared by dissolving 1 g methyl red crystals in 3 ml 0.1N NaOH. The gas holder solution is acidic (5 percent w/w H_2SO_4) to prevent CO_2 from going into solution. Since the solubility of gas decreases as salt content increases, the 10 percent w/w NaCl is used to minimize gas solubility. The gas, as it enters



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

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

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Figure 2. Schematic of anaerobic acclimation system. (a) Digester's contents are mixed and kept at constant temperature (36 ± 1°C) by means of a hot plate-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.

the gas holder, displaces some of the acidified solution which is collected in a graduated cylinder. The volume of acidified solution collected in the graduated cylinder can be related to the volume of gas produced by the formula shown in Figure 2. Gas that is captured in the gas holder can be sampled via the gas recovery line with a syringe. The basic operational procedure of the system described in Figure 2 involves flushing with nitrogen gas before startup to prevent oxygen toxicity, periodic introduction of substrate, and periodic removal of effluent from the digester. Gas is captured in the gas holder and periodically sampled for analysis. The volume of substrate introduced is equal to the volume of effluent removed and, thus, a constant volume is maintained within the reactor. The volume of substrate introduction/effluent sampling is based on the selected value of mean hydraulic residence time.

The laboratory-scale digesters are operated as "batch" reactors. A designated volume of influent is periodically introduced and a corresponding volume of effluent is periodically withdrawn. The mean cell residence time of a batch reactor, such as the one used in this work, is defined to be:

$$\theta_c = \theta = \frac{V}{\Delta V/t}$$

where ΔV = volume of influent or effluent periodically introduced or withdrawn, and t = time increment. The volume of the reactor shown in Figure 2 is 750 ml.

The digesters described in Figure 2 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 Table 5.

Analytical Methods

The analytical methods used by the University of California to characterize the retort water and to measure the parameters evaluated in this study are summarized in Table 6.

Acclimation

The microbial population in the digested sludge described in Table 5 was acclimated to a municipal waste containing some industrial wastes. Therefore, it was necessary to acclimate it to retort water. The acclimation schedule used is summarized in Table 7. The composition of the artificial substrate used during the acclimation procedure is shown in Table 5.

Table 5. 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 HAc	77 mg/l	550 mg/l
Organic nitrogen	-	3,960 mg/l
Total NH_3-N	-	125 mg/l
Total phosphate as $PO_4^{\equiv}$	-	1,020 mg/l
Reactive (inorganic) phosphate as $PO_4^{\equiv}$	-	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 g/l tryptone, 10 g/l dextrose, and 6 g/l beef extract (Ref. 19).

Table 6. Analytical methods for chemical characterization.

Parameter	Method
Al,Br,Cl,Cu,Pb,Mn,Na,V,Zn	Neutron activation analysis by J. S. Fruchter and M. R. Smith of Battelle PNL.
Ca,Mg,K,Na,Si,P,Cl,S	X-ray fluorescence spectrometry on freeze-dried sample (Ref. 20).
COD, BOD_5, total alkalinity, solids, volatile acids, hardness, pH	Standard Methods, 13th Ed. (Ref. 21).
Sulfides	Standard Methods, 12th Ed. (Ref. 22).
Inorganic and organic carbon	Beckman Model 915 Total Carbon Analyzer with a Model 215A Infrared Detector. Organic carbon determined according to Standard Methods, 14th Ed. (Ref. 23).
Gas analysis	Varian Aerograph Model 90-P gas chromotography unit with He carrier gas.
Ammonia, ammonium	Standard Methods, 13th Ed. (Ref. 21) modified to accommodate small sample size.

Table 7. Acclimation schedule.

Step	Artificial Substrate, Percent of Organic Load	Retort Water, Percent of Organic Load
1	100	0
2	75	25
3	50[a]	50[a]
4	34	66
5	25	75
6	0	100

[a]Step 3 was modified in experiment II to consist of the addition of 50 percent retort water and 50 percent artificial substrate by volume instead of by organic load.

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 (VSS)
- Volatile acids (VA)
- Volume and composition of digester gas

Volatile suspended solids are a measure of the concentration of microorganisms present in the digester. Volatile acids are intermediate degradation products of anaerobic fermentation and are a measure of the relative degree of anaerobic fermentation that is occurring. Digester gas (usually 60 percent methane) is an end product of anaerobic fermentation and is also indicative of the relative degree of anaerobic fermentation that is occurring.

Digester performance was evaluated by monitoring biochemical oxygen demand (BOD_5) and chemical oxygen demand (COD) in the process influent and effluent. BOD_5 is a measure of the soluble, biodegradable organics present; COD additionally includes oxygen demand due to nonbiodegradable constituents such as sulfate and thiosulfate. In addition, volatile matter, an indicator of effluent putrescibility, was monitored.

Four experiments were conducted to investigate toxic and nutrient deficient conditions within the digester. Each of these is summarized in Table 8 and described in detail in the next section. The reader may skip this section without loss in overall continuity.

Table 8. Summary of experiments I-IV.

Experiment	Purpose	Pretreatment	Digester	Acclimation Step % Organic Load: Retort Water	Acclimation Step % Organic Load: Artificial Substrate	Influent: Total NH_3-N (mg/l)	Influent: Organic Loading (lb Vm/ft^3-day)	Influent: Hydraulic Residence Time (days)	Influent: Mean Cell Residence Time (days)	Mixed Liquor: NH_4^+-N (mg/l)	Mixed Liquor: $S^=$ (mg/l)	Results: BOD_5 Removal (%)	Results: Failure Caused By
I	Assess effect of ammonia on digester performance	Retort Water A pH elevation to 11 with 1N NaOH; 24 hr aeration; skimming; pH adjustment to 7.3 with 1N H_2SO_4 Retort Water B pH adjustment to 7.3 with 1N H_2SO_4	A	0%	100%	125	0.065	25	25				Digester A Sulfide toxicity
			B			125	0.065	25	25				
			A	25%	75%		0.013	58	58				Digester B Ammonia toxicity
			B				0.020	58	58				
			A	50%	50%		0.013	38	38				
			B				0.026	38	38		122		
			A	66%	34%		0.014	30.5	30.5		335		
			B										
II	Resolve sulfide toxicity problem	pH elevation to 11 with $Ca(OH)_2$; skimming; pH adjustment to 7.3 with CO_2	C	0%	100%	125	0.065	25	25				Ammonia toxicity & nutrient deficient conditions
						259	0.036	25	25	1565			
III	Resolve 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
				100%	0%	357	0.0087	15	∞				
IV	Solve nutrient deficient condition	Same as III; Ca, Mg and P added	D	100%	0%	357	0.0026	50	∞			89%	No failure occurred
			E	100%	0%	357	0.0026	50	50			90%	
	Control	None; 100% artificial substrate used	F	0%	100%		0.034	50	50			84%	No failure occurred

EXPERIMENT DESCRIPTION

Experiment I

The purpose of this experiment was to assess the effect of ammonia concentration on the performance of an anaerobic system receiving retort water. This was achieved by preparing two batches of retort water: A and B. Each batch of retort water was treated separately in two digesters, digesters A and B. Retort water preparation (pretreatment) and the acclimation procedure used for each system are discussed below.

The results of this experiment are summarized in Table 9 and in Figures 3 and 4.

Pretreatment of Retort Water. Two batches of retort water were prepared. The pretreatment procedures used for each water are summarized below. The final composition of each retort water is shown in Table 10.

Retort Water A--The following procedure was used:

1. The pH of the retort water was raised to 11 using 1N NaOH. At this pH, 98 percent of the ammonia in solution occurs as ammonia gas (NH_3) while only 2 percent occurs in the ionic form (NH_4^+).

2. After pH adjustment to 11, the retort water was aerated for 24 hr to strip out the ammonia gas.

3. Material floating on the liquid surface including oil and suspended solids was removed by skimming.

4. The pH of the retort water was then readjusted to a final value of 7.3 with 1N H_2SO_4. The volume of acid per unit volume of retort water was 1.14 ml 1N H_2SO_4 per ml retort water.

The final ammonia concentration in retort water A was reduced from the original concentration 10,150 mg-N/l as shown in Table 10 to 760 mg-N/l. Therefore, the above procedure removed 93 percent of the ammonia. However, the acid adjustment step, which uses 1 N H_2SO_4, resulted in a sulfide toxicity problem which became apparent in step 4 of the acclimation procedure. This will be discussed subsequently.

Retort water B--The only pretreatment used for retort water B was pH adjustment to 7.3 using 1N H_2SO_4. The volume of acid added per unit volume of retort water for pH adjustment was 0.24 ml 1N H_2SO_4 per ml retort water. The final ammonia concentration was 6,600 mg-N/l. This corresponds to a 35 percent reduction in total ammonia in the retort water. The precise cause for this reduction is

Table 9. Characteristics of steady-state conditions: experiment I.[a]

	Step 1		Step 2		Step 3	
	Digester A	Digester B	Digester A	Digester B	Digester A	Digester B
Mixed liquor volatile suspended solids, mg/l	8860	9300	5620	4500	2300	2800
Gas composition, percent						
CH_4	59.4	50.8	67.5	55.0	49.0	b
CO_2	34.9	45.2	26.5	39.0	33.0	b
Other	5.7	4.0	6.0	6.0	18.0	b
Gas production:[c]						
ft^3 gas/lb BOD_5-day	11.5	11.1	5.8	5.6	1.2	0.8

[a]Steady-state conditions not achieved in step 4.

[b]Steady-state gas composition not achieved in step 3.

[c]Gas production is expressed as volume of gas per weight of BOD_5 added per day.

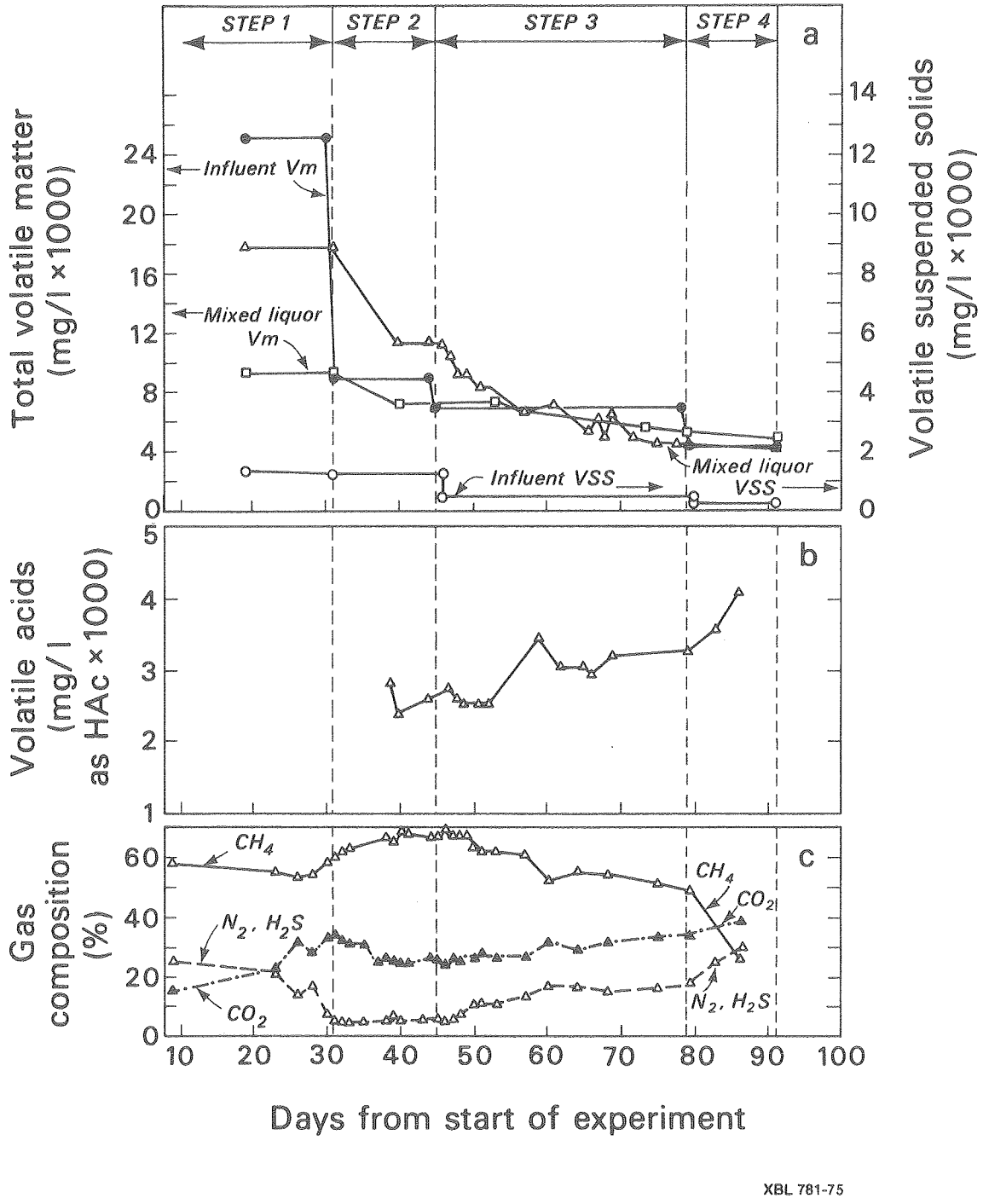

Figure 3. Time variation in volatile suspended solids, volatile matter, volatile acids, and gas composition in Digester A during experiment I.

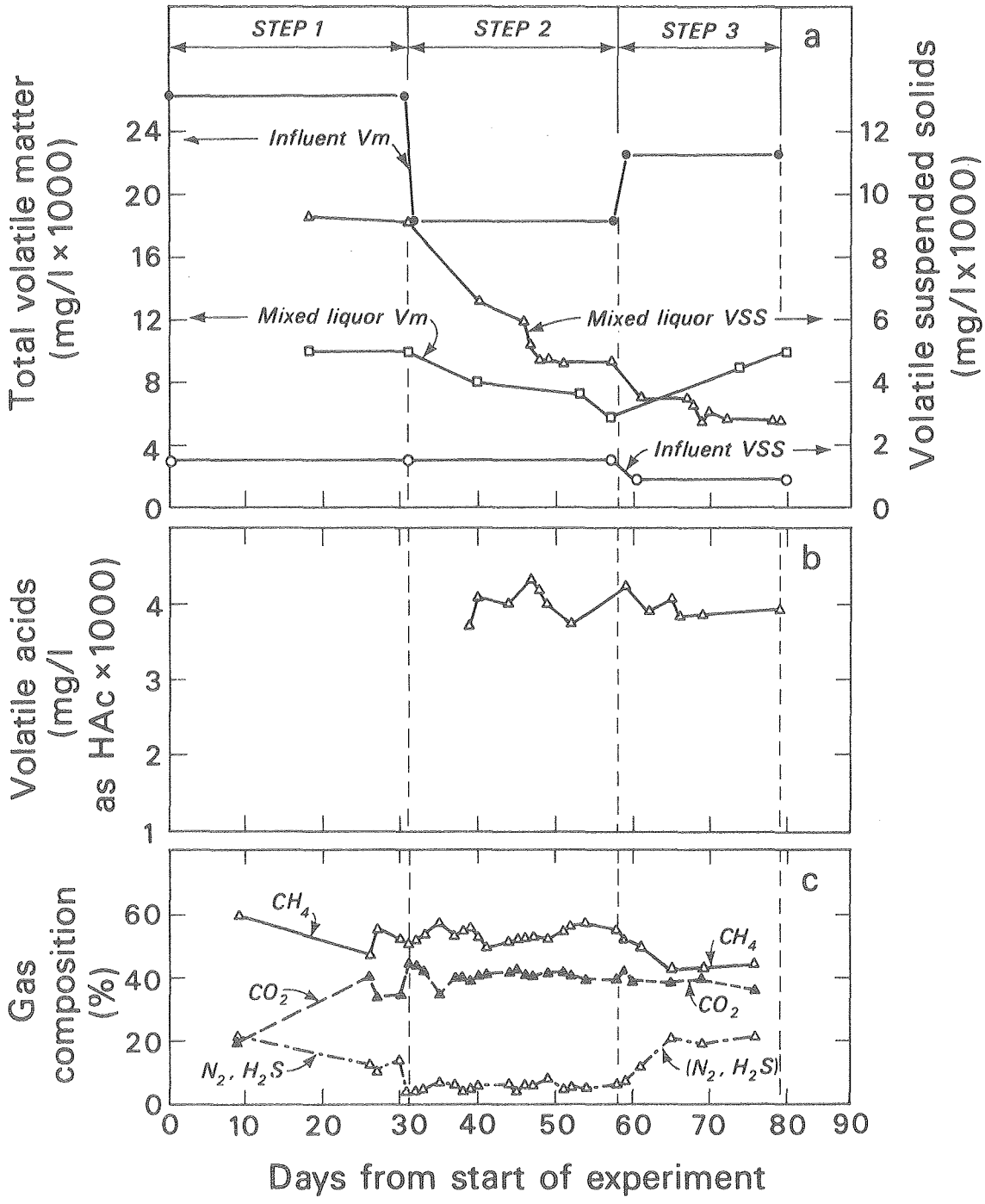

Figure 4. Time variation in volatile suspended solids, volatile matter, volatile acids, and gas composition in Digester B during experiment I.

Table 10. Characteristics of pretreated retort water: experiment I.

Parameter	Original Water	Digester A	Digester B
Total solids, mg/l	---	64,900	21,530
Volatile matter, mg/l	---	5,160	14,240
Total suspended solids, mg/l	---	2,100	2,680
BOD_5, mg/l	5,325	3,255	2,660
COD, mg/l	8,800	7,760	9,380
pH	8.62	7.3	7.3
Volatile acids (as HAc)	3,330	780	540
Total NH_3 (as N)	10,150	760	6,600

unknown. Mechanical stirring during pH adjustment is the most likely cause.

It is interesting to note that pH adjustment to 7.3 resulted in a 50 percent reduction in BOD_5 and an 84 percent reduction in volatile acids for retort water B. Likewise, pretreatment of retort water A resulted in a 39 percent reduction in BOD_5 and a 77 percent reduction in volatile acids. This suggests that volatile acids are being removed from the retort water during pretreatment. Acid addition shifts the following equilibrium expression to the left:

$$RCOOH(aq) \rightleftharpoons RCOO^- + H^+$$

Thus, the BOD_5 and volatile acid reduction may be due to the precipitation of carboxylic acids. This was supported by visual observation of a white precipitate in the sample container.

The acclimation schedule given previously in Table 7 was used during experiment I (steady-state conditions for both digesters for experiment I are summarized in Table 9). Procedures for steps 1 through 4 are described below.

Acclimation Procedure--Step 1. Both digesters A and B were initially fed 30 ml/day of artificial substrate. The resulting organic loading applied to each digester was 0.065 lb Vm/ft^3-day. Mean cell-residence time was 25 days.

Steady state was reached after about 30 days. Steady-state conditions for step I are summarized later in Table 9. Time variations in VSS and Vm for digesters A and B are shown in Figures 3a and 4a, respectively. Production of volatile acids is presented in Figures 3b and 4b. Gas compositions during the steps are shown in Figures 3c and 4c for the two digesters.

Acclimation Procedure--Step 2. The organic loading rate for step 2 was 0.013 lb Vm/ft^3-day for digester A and 0.020 lb Vm/ft^3-day for digester B; the mean cell residence time was 58 days for both digesters. The time variations in VSS, Vm, volatile acids, and gas composition are plotted in Figures 3 and 4. The plots show that there was a substantial reduction in mixed liquor VSS in both digesters during step 2. The reduction was expected because of the system's response to the new organic loading and substrate composition. The composition of the gas from digesters A and B is shown in Figures 3c and 4c, respectively. They indicate that for digester A there was an increase in CH_4 production and a decrease in trace gas production over the period of the step. For digester B the net change in CH_4 and CO_2 production during the step was small.

Digester A was the first one to reach steady state. This condition was maintained for 6 days before step 3 of the acclimation procedure was begun. Digester B took longer to reach steady state. At this point the VSS in system B was lower than the corresponding steady-state VSS in digester A. Digester B was maintained at steady state for 9 days before proceeding to step 3. This is likely related to the higher NH_3 concentrations in digester B influent.

Table 11 compares the digester influent at the beginning of step 2 with the mixed liquor at the end. This table indicates that in spite of the considerable difference in the influents to A and B, there is little difference in the mixed liquor.

The difference in the total solids and volatile matter concentrations in the influents to the two digesters for step 2 is due primarily to the difference in pretreatment received by the two influents (Table 11). The total solids in retort water A is significantly higher relative to B due to the addition of NaOH and to a larger volume of H_2SO_4 during pH adjustment. This is also reflected in the pretreated retort water compositions in Table 10. The difference in Vm concentration is probably due to the loss of volatile components when adjusting the pH to 13 and to subsequent stirring. The component responsible for the difference in Vm in waters A and B was probably not solely ammonia as the difference in ammonia between the two waters in only 5800 mg NH_3/l and the difference in Vm is 9080 mg/l. In addition, over 90 percent of the ammonia present in a retort water is lost during the Vm determination. Therefore, irrespective of how much ammonia was initially present, it would not be detected by this test. The four-fold increase in total suspended and volatile suspended solids in the mixed liquors is due to the presence of new cells (Table 11).

Table 11. Total and suspended solids in digester influent and mixed liquor: experiment I, step 2.

	Influent		Mixed Liquor	
	Digester A[a]	Digester B[b]	Digester A	Digester B
Total solids, mg/l	52,060	24,300	17,060	14,220
Volatile matter, mg/l	9,100	18,160	7,340	5,760
Total suspended solids, mg/l	2,100	2,680	8,800	9,760
Volatile suspended solids, mg/l	1,380	1,440	5,620	4,500

[a] 8.3 ml of retort water with ammonia stripping and pH adjustment to 7.3 plus 4.6 ml artificial substrate.

[b] 8.3 ml of retort water without ammonia stripping and with pH adjustment to 7.3 plus 4.6 ml artificial substrate.

Acclimation Procedure--Step 3. In step 3 of the acclimation procedure, 50 percent retort water and 50 percent artificial substrate by organic load were added to each digester. The organic loading rate was 0.013 lb Vm/ft^3-day for digester A and 0.026 lb Vm/ft^3-day for digester B, resulting in a residence time of 38 days. During this acclimation step there was a marked reduction in volume of gas produced per unit weight of BOD_5 added per day (from 5.8 ft^3/lb BOD_5-day to 1.2 ft^3/lb BOD_5-day for digester A and from 5.6 ft^3/lb BOD_5-day to 0.8 ft^3/lb BOD_5-day for digester B). Figures 3a and 4a, and Table 9 show that the volatile suspended solids stabilized at 2300 mg/l and 2800 mg/l for digesters A and B, respectively. Digester A took longer than B to reach steady state. Both systems showed a reduction in the percentage of CH_4 in the fermented gas and an increase in the percentage of trace gases.

The acidified water in the gas holder unit was discolored in both digesters during step 3. Discoloration was probably due to oxidation of the methyl red indicator by H_2S produced during fermentation. Discoloration was not caused by NH_4 absorption since the pH values of the red and discolored layers were the same.

Several BOD_5 and COD tests were run during this phase of the acclimation procedure to check removal efficiencies. Table 12 summarizes these data, which show that digester A was working more efficiently than digester B. The BOD_5 and COD removal efficiencies associated with each digester are almost the same. Volatile acids and gas composition are shown in Figures 3b, 4b, 3c, and 4c for the step. Digester B failed by the end of the step.

Table 12. Influent and effluent BOD_5 and COD during step 3 of the acclimation procedure: Experiment I.

	Digester A	Digester B
Influent BOD_5, mg/l	8,840	7,000
Effluent BOD_5, mg/l	5,463	6,200
Percent BOD_5, removed	38	11
Influent COD, mg/l	12,080	13,200
Effluent COD, mg/l	7,280	11,040
Percent COD removed	40	16

Acclimation Procedure--Step 4. In step 4 of the acclimation procedure, 66 percent retort water and 34 percent artificial substrate by organic load were added to digester A. The organic loading applied to this digester was 0.014 lb Vm/ft^3-day and the corresponding mean cell residence time was 30.5 days. Gas production was significantly reduced after initiation of step 4 and the digester failed by the seventh day. The predominant gas component prior to failure was CO_2. Methane, which was previously of the order of 50 to 60 percent of the total gas produced, dropped to 27.5 percent while trace gases, such as H_2S, increased. Gas composition for digester A for step 4 is shown in Figure 3c. The significant change in gas production suggests that failure was due to a toxicity problem. In contrast, if no change in gas composition accompanies failure then nutrient deficiencies most likely exist.

Results. Possible explanations for reduced gas production and the concomitant failure of both digesters are discussed below for each digester.

Digester A--The concentration of soluble sulfides in digester A at failure was 335 mg-S/l. McCarty (Ref. 15) has reported that the basic threshold of soluble sulfide ranges from 200 to 400 mg-S/l (Ref. 15). Therefore, the failure of digester A was probably due to sulfide toxicity. Sulfide was a problem in digester A but not in digester B because 4.75 times as much H_2SO_4 was used for pH adjustment of digester A as was used for digester B. The sulfate from H_2SO_4 may be converted to sulfide through microbial action as follows:

$$8H^+ + 8e^- + SO_4^{=} \xrightarrow[\text{desulfuricans}]{\text{Desulfovibrio}} S^{=} + 4H_2O$$

This reaction has been found (Ref. 24) to be one of the major sources of sulfides in the anaerobic fermentation process.

Digester B--Sulfide toxicity is not believed to be the cause for the failure of digester B, although the pH was also adjusted with H_2SO_4. In the case of digester A, the pH was first raised to 11 and then adjusted to 7.3 with 1N H_2SO_4. In digester B, the pH was adjusted from 8.6 directly to 7.3. Therefore, for digester B, much less $SO_4^{=}$ was added during the pH adjustment step. The sulfide concentration in digester B at failure was 122 mg-S/l which was below the toxic threshold range of 200-400 mg-S/l.

The high ammonia level in the influent to digester B is believed to be the reason for its failure. The influent concentration was 6600 mg-N/l. The toxicity threshold for ammonia has been reported to be 1350 mg-N/l (Ref. 15).

Experiment II

The purpose of experiment II was to investigate and resolve the sulfide toxicity problem encountered in experiment I. This was accomplished by revising the pretreatment procedure used in experiment I. The pretreatment procedure and acclimation steps used in experiment II are discussed below. The digester and retort water are given the designation, C.

Pretreatment. The revised pretreatment procedure is:

1. The pH of the retort water was raised to 11 using $Ca(OH)_2$.
2. The pH 11 water was aerated for 24 hr.
3. Floatables were removed by skimming.
4. The pH of the retort water was readjusted to a final pH of 7.2 using compressed CO_2.

The primary difference between the new procedure and the one used in experiment I is the substitution of $Ca(OH)_2$ for NaOH, and CO_2 for H_2SO_4 for pH adjustment. The final composition of the retort water subjected to this pretreatment is summarized in Table 13. Note that this treatment results in a 42 percent reduction in BOD_5 which is equivalent to that obtained previously during pretreatment; however, this revised procedure gives a much lower total solids and Vm concentration than previously.

Table 13. Characteristics of pretreated retort water: experiment II.

Parameter	Digester C
Total solids, mg/l	6420
Volatile matter, mg/l	2400
Total suspended solids, mg/l	nil
Total ammonia, mg-N/l	1800
BOD_5, mg/l	3080
COD, mg/l	9050
pH	7.2

Acclimation. The acclimation schedule outlined in Table 7 was reinitiated using a new batch of retort water as influent and a single digester, digester C. The organic loading and mean cell residence time for step 1 were 0.065 lb Vm/ft^3-day and 25 days, respectively. Steady state was reached in 39 days. After step 1 steady state was reached, a modified step 3, consisting of a 50 percent by volume mixture of retort water and artificial substrate (15 ml each), was initiated. The organic loading and mean cell residence time for modified step 3 were 0.036 lb Vm/ft^3-day and 25 days, respectively.

Results. The results of this experiment are summarized in Figure 5. Figure 5a shows the time history of total and unit gas production. This figure indicates that a marked decrease in gas production occurred on initiation of step 3 and that gas production ceased on day 62 of operation (the process failed). Figure 5b shows the variation in gas composition. This figure indicates that there was a slight shift in gas composition during experiment II. Methane decreased and CO_2 and trace gases increased. However, at failure, the gas composition was within acceptable ranges for the anaerobic fermentation process. The slight shift in gas production, however, suggests that the methane fermenters were not functioning properly. This explains the accumulation of volatile acids and COD by the end of the run shown in Figure 5c. This suggests that the system was nutrient limited.

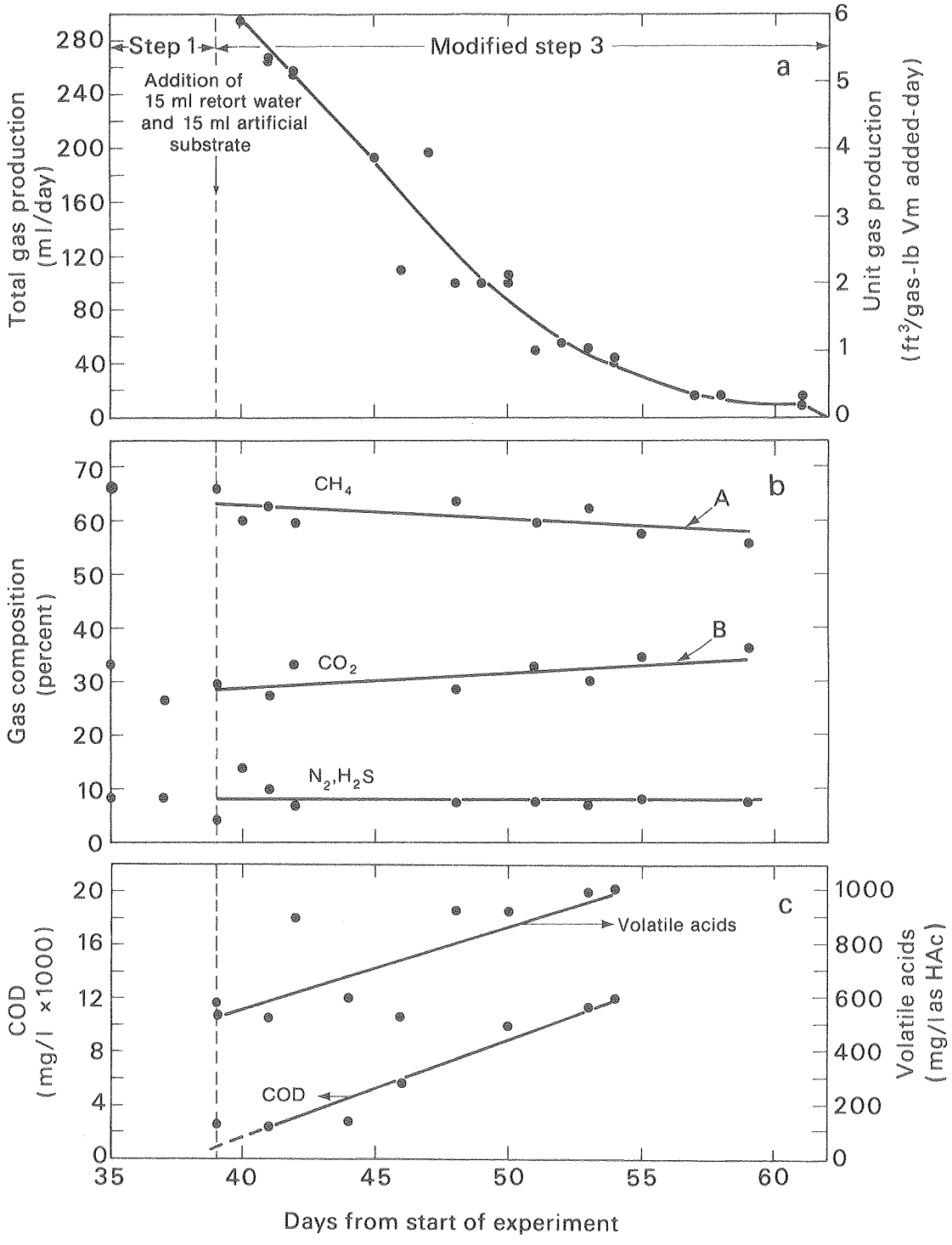

Figure 5. Time variation of total gas production, gas composition, COD, and volatile acids in Digester C during experiment II.

At the termination of this experiment, the influent and digester mixed liquor were subjected to chemical analyses to identify the cause of failure. The results of these analyses are shown in Table 14 along with average measurements previously reported in Table 3 for raw retort water. This tabulation indicates that no change in Na and Mg occurred during pretreatment, while ammonia was significantly reduced and P, Si, Cl, and Ca were elevated. The elevation in Ca is due to lime addition while the elevation in P and Si may be related to analytical error. A significant elevation in Si, P, Cl, and K was observed during digestion while sulfur and ammonia were reduced, presumably due to gas formation. Only Ca was unchanged by digestion.

Experiment II data in Table 14 indicate that those elements that are nutrients, for example, Mg, P, K, and Ca, are enriched in the mixed liquor relative to the influent. This is because the organisms within the digester remove the nutrients from the influent and concentrate them. The significant decrease in Na and increase in Cl cannot be readily explained but may be due to analytical bias. The 77 percent decrease in sulfur is due to hydrogen sulfide (H_2S) production within the digester. This is consistent with results reported by other investigators (Ref. 24) and, also, with experiment I results; that is, H_2S production was responsible for the discoloration of methyl red in the gas holder unit.

Table 14. Elemental composition of influent and mixed liquor at termination of Experiment II. Digester C.

		Experiment II	
Element	Raw retort water[a] mg/l	Pretreated retort water mg/l	Mixed liquor mg/l
Sodium	575	420	231
Magnesium	19	14	49
Silicon	29	50	440
Phosphorus	3.5	101	333
Sulfur	406	1330	304
Chlorine	57	86	270
Potassium	37	90	184
Calcium	3.7	65	72
Nitrogen, total NH_3 (as N)	10,025	1813	1565

[a] From Table 3.

Comparison of data in Tables 2 and 14 indicates that failure of digester C may have been caused by either ammonia toxicity or nutrient deficient conditions. Ammonia toxicity is studied in experiment III and nutrient deficiencies in experiment IV.

Experiment III

The purpose of experiment III was to resolve the ammonia toxicity problem noted in experiments I and II and to implement a method to simulate cell recycle in a batch reactor. The digester and retort water are designated as D. The ammonia toxicity problem was resolved by devising a new pretreatment procedure to remove most of the ammonia. This is described below under "Pretreatment." Cell recycle was simulated by removing a sample of digester mixed liquor, centrifuging it, and returning the centrate (the biological mass) to the digester. This procedure is described under "Acclimation."

Pretreatment. The pretreatment procedure used in experiment III removed about 96 percent of the ammonia present in the retort water. This procedure is as follows:

1. The pH was raised to 11 using $Ca(OH)_2$.

2. The pH 11 water was injected into an aeration basin with compressed air. Spraying the retort water with compressed air enhances liquid-air contact, thereby stripping a larger percentage of the NH_3 from the water. The procedure is shown schematically in Figure 6.

3. Floatables are removed by skimming.

4. The pH of the retort water was readjusted to a final pH of 7.0 using compressed CO_2.

The primary difference between this procedure and the one used in experiment II is the revised method for ammonia removal. The final ammonia concentration was 357 mg-N/l. Final retort water composition is shown in Table 15.

Acclimation. The acclimation procedure outlined in Table 7 was reinitiated using a new batch of retort water, D, and a single digester, D. The digester was set up in a room maintained at a constant temperature of 36 ± 1°C throughout the experiment. The organic loading and mean cell-residence time for step 1 were 0.035 lb Vm/ft^3-day and 50 days, respectively. After steady state was reached in step 1, step 6 was initiated. Intermediate steps used in previous experiments were skipped to minimize the effect on the digesters caused by continually modifying the retort water and artificial substrate mixture.

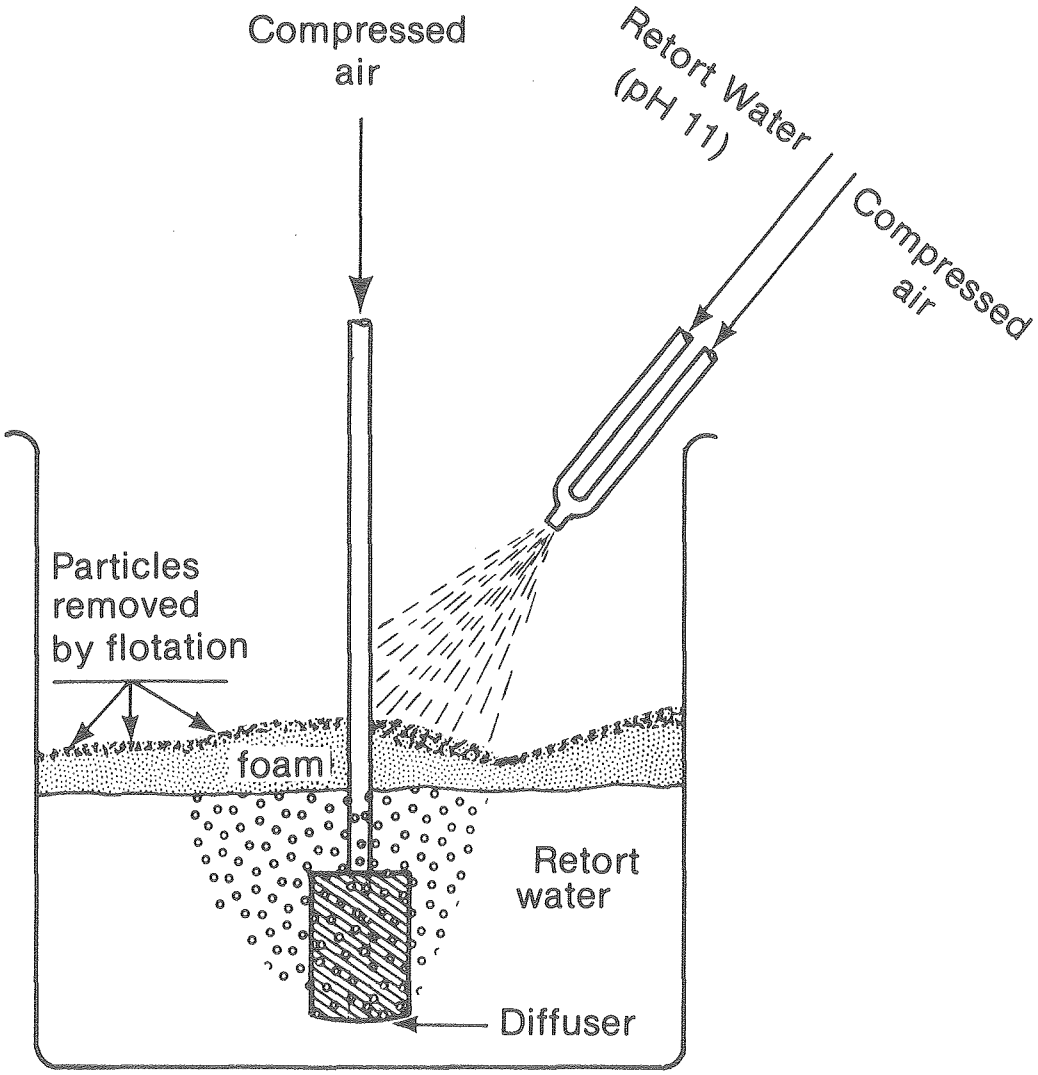

Figure 6. Schematic of ammonia stripping system.

Table 15. Characteristics of pretreated retort water: Experiment III.

Parameters	Digester D
BOD_5, mg/l	2694
Calcium, mg/l	67
Chlorine, mg/l	21
COD, mg/l	9440
pH	7.0
Phosphorus, mg-P/l	42
Potassium, mg/l	24
Silicon, mg/l	28
Total ammonia, mg-N/l	357
Total solids, mg/l	8780
Total sulfur, mg-S/l	860
Total suspended solids, mg/l	nil
Volatile matter, mg/l	2100
Volatile acids, as HAc	900

Cell recycle was implemented in step 6. A sample of mixed liquor was removed and centrifuged for 10 min at 2500 rpm. The centrate mixed with an amount of pretreated retort water so that the total volume returned was equal to the volume of sample removed for centrifuging, was then returned to the digester. This resulted in an infinitely large cell residence time and a hydraulic residence time of 15 days. The purpose of the cell recycling was to increase the cell concentration and to return to the digester the active cells which had become acclimated to the system.

The resulting organic load was 0.0087 lb Vm/ft^3-day. This is a low loading compared to conventional anaerobic digestion systems used for municipal sewage treatment which typically have organic loadings of 0.03 to 0.10 lb Vm/ft^3-day.

Results. Figure 7 summarizes the results of this experiment. Figure 7a shows the time history of total gas production. It is apparent that the decrease in gas production from day 19 to day 23 was due primarily to the significant reduction in organic loading. Figure 7b shows the time variation in gas composition; Figure 7c shows the time variation in volatile acids and COD. By considering these figures in conjunction with Figure 7a, it may be concluded that digester performance is limited by a lack of nutrients. In Figure 7a, retort water addition on day 26 did not produce the expected volume of fermentation gas (65 ml) and gas production per pound of added volatile solids decreased. The decrease in gas production is indicative of a malfunctioning digester. However, Figure 7b, gas

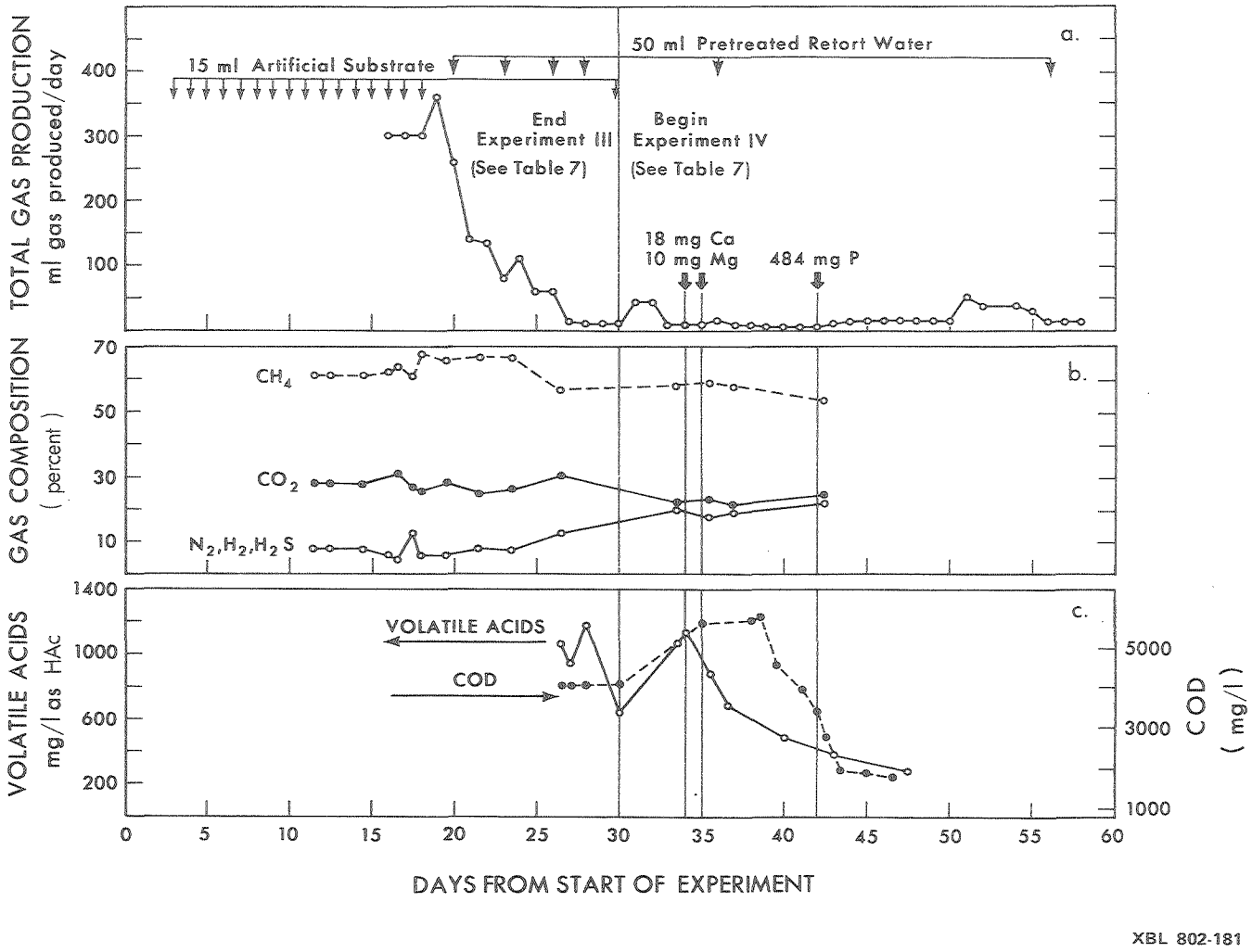

Figure 7. Time variation of total gas production, gas composition, COD, and volatile acids in Digester D during experiments III and IV.

composition, shows no change in the composition of the gases produced. Figure 8c reveals that both volatile acids and COD increased after retort water addition. This suggests that the retort water added was not being assimilated completely. This combination of factors suggests that nutrients were deficient in the influent retort water; this deficiency was the cause of the failure. Failure was clearly not due to toxicity or high loading rates.

Composition data from Tables 2 and 3 indicate that Ca, Mg, and P were probably the deficient nutrients. The low concentration of Ca, Mg, and P is due primarily to the high pH and alkalinity of retort water. At the reported pH and in the presence of high alkalinity, all three of these constituents are relatively insoluble.

Experiment IV

The purpose of experiment IV was to resolve the nutrient deficiency problem noted in experiments II and III. This was investigated by adding Ca, Mg, and P to digester D. Since nutrient addition resulted in the recovery of digester D, a fifth digester, digester E, was set up and acclimated as reported below.

Pretreatment. The retort water used in digesters D and E was pretreated as described for experiment III. Calcium and magnesium were added as calcium and magnesium versenate, and phosphorous was added as phosphate buffer solution. Calcium and Mg were added as an organic complex to prevent their precipitation. Those nutrient solutions were prepared as follows:

- Phosphate Buffer

  8.5 g of KH_2PO_4, 21.75 g K_2HPO_4, 33.4 g Na_2HPO_4, 7 g H_2O, and 1.7 g NH_4Cl were dissolved in 500 ml distilled water and diluted to 1000 ml.

- Calcium/Magnesium Versenate Solution

  The solution used for digester D was prepared by adding 10 ml versine (EDTA) to 0.1 g each of $CaCl_2$ and $MgSO_4$ and a 2 ml solution of distilled water. The digester E solution was prepared by adding 10 ml versine to a solution of 0.05 g each $CaCl_2$ and $MgSO_4$ and 2 ml distilled water. The amount of versine required to complex the Ca and Mg was determined titrimetrically on three separate aliquots according to the hardness determination in Standard Methods, 13th Edition (Ref. 21). These solutions were added in different amounts to each digester as follows:

- Digester D

  Six ml of the calcium/magnesium versenate solution were added to the digester on the 34th and 35th days of the experiment. Fifty ml of phosphate buffer solution were added on the 42nd day. These additions resulted in an increase of 36 mg Ca, 20 mg Mg, and 484 mg P.

- Digester E

  2.5 ml of the calcium/magnesium versenate solution were added to the digester on the 44th and 51st days of the experiment; 15 ml phosphate buffer solution were added on days 47 and 58. These additions resulted in an increase of 9 mg Ca, 5 mg Mg, and 290 mg P.

Acclimation. Experiment IV, digester D, was initiated following steps 1 and 6 of the acclimation procedure reported for experiment III. The nutrients Ca, Mg, and P were added directly to digester D in stages as shown in Figure 7 and described above. Each time nutrients were added, an increase in gas production occurred (Figure 7a). Concomitant with nutrient addition, the COD and volatile acids in digester D decreased steadily (Figure 7b).

The results of this experiment were verified by setting up digester E in a constant temperature room. The acclimation procedure consisted of steps 1 and 6 of the procedure outlined in Table 7. The results of this experiment are summarized in Figure 8; the figure demonstrates that the behavior noted with digester D is reproducible.

Results. The performance of digesters D and E is summarized in Table 16. Pretreated retort water having a BOD_5 and COD of 2695 and 9440 mg/l, respectively, was treated by anaerobic digestion to remove from 65 to 70 percent of the COD and 89 to 90 percent of the BOD_5.

A control digester, digester F was set up and fed with 15 ml/day of artificial substrate during the entire period of the study. Hydraulic and cell residence time were equal to 50 days. The organic loading rate was 0.034 lb Vm/ft^3-day.

The effect of nutrient addition on digester performance is indicated in Figures 7 and 8. Four times as much Mg and Ca and 1.7 times as much P was added to digester D as to digester E. These figures indicate that each time nutrients were added the total and unit gas production increased. However, the unit gas production ultimately reached by digesters D and E are significantly different. In digester D, unit gas production stabilized at 12 ft^3 gas/lb Vm added-day while digester E stabilized at approximately 5 ft^3 gas/lb Vm added-day. Gas production for digester D is comparable to that obtained with more conventional wastes (Ref. 14). The relatively low

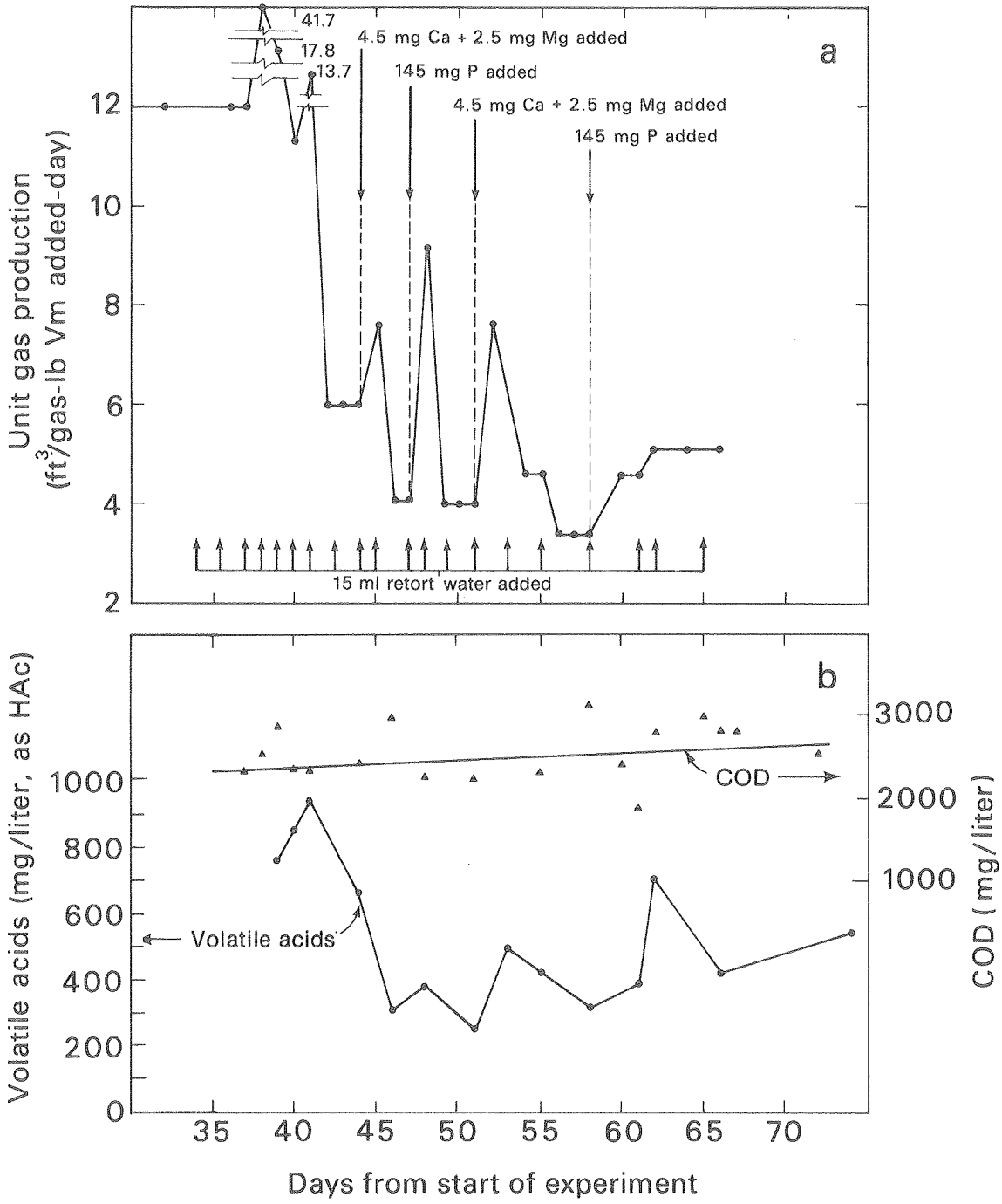

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Figure 8. Time variation of unit gas production, COD, and volatile acids in Digester E during experiment IV.

Table 16. Performance of digesters: experiment IV.

Item	Digester D (100% retort water)	Digester E (100% retort water)	Digester F (100% Artificial Substrate)
Influent COD	9440[a]	9440[a]	29,000
Effluent COD	2250	1995	5220
Percent removal	65[b]	70[b]	82
Influent BOD_5	2695[a]	2695[a]	38,340
Effluent BOD_5	580	530	6134
Percent removal	89[b]	90[b]	84

[a] Pretreated retort water.
[b] Calculation procedure as discussed under "Treatability" in the "Experimental Results and Conclusions" section.

value for digester E may be due to either insufficient nutrient addition (less nutrients were added to this digester) or the lower cell-residence time (cell recycle was used for digester D which increases the cell residence time). The results of the experiment indicate that nutrients are deficient in the retort water. The optimum combination and quantity of nutrients required, however, was not determined. Additional work is required in this area.

EXPERIMENTAL RESULTS AND CONCLUSIONS

The results of the four experiments are summarized in Tables 8 and 17. Based on these results, the following conclusions are made:

- Pretreatment

  Retort water must be pretreated before it can be successfully treated with the anaerobic fermentation process. Pretreatment used in this study included adjustment of pH to 7, ammonia reduction to 360 mg-N/l, and the addition of the nutrients calcium, magnesium, and phosphorus.

- Acclimation

  Digested sludge from a conventional municipal sewage treatment plant can be successfully acclimated to retort water.

- Treatability

  Retort water can be successfully treated using the anaerobic fermentation process and the prescribed pretreatment. BOD_5 and COD removal efficiency is ranged from 65 to 70 percent and 89 to 90 percent, respectively.

The four experiments summarized in Table 8 led to the development of a method to pretreat and acclimate a microbial population to retort water and to stabilize 65 to 70 percent of the COD present in the pretreated retort water.

Table 17. Summary of retort water BOD_5 and COD removal efficiencies.

	Digester D (100% Retort Water)	Digester E (100% Retort Water)	Digester F (100% Artificial Substrate)
Pretreatment			
Influent COD	8,800	8,800	-
Effluent COD	9,440[a]	9,440[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	-
Anaerobic treatment			
Influent COD	9,440	9,440	29,000
Effluent COD	2,250	1,995	5,220
Percent removal	65	70	82
Influent BOD_5	2,695	2,695	38,340
Effluent BOD_5	580	530	6,134
Percent removal	89	90	84

[a] Before nutrient addition.

In experiments I to 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 fermenters. 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 to successfully stabilize organics in pretreated retort water. The reproducibility of the results was verified by setting up a second digester, E (see Table 8 for designation 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 8.

Pretreatment

Before anaerobic treatment can be successfully used for retort water, sulfides, ammonia, and pH have to be reduced and nutrients added. This work suggests that Ca, Mg, and P may have to be added. However, additional work is required to determine optimum levels. This was substantiated by the experiments described in Table 8 and is indicated by comparing Tables 2 and 3. The method developed for the pretreatment of retort water in the laboratory is as follows:

1. The procedure used to remove ammonia was shown schematically in Figure 6. The pH is first raised to 11 using lime [$Ca(OH)_2$]. This converts ammonium ion to ammonia gas. The pH 11 water is then injected into an aeration basin with compressed air and aerated for 24 hr with a sparger; 97 percent removal of ammonia was achieved.

2. During aeration, suspended materials and oil and grease are transported to the surface of the retort water. These are removed by skimming.

3. The pH is then adjusted to 7, the optimum level for anaerobic fermentation, by recarbonation (injection of CO_2).

4. The nutrients calcium, magnesium, and phosphorous are added. Calcium and magnesium are added as calcium and magnesium versenate to prevent their precipitation. Phosphorous is added as phosphate buffer solution.

The pretreatment method described above would not be used in a full-scale treatment system because of 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 equipment and because it simulates the processes that would be used in practice.

In practice, dissolved solids and oil and grease might be removed by sedimentation or dissolved air flotation. Ammonia and sulfides might be reduced by steam stripping. At an oil shale plant, nutrient addition might be achieved, in part, by blending retort water with other waste streams that are rich in the required nutrients such as municipal sewage.

The effect of pretreatment on the chemical composition of the retort water may be determined by comparing Tables 3 and 15. This comparison shows that BOD_5 is reduced by 49 percent, volatile acids by 73 percent, TOC by 55 percent, total NH_3 by 96 percent, and alkalinity by 95 percent. The decrease in BOD_5, TOC, and volatile acids is due to the conversion and removal of fatty acids during pH adjustment. The BOD_5, 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 alkalinity (CO_2, NH_3) is removed by stripping during aeration. 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 increase in COD is believed to be due to conversion of some organics that are initially resistant to chemical oxidation to forms that are more readily oxidized. 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.

Acclimation. Digested sludge from a conventional municipal sewage treatment plant can be acclimated to retort water pretreated as described above and using the artificial substrate described in Table 6. Experiments I-IV indicate that the acclimation procedure should consist of steps 1 and 6 in Table 7.

Steady-state conditions can be easily and successfully monitored by total gas production, volatile acids, and volatile suspended solids. Digester performance was monitored by BOD_5 and COD. The COD test is of questionable use for biological treatment performance on retort waters because it includes inorganic species such as S_2O_5 (Ref. 17) and excludes many organonitrogen compounds which are predominant in retort waters. Organic carbon is recommended for routine analysis because of the simplicity of the analytical method. BOD_5 should be run periodically to monitor organic carbon results.

Treatability. Digesters D (Figure 7) and E (Figure 8) successfully biodegraded the organics in 150-ton retort water pretreated to removed ammonia, adjust the pH, and supplement nutrients. The final effluent BOD_5 and COD concentrations achieved by these two digesters are summarized in Table 16. These digesters were not operated to steady state because the purpose of the three experiments was to demonstrate the feasibility of the anaerobic fermentation process. These experiments were subsequently repeated on separate digesters using the procedures developed here and equivalent COD reductions were obtained when the digesters were operated to steady state.

The digesters used in this study were operated in the batch mode. The percent reductions in COD and BOD_5 can be computed by using a simple material balance about the reactor which takes into account the dilution due to the original reactor contents. This approach is necessary since the reactors were not operated to steady state.

Recalling that equivalent volumes of reactor contents were removed prior to adding the retort water, the mass balance equation is:

$$\begin{bmatrix}\text{Mass of Substance}\\ \text{Added in}\\ \text{Pretreated Retort}\\ \text{Water}\end{bmatrix} + \begin{bmatrix}\text{Mass of Substance}\\ \text{in Digester Before}\\ \text{Adding the Pretreated}\\ \text{Retort Water}\end{bmatrix} = \begin{bmatrix}\text{Mass of Substance}\\ \text{in Digester}\\ \text{After Adding the}\\ \text{Pretreated Retort}\\ \text{Water}\end{bmatrix}$$

Now, since the digester contents were well stirred, we may safely assume that the concentration of the substance is the same throughout the reactor, or

$$C_R V_R + C_D V_D = C_o V_o$$

The percent removal of the substance in the reactor under batch operation would then be

$$\left(\frac{C_o - C_f}{C_o}\right) \times 100$$

where

C_R = Concentration of substance in pretreated retort water.

C_D = Concentration of substance in digester after sample withdrawal.

C_o = Concentration of substance in digester after addition of retort water.

C_f = Concentration of substance in reactor after completion of digestion.

V_R = Volume of retort water added.

V_D = Volume of mixed liquor before retort water is added.

V_o = Total reactor volume.

These equations were used to compute COD and BOD_5 removal efficiencies for Digester D and E. Digester F, a control operated on artificial substrate, was run to steady state and the BOD_5 and COD reductions were computed in the usual way. The result of these calculations are summarized in Table 17.

Note that this approach includes the biological degradation of the substances being determined which are contained in the reactor at time zero plus that of the retort water. Consequently, the precise reduction in the retort water itself cannot be ascertained. The only way that this can be done with such measures as BOD_5 and COD is to run the reactor to steady state with constant retort water feeding.

It must be recognized that when one switches from batch to CSTR operation, one has to pay a penalty in terms of percent reduction of the substance of concern. This is caused by the fact that the majority of the retort water has a residence time in the digester less than that of the theoretical detection time.

These calculations indicate that the anaerobic fermentation process holds promise for the reduction of organics in oil shale retort waters. This process removed 65 and 70 percent of the COD and 89 and 90 percent of the BOD_5 from pretreated 150-ton retort water for a hydraulic residence time of 50 days. Such a large residence time 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. Additional work is required to determine if the hydraulic residence time can be decreased by operating with cell recycle or by other modifications.

SUMMARY

Anaerobic fermentation was successfully used in a laboratory-scale batch digester to remove soluble organics from retort water. Required pretreatment includes reduction of ammonia levels to 360 mg-N/l, pH adjustment to 7.0, sulfide control, and the addition of the nutrients calcium, magnesium, and phosphorus. If the prescribed pretreatment is used, BOD_5 and COD removal efficiencies of 89 to 90 percent and 65 to 70 percent are achieved, respectively.

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