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Pilot-Scale Biotreatment of Refinery Spent Sulfidic Caustics

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ABSTRACT

Caustics are used in petroleum refining to remove hydrogen sulfide from various hydrocarbon streams. It was previously demonstrated that spent sulfidic caustics from two Conoco refineries could be successfully biotreated at the bench scale, resulting in neutralization and removal of active sulfides. Sulfides were completely oxidized to sulfate to *Thiobacillus denitrificans*. Microbial oxidation of sulfide produced acid, which at least partially neutralized the caustic. Biotreatment of a Conoco spent sulfidic caustic has now been demonstrated at pilot scale (1000 gal or 3875 L). Results were comparable to those obtained at the bench scale. The economics and design of a commercial system to treat 1 gpm (3.8 L/min) of spent caustic are presented.

Index Entries: *Thiobacillus denitrificans*; hydrogen sulfide; spent sulfidic caustic; refinery wastes.

INTRODUCTION

Sodium hydroxide (NaOH) solutions are used in petroleum refining to remove hydrogen sulfide (H_2S) from various hydrocarbon streams. Once H_2S reacts with the majority of NaOH, the solution becomes known as a spent-sulfidic caustic. Spent caustics typically have a pH >12 and sulfide concentrations exceeding 2–3 wt%. Depending on the source, spent caustic may also contain phenols, mercaptans, amines, and other organic compounds that are soluble or emulsified in the caustic (*1*).

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Table 1
Characteristics of Spent Sulfidic Caustic Successfully Biotreated at Bench-Scale (3)

Sample	Sulfide, *M*	COD, mg/L	MDEA, wt%	OH, *M*
D1	1.06	82100	2.37	2.60
D2	1.05	113800	3.17	1.04
D3	1.06	107000	3.81	1.03
PC1	0.60	73300	2.08	2.46
PC2	0.58	40200	—	2.91

MDEA = methyl diethanolamine.

Currently, most spent sulfidic caustics generated by refineries are either sent off-site to commercial operations for recovery or reuse (pulp and paper mills, for example) or for disposal by deep-well injection. Biological treatment in the refinery waste water treatment unit is an inexpensive disposal option. However, many refineries do not have the waste-water treatment capacity to treat the entire amount of spent caustic generated, and concerns regarding odors and toxicity frequently prohibit this practice.

Future regulatory changes could result in more stringent controls and increased cost for off-site management of spent caustic. In such an event, low-cost on-site treatment options would be desired. Even without regulatory changes, current off-site transportation and disposal costs warrant further investigation of on-site management alternatives. Wet-air oxidation (WAO) is a commercially available process for on-site management of spent caustic (2), but WAO can result in significant capital investment and high operating costs. WAO can be particularly expensive for spent caustic streams from small- to medium-size refineries owing to an insufficient economy of scale.

The objective of this work has been to evaluate the feasibility of biologically treating refinery spent sulfidic caustic using a bioreactor containing a microbial culture augmented with a sulfide-tolerant strain (strain F) of the chemoautotroph *Thiobacillus denitrificans*. It is envisioned that this process could be implemented either by augmenting an existing refinery-activated sludge unit so that it could handle higher concentrations of sulfides without toxicity or odor problems or by using a relatively small bioreactor that would be specialized for treating spent sulfidic caustic streams.

We have previously reported the bench-scale (1.5-L) biotreatment of sulfidic caustic samples from two Conoco refineries (Table 1), resulting in neutralization and removal of active sulfides (3). Sulfides were completely oxidized to sulfate by *T. denitrificans*. Microbial oxidation of sulfides produced acid that at least partially neutralized the caustic. Mixed heterotrophs in the treatment culture acclimated to methyl diethanolamine (MDEA) present in these samples, resulting in complete degradation of the amine. Results of these treatability studies are summarized in Table 2. Biotreat-

Table 2
Stoichiometry of Sulfide Oxidation by *T. denitrificans* in a Bench-Scale Fed-Batch Reactor with a Feed of Spent Sulfidic Caustic (3)

Sample	SO_4^{-2}/S^{-2}, mol/mol	HNO_3/S^{-2}, mol/mol	H^+ prod/S^{-2}, mol/mol	g MLSS/mol S^{-2}
D1	1.00	1.06	1.39	4.1
D2	1.07	0.048	0.94	6.1
D3a	1.10	0.040	0.94	18.3
D3b	1.01	0.040	0.94	15.9
PC1	0.98	3.0	1.10	8.5
PC2	1.00	4.0	1.02	11.8

HNO_3/S^{-2} is the mol HNO_3/mol sulfide oxidized required to maintain the pH at 7.0–7.1. This acid utilization represents a cost to the treatment process.

H^+ prod/S^{-2} is the mol of acid produced/mol of sulfide oxidized. This amount of acid was available to at least partially neutralize the caustic.

ment of a Conoco spent sulfidic caustic has now been demonstrated at a pilot scale (1000 gal or 3875 L). The economics and design of a commercial system to treat 1 gpm (3.8 L/min) of spent caustic are presented.

MATERIALS AND METHODS

Organism and Stock Cultures

T. denitrificans (ATCC 23642) was originally obtained from the American Type Culture Collection (Rockville, MD). A sulfide-tolerant strain (strain F) was isolated by enrichment as described previously (4). Stock cultures were grown anoxically in 10-mL culture tubes at 30°C in thiosulfate medium described previously (5). In this medium thiosulfate is the energy source, nitrate the terminal electron acceptor, bicarbonate the carbon source, and ammonium ion the source of reduced nitrogen. The medium also contains a phosphate buffer (pH 7.0) and sources of Mg^{+2}, Ca^{+2}, Fe^{+3}, Mn^{+2}, and trace elements. *T. denitrificans* was initially flocculated by aerobic coculture with floc-forming heterotrophs from a refinery-activated slude system as previously described (6).

Spent Caustic Samples

Two samples of refinery spent sulfidic caustic were obtained in 0.23-m^3 plastic drums from Conoco's Ponca City refinery. Sample characteristics are given in Table 3. All samples were odorous and likely contained organic compounds that were not identified. No MDEA was detected.

Table 3
Characteristics of Spent Sulfidic Caustic Samples

Sample	Sulfide, *M*	COD, mg/L	OH^- *M*
PC2	0.58	40200	2.91
PC3	0.73	46300	2.80

Pilot-Scale Biotreatment of Spent Sulfidic Caustic

Pilot-scale biotreatment of spent sulfidic caustic was conducted in a 3.8-m^3 stainless-steel milk-holding tank manufactured by the Paul Mueller Co. (Springfield, MO). The tank was horizonal and semicylindrical, 170 cm deep, and 660 cm long on the inside. The tank was jacketed with cooling/heating coils running lengthwise in the jacket annular space. A 2 horse power (hp) variable-speed DC motor and gearbox were mounted on a platform that bridged the center of the vessel. The motor drove a paddle-type stirrer that was 81 cm in diameter and 12 cm wide. The agitation rate was 50 rpm. On either side of the stirrer platform were stainless-steel lids that completely closed the top of the vessel. The tank was modified by fitting with stainless-steel baffles, each 1/10 of the major or minor dimensions of the tank, and a sparger. The sparger was fabricated from 2.5-cm stainless-steel tubing in a U-shape. It was fed with air at the bottom of the U through a 2.5-cm stainless-steel tube that extended through the wall of the vessel at the center and bottom. The sparger was centered under the stirrer with the branches of the U equal in length to the stirrer diameter. The U branches had equally spaced 0.32-cm holes drilled on the bottom such that the total hole area on each branch was two times the cross-sectional area of the tube.

Air was fed to the reactor using both a Fugi model VFC504A-7W ring compressor and line air from an in-house compressor. About 0.85 standard m^3/min of air was supplied by the blower to the sparging system. Air from the compressor was cooled with a Speedaire Model 5Z267 after-cooler or heat-exchanger using house water at 15°C. Line air was introduced into the reactor at each end with two supplemental spargers which consisted of 1.25-cm stainless-steel tubes bent at one end to produce a 0.3-m section that was perforated with 0.32-cm holes. An additional 0.42–0.57 standard m^3/min could be provided to the reactor in this manner.

Temperature control in the 3.8-m^3 tank was achieved by circulating water from a Neslab Model HX-300 refrigerated recirculator through the jacket coils. Some heating could also be obtained as needed by reducing the cooling water flow rate to the blower after-cooler, thereby increasing the temperature of the air. The temperature was maintained at 30 ± 1°C. The pH was monitored and controlled at 7.0 ± 0.05 by a Cole-Parmer (Chicago, IL) Model 5651-50 pH meter/controller, which activated a Cole-Parmer Chem-Feed Pump to deliver acid or alkali as needed.

Table 4
Sources and Grades of Components of Medium Used to Grow Flocculated *T. denitrificans* Strain F in 3.8-m^3 Stirred-Tank Reactor

Component	Grade	Source	Quantities
Na_2HPO_4	Food grade	Monsanto St. Louis, MO	50-lb bags (22.7 kg)
KH_2PO_4	Food grade	Monsanto St. Louis, MO	50-lb bags (22.7 kg)
$MgSO_4 \cdot 7H_2O$	Food grade	PQ Corporation Valley Forge, PA	50-lb bags (22.7 kg)
NH_4Cl	Technical, treated	Dallas Group of America Liberty Corner, NJ	50-lb bags (22.7 kg)
$CaCl_2 \cdot 2H_2O$	AR	Mallinckrodt Specialty Chemicals, Paris, KY	5-lb bottles (2.3 kg)
$MnSO_4$	FCC grade	Tomco Chemicals Tulsa, OK	5-lb buckets 2.3 kg)
$FeCl_3 \cdot 6H_2O$	AR	Mallinckrodt Specialty Chemicals, Paris, KY	5-lb bottles (2.3 kg)
$NaHCO_3$	Food grade	Church & Dwight Co. Princeton, NJ	100-lb bags (45.4 kg)
$Na_2S_2O_3$	Technical	General Chemical Parsippany, NJ	50-lb bags (22.7 kg)

The flocculated *T. denitrificans* biomass required to operate the pilot-scale bioreactor was produced as follows. *T. denitrificans* strain F was immobilized by aerobic coculture with floc-forming heterotrophs at the bench scale as described above. When a sulfide-active, gravity-settleable floc was obtained, this culture was used to inoculate 0.19 m^3 of thiosulfate medium (without nitrate) in a jacketed stainless-steel stirred-tank reactor. The culture was maintained at 30°C by circulating water at this temperature through the jacket from the Neslab refrigerated recirculator. The pH was monitored and maintained at 7.0 ± 0.05 by a Cole-Parmer Model 5651-50 pH meter/controller, which activated a Cole-Parmer Chem-Feed Pump to deliver 50% NaOH (Kjeldahl-N grade, Ricca Chemicals, Arlington, TX) as needed. The culture was aerated with line air from an in-house compressor at 0.085–0.14 standard m^3/min. The reactor also received a gas feed of pure CO_2 from a compressed gas tank at a rate of about 5% of the aeration rate. The culture was agitated by means of a single 15-cm, six-bladed, disk-type impeller at 30–50 rpm. When the thiosulfate was depleted (2–3 d), the contents of this reactor were used to inoculate the 3.8-m^3 reactor described above.

Each batch of flocculated *T. denitrificans* biomass was produced as follows. The 3.8-m^3 tank was filled with tap water and agitated with the stirrer. Components of thiosulfate medium (*see* Table 4) were then added

and allowed to dissolve one at a time. The thiosulfate medium used in the 3.8-m^3 reactor was identical to that described previously (*5*), except that the $NaHCO_3$ concentration at this scale was higher (3.0 g/L). The smaller-volume cultures described above used CO_2 as a source of carbon. At the 3.8-m^3 scale, this was prohibitively expensive; therefore, $NaHCO_3$ was used as the sole carbon source. The pH was initially adjusted to 7.0 with 50% NaOH. When the temperature reached 30°C, the culture was inoculated.

The first inoculum for the 3.8-m^3 reactor was produced in the 0.19-m^3 stirred-tank reactor described above. Subsequent inocula consisted of a fraction of the biomass produced in the previous batch. Following inoculation, each batch was maintained at pH 7.0 and 30°C until the thiosulfate was depleted. The medium was thiosulfate-limiting. When the thiosulfate was completely utilized, the contents of the reactor were pumped to a 0.23-m^3 open-top, conical-bottom tank (in two batches) to allow the flocculated biomass to settle under gravity for about 2 h. A concentrated suspension of biomass was then drawn from the bottom of the tank. On average, about 20 L of concentrated suspension were obtained. About 20% was used to inoculate the next batch. The remainder was stored at 4°C in a 0.23-m^3 polypropylene barrel in a walk-in cold room. Several batches of *T. denitrificans* biomass were prepared in this way for subsequent pilot-scale biotreatment of sulfidic caustic and other purposes.

The 3.8-m^3 stirred-tank reactor was utilized for pilot-scale biotreatment of spent sulfidic caustic in a fed-batch mode as follows. About 40 L of the concentrated suspension of flocculated *T. denitrificans* strain F was used to inoculate 3.0 m^3 of thiosulfate-free medium. The initial MLSS was 630 mg/L. Spent sulfidic caustic (samples PC2 and PC3, about 180 L of each) was fed (undiluted) from 0.23-m^3 barrels by a Cole-Parmer Chem-Feed Pump (Model 5000-076) connected to a Chron Trol Model CD-4 timer (Lindberg Enterprises, San Diego, CA). Since the desired feed rate of 30 mL/min was less than the lowest steady flow rate of the pump, the timer was used. At a pump feed rate of 150 mL/min, the timer switched on the pump for 12 s every minute giving an effective feed rate of 30 mL/min. The caustic was conveyed to the reactor through 0.95-cm PTFE tubing and introduced below the liquid surface near the impeller tip. The temperature was maintained at 30°C and pH at 7.2 ± 0.1 with 85% H_3PO_4, industrial-grade (Delta Distributors, Dallas, TX). The agitation rate was 50 rpm, and aeration rate was about 1.1 standard m^3/min (blower + line air). The culture was operated with spent sulfidic caustic feed intermittently during the evenings and on weekends because of the odor from the caustic. When not receiving a caustic feed (10–12 h at a time), the culture was maintained at temperature with aeration. The total operating time with spent caustic feed was 200 h. A schematic diagram of the pilot-scale biotreatment system is shown in Fig. 1.

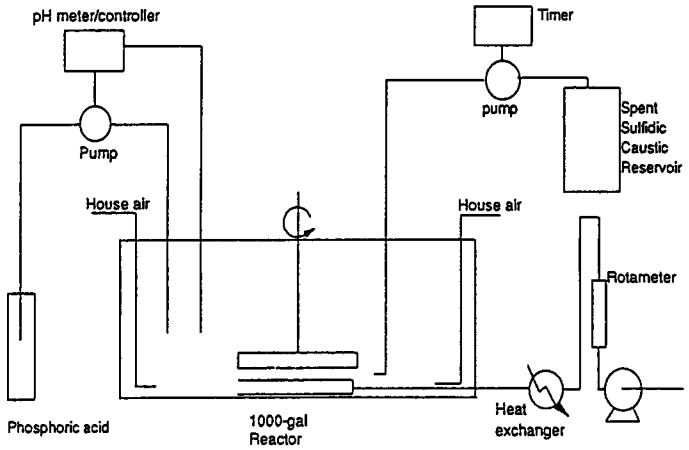

Fig. 1. Schematic diagram of the 3.8-m³ pilot-scale system for biotreatment of spent sulfidic caustic.

Analytical

The hydrogen sulfide concentrations in the vapor space of the 3.8-m³ stirred-tank reactor were estimated using Gastec Analyzer tubes (Yokohoma, Japan). The range of the analyzer tubes was 2.5–60 ppm ± 2 ppm using 100-mL samples.

Total aqueous sulfide in spent caustic samples was determined colorimetrically using the methylene blue method (*7*). Sulfides were precipitated with 0.3 wt% zinc acetate as ZnS prior to analysis. A 1*M* sulfide stock solution was prepared by dissolving $Na_2S{\cdot}9H_2O$ crystals (Sigma Chemical Co., St. Louis, MO) in distilled water. The stock solution was standardized by titration with 0.01*M* $Pb(ClO_4)_2$ using an Orion Research Model 94-16 sulfide/silver electrode and an Orion Research Model 701a pH/mV meter to detect the end point. Sulfide standards in the range of 0–500 μM were prepared by dilution of the stock solution with 0.3 wt% zinc acetate and a standard curve obtained.

The medium in the 3.8-m³ reactor was sampled for sulfide using sulfide ion analyzer tubes (Yokohoma, Japan) with a range of 1–100 mg/L. Sulfate was determined turbidimetrically following precipitation with $BaCl_2$ (*8*). Elemental sulfur was determined by reaction with cyanide to produce thiocyanate, which was quantitated as $Fe(SCN)_6^{-3}$ (*9*). Ammonium ion was determined by the Nessler method without distillation (*8*). Nitrate was determined by the cadmium reduction method. Chemical oxygen demand (COD) was determined using Hach Chemical Co. (Loveland, CO) premeasured reagents.

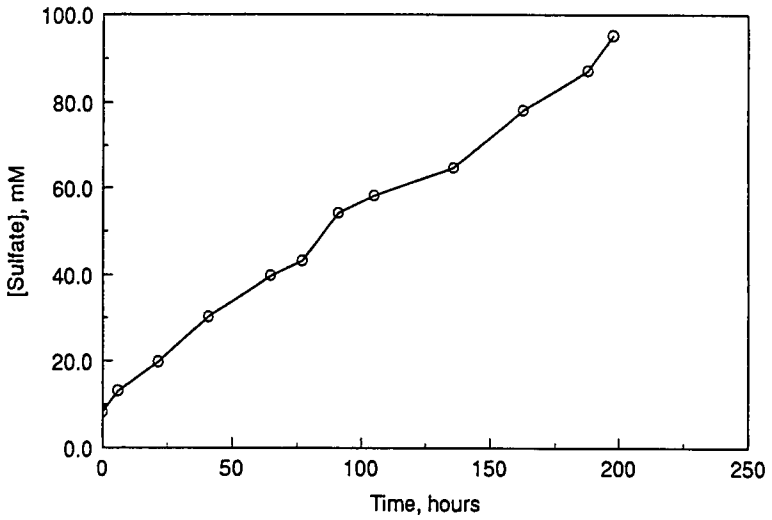

Fig. 2. Sulfate concentration in the pilot-scale bioreactor operating with a feed of undiluted spent sulfidic caustic (PC-series samples).

RESULTS AND DISCUSSION

Pilot-Scale Biotreatment of Spent Sulfide Caustic

Figures 2–4 show the results of biotreatment of samples PC2 and PC3 in the 3.8-m^3 stirred-tank reactor. Sulfate accumulated in the reactor medium as caustic was fed to the reactor (Fig. 2). No hydrogen sulfide emissions were detected from the reactor at any time during the 200 h of operation, and no sulfide was detected in the culture medium. The overall sulfate/sulfide ratio observed was 1.3. However, only the soluble sulfide concentrations in these samples were used to calculate this ratio. These samples contained copious amounts of iron sulfides. Iron sulfides in the feed were most notable when feed was initiated from a new barrel (after some agitation in getting the barrel in place) and after about 75% of the caustic in each barrel had been pumped out. In the latter case, the solids had concentrated at the bottom of the barrel. In fact, the sludges were so viscous at the bottom of the barrel that they could not be pumped out.

The elemental sulfur concentration in the reactor medium averaged about 0.3 mg/L, except for one 5-h period when we attempted to double the caustic feed rate. This increase in feed rate caused an upset condition in which the elemental sulfur concentration became high enough to give the culture a white color. The caustic feed was stopped and the culture aerated overnight. The next day, the elemental sulfur was gone (oxidized to sulfate), and the caustic feed was resumed at 30 mL/min with no further difficulties.

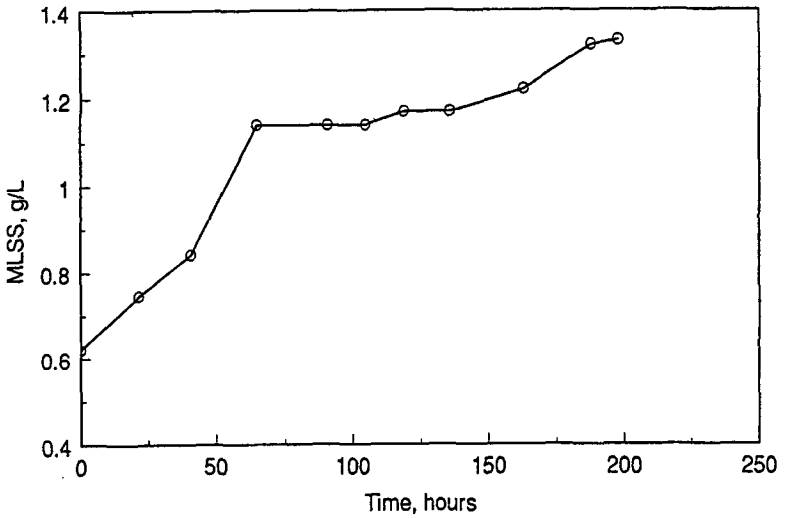

Fig. 3. MLSS concentration in the pilot-scale bioreactor operating with a feed of undiluted spent sulfidic caustic (PC-series samples).

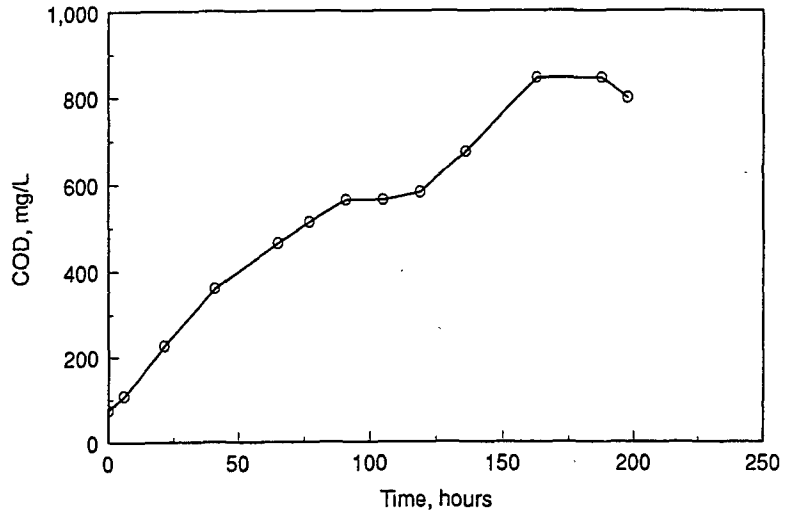

Fig. 4. COD concentration in the pilot-scale bioreactor operating with a feed of undiluted spent sulfidic caustic (PC-series samples).

The MLSS concentration (Fig. 3) rose rather sharply following initiation of caustic feed; however, the rate of increase showed after about 70 h. This may have been because of increased solids in the feed during this time, since the barrel was agitated somewhat during setup. Once the iron sulfide solids settled down below the intake to the pump, the solids concentration in the feed fell. The overall MLSS yield was 10.8 g/mol of soluble sulfide.

Table 5
Estimated Operating Cost of a Commercial-Scale Bioreactor System for Treatment of Spent Sulfidic Caustic[a]

	$/gal	$/yr[e]
Nutrients[b]	$0.010	$ 4208
Power[c] (agitator & blower)	$0.043	$18,094
Capital costs[d]	$0.068	$35,400
Total	$0.121	$57,702

[a]1 gpm (3.8 L/min) with 3 wt% sulfide.
[b]NH_4NO_3 and P_2O_5.
[c]Assumes $0.05/kW/h.
[d]Assumes $200,000, 10-yr useful life and i = 12%.
[e]Assumes 80% on time.

The ammonium ion concentration was seen to decrease as caustic was fed to the reactor as ammonium ion was used as a source of reduced nitrogen by the organisms (data not shown). The COD concentration (Fig. 4) was seen to increase as caustic was fed to the reactor. This is likely because of the presence of an unidentified organic compound present in the caustic that was not degraded by the culture. Such a compound was detected (but not identified) by gas chromatography. About 2.8 mol of H_3PO_4 were required/mol of soluble sulfide in the caustic to maintain the pH at 7.2. A total of 360 L of refinery spent sulfidic caustic was successfully treated in about 200 h of run time.

Commercial Biotreatment of Spent Sulfidic Caustic

The initial MLSS concentration in the 3.8-m^3 reactor was only 620 mg/L. A commercial system would operate with an MLSS of about 4000–5000 mg/L (similar to an activated sludge system). Past experience with flocculated *T. denitrificans* indicates that 1 mmol sulfide/h/g MLSS is a conservative design figure for the specific activity of flocculated *T. denitrificans* for sulfide oxidation (*10*). Based on this specific activity and assuming the MLSS concentration in the bioreactor of 4000 mg/L, a 3.8 L/min (1 gpm) stream with 3 wt% sulfide will require a 53-m^3 bioreactor. A secondary settler and capacity for biomass recycle will also be required for continuous operation. The sulfidic caustic biotreatment system will resemble a small activated sludge treatment system. In fact, the system can be thought of as a specialized activated sludge treatment system.

Estimated cost of a commercial system treating a 3.8 L/min (1 gpm) caustic stream containing 3 wt% sulfide is given in Table 5. The system was assumed to be on-line 80% of the time. Nutrient costs were estimated assuming that treated effluent from the refinery supplemented with only NH_4NO_3 and P_2O_5 (common fertilizers) would serve as the nutrient feed to the bioreactor. All other mineral requirements of the organism could likely be supplied by the refinery effluent. In a field test of microbial sul-

fide oxidation for treatment of sour water, produced water supplemented with just these two nutrients resulted in successful operation for 6 mo (*10*). Estimated nutrient costs in Table 5 are based on nutrient costs per unit weight of sulfide determined in the field test. Power requirements (for an agitator and blower) were estimated by scaling up the power requirements of the 3.8-m^3 bioreactor for treatment of the spent sulfidic caustic sample. A cost of \$0.05/kW/h was assumed. The capital costs of the system were estimated to be about \$200,000. These costs were annualized assuming a 10-yr useful life and a 12% interest rate. Operating costs are assumed to be minimal. When properly instrumented for pH control, the 3.8-m^3 reactor was operated for 8 h at a time without an attendant and without problems. The costs of acid for pH control is also not included in Table 5. The costs of acid will be dependent on the relative amounts of sulfide and alkalinity in the caustic. The greater the sulfide concentration relative to the alkalinity, the less acid that will be required since sulfide oxidation is acid-producing. The particular samples biotreated in the 1000-gal reactor had relatively low sulfide concentrations and high residual alkalinities.

CONCLUSIONS

Refinery spent sulfidic caustics have been successfully biotreated at the pilot scale, resulting in neutralization and removal of reactive sulfides. Spent caustic could be fed to the bioreactor undiluted and without prior neutralization. A preliminary economic analysis shows that the caustics can be treated for roughly 12¢/gal (\$0.33/L) plus the cost of any additional acid required to maintain a near-neutral pH over and above that produced by the microbial oxidation of sulfide.

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