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# A Preliminary Cost Analysis of the Biotreatment of Refinery Spent-Sulfidic Caustic

KERRY L. SUBLETTE

*Center for Environmental Research & Technology, University of Tulsa, 600 S. College Avenue, Tulsa, OK 74104*

## ABSTRACT

Caustics are used in petroleum refining to remove hydrogen sulfide from various hydrocarbon streams. Spent-sulfidic caustics from three refineries have been successfully biotreated on the bench and pilot scale, resulting in neutralization and removal of active sulfides. Sulfides were completely oxidized to sulfate by *Thiobacillus denitrificans* strain F. Microbial oxidation of sulfide produced acid, which at least partially neutralized the caustic. A commercial-scale treatment system has been designed that features a bioreactor with a suspended culture of flocculated *T. denitrificans*, a settler and acid and nutrient storage and delivery systems. A cost analysis has been performed for nine cases representing a range of spent caustic sulfide and hydroxide concentrations at a base treatment rate of 10 gpm. This analysis shows that refinery spent-sulfidic caustic can be biotreated for 4–8.3¢/gal.

**Index Entries:** Sulfidic caustic; sulfide; *Thiobacillus denitrificans*; cost analysis; refinery waste.

## 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 in the solution, the solution becomes known as spent-sulfidic caustic. Spent caustics typically have a pH >12.0, sulfide concentrations exceeding 2–3 wt%, and a large amount of residual alkalinity. 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)*.

Author to whom all correspondence and reprint requests should be addressed.

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.

Recently biotreatment of refinery spent-sulfidic caustic using a microbial culture augmented with the sulfide-oxidizing bacterium *Thiobacillus denitrificans* strain F was shown to be feasible *(2,3)*. 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, which would be specialized for treating spent-sulfidic caustic streams. Reported here are the results of a cost analysis of the biotreatment of refinery spent sulfidic caustic using the sulfide–tolerant strain F of *T. denitrificans* in flocculated, suspended culture.

## BIOTREATMENT OF SPENT-SULFIDIC CAUSTIC

### Bench-Scale, Stirred-Tank Reactor

The biotreatment of spent-sulfidic caustic was first demonstrated at the bench scale using a B. Braun Biostat M fermenter *(2)*. The reactor was initially charged with 1.5 L of a mineral salts medium containing 1700 mg/L of flocculated *T. denitrificans* strain F *(4)*. The pH and temperatures were maintained at 7.0 and 30°C, respectively. The acid used for pH control was 10*N* $HNO_3$. This particular acid was used so that acid addition could be monitored by following the nitrate concentration in the culture medium. The culture received a gas feed of 0.3–0.4 L/min of air with 5% $CO_2$. The outlet gas from the bioreactor was passed to a 500-mL Erlenmeyer flask, where the gas was sparged into 300 mL of 0.3 wt% zinc acetate to trap fugitive $H_2S$ from the bioreactor. A tee connection was located between the bioreactor of zinc acetate trap for gas sampling.

Sample characteristics of all caustics used in these studies are given in Table 1. The spent caustic feed reservoir consisted of a 250-mL graduated cylinder with a cork stopper. Spent-sulfidic caustic samples were diluted 1/5 with deionized water, but not neutralized (pH > 12.0). Diluted caustic was withdrawn through a stainless-steel tube that extended to the bottom of the cylinder. Feed was pumped to the bioreactor at 0.12 mL/min. In this manner, 150 mL of feed (1/10th the culture volume) could be delivered in 21 h. The feed was introduced into the bioreactor at a point about 2.5 cm from the bottom of the vessel and adjacent to one of the agitator impellers.

At start-up 150 mL of the process culture were removed from the bioreactor with the biomass recovered by centrifugation and returned to

Table 1
Characteristics of Spent-Sulfidic Caustic Samples[a]

| 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 |
| PC3 | 0.73 | 46300 | | 2.80 |
| T1 | 0.18 | 26700 | | 2.11 |

[a]The D, P, and T series caustics were obtained from three different refineries.

the culture. The supernatant from this centrifugation was the initial sample for sulfate, ammonium ion, nitrate, and chemical oxygen demand (COD) determination. At this time, the feed pump was activated, and the 1/5 dilution of spent-sulfidic caustic (sample D1) was delivered to the bioreactor. As noted above, the feed reservoir contained 150 mL of diluted caustic. Therefore, the feed reservoir was emptied in 21 h. The reactor received no feed for the next 3 h. At the end of this time, and each day thereafter, the feeding procedure was repeated with 150 mL removed from the bioreactor, the biomass recovered and returned to the culture. At the end of the 7th day of fed batch operation (after a total of 1050 mL of diluted caustic had been fed to the reactor), the agitation and gas feed were turned off and the biomass allowed to settle under gravity. The biomass settled to 25% of the original volume in <10 min. The clarified liquor was then siphoned off and replaced with fresh medium to a final volume of 1.5 L. The agitation and aeration were then resumed. At this time, 150 mL of the culture were removed, the biomass recovered and returned to the culture, and the feeding schedule resumed as described above using a second sample of caustic (D2). This replenishment of the culture medium was also repeated after 5 d of operation at which time the caustic feed was changed to the D3 sample for the duration of the experiment. The experiment was terminated after 21 full days of operation on the D series feeds.

The PC1 and PC2 samples (Table 1) were biotreated using the same reactor system at a later time using a second flocculated culture of *T. denitrificans* strain F developed for this purpose. The bioreactor was operated as described above for 6 d using PC1 as feed and 10 d using PC2 as feed.

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

| Sample | $SO_4^{-2}/S^{-2}$ (mole/mole) | $HNO_3/S^{-2}$ (mole/mole) | $H^+$ prod/$S^{-2}$ (mole/mole) | g MLSS/mole $S^{-2}$ |
|---|---|---|---|---|
| D1 | 1.00 | 1.06 | 1.39 | 4.1 |
| D2 | 1.07 | 0.048 | 0.94 | 6.1 |
| D3 | 1.10 | 0.040 | 0.94 | 18.3 |
| D3 | 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 |
| T1 | 1.02 | | | |

[a]$HNO_3/S^{-2}$ is the mol $HNO_3$/mol sulfide oxidized required to maintain the pH at 7.0–7.1. $H^+$ prod/$S^{-2}$ is the mol of acid produced/mol of sulfide oxidized.

It is important to note that the spent-sulfidic caustic was introduced into the bioreactor without neutralization. Sulfide oxidation by *T. denitrificans* is acid-producing *(5)*. Therefore, if the reactor is operated on a sulfide-limiting basis, at least partial neutralization of the added caustic can be achieved by the oxidation reaction if the reaction is sufficiently fast. This was indeed the case in this experiment. During the entire course of the experiment, the pH was maintained at 7.0–7.1 with only a small amount of acid addition as shown in Table 2. All of the acid produced by sulfide oxidation by the organism was neutralized by the hydroxide ion in the samples. The amount of $HNO_3$ required to maintain the pH in the 7.0–7.1 range was dependent on the extent to which the alkalinity in the sample exceeded the acid produced by sulfide oxidation. Greater addition of nitric acid was required when the D1 sample was used as feed because of the much greater alkalinity of the sample (Table 1).

Sulfate accumulated in the culture media as the sulfidic caustics were fed to the bioreactor. A sulfur balance showed complete conversion of sulfide to sulfate (Table 2). No elemental sulfur was detected in the culture medium, and no $H_2S$ was detected in the outlet gas or collected in the zinc acetate trap. It was also observed in these experiments that the process culture acclimated to methyldiethylamine (MDEA), resulting in complete removal of MDEA as well as oxidation of sulfides. The MDEA was metabolized by the mixed heterotrophs of the culture, whereas sulfides were oxidized to sulfate by *T. denitrificans*.

Similar results were obtained with samples PC1 and PC2 (Table 2). Subsequently, bench-scale testing with a similar suspended culture of *T. denitrificans* strain F and a caustic from a third refinery showed that caustic could be fed to the stirred-tank bioreactor undiluted as well as without neutralization *(6)*. The stoichiometry of sulfide oxidation with this caustic (T1, Table 1) is also given in Table 2. With the T1 caustic, the specific activity of flocculated *T. denitrificans* strain F was shown to be 1.1–1.3 mmole sulfide/h/g (MLSS). This agrees well with the specific activity observed in the biotreatment of sour water with this organism in an upflow bubble column *(7)*. Experiments with undiluted T1 caustic also demonstrated that carbonates present in the caustic provided sufficient inorganic carbon to *T. denitrificans* that no other source was necessary to support autotrophic oxidation of caustic sulfide.

## Pilot-Scale, Stirred-Tank Reactor

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 horizontal 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-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, which 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, which 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, which 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.

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 a concentrated suspension of flocculated *T. denitrificans* strain F were used to inoculate 3.0 $m^3$ of mineral salts medium. The initial (MLSS) concentration 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 at a feed rate of 30 mL/min. The caustic was conveyed to the reactor through 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. 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 during the evenings and on weekends only 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 total of 360 L of refinery spent-sulfidic caustic were successfully treated *(3)*.

Sulfate accumulated in the reactor medium as caustic was fed to the reactor. 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 caustic 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 the caustic feed rate was doubled. 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.

## 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 mg/L (similar to an activated sludge system). *T. denitrificans* strain F can easily be cultivated to this concentration by growth on thiosulfate *(8)*. As noted above, 1 mmol sulfide/h-g MLSS is a reasonable design figure for the specific activity of flocculated *T. denitrificans* for sulfide oxidation. Based on this specific activity and assuming an MLSS concentration in the bioreactor of 4000 mg/L, a 38 L/min (10 gal/min or gpm) stream with 3 wt% sulfide will require a 535-$m^3$ 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.

A preliminary economic analysis has been conducted for a base case of treating 10 gpm of spent-sulfidic caustic using a suspended culture of flocculated *T. denitrificans* strain F. A commercial-scale treatment system was designed for nine cases: three different sulfide concentrations, 0.2, 0.6, and 1.0 *M*, and three different $OH^-$ alkalinities, 1.0, 2.0, and 3.0*N*. Design

Table 3
Refinery Spent Caustic Treatment System Design Assumptions

| |
|---|
| Caustic flow rate = 10 gpm |
| T = 25 C |
| 1 mole $H^+$ per mole sulfide oxidized to sulfate |
| 1.86 moles $O_2$ required per mole of sulfide oxidized to sulfate |
| Specific activity of biomass = 1.0 mmoles/hr-g MLSS |
| [MLSS] = 4000 mg/L |
| $[H_2SO_4]$ = 18 N |
| Critical DO concentration = 0.05 mM |
| Nutrient stock solution = 35 wt% $NH_4NO_3$ and 6.3 wt% $P_2O_5$ |
| Settler design: overflow rate = 8 $m^3/m^2$-d |
| solids loading = 1.0 $kg/m^2$-hr |
| depth = 3 m |

assumptions are summarized in Table 3. Figure 1 gives a schematic diagram of a commercial-scale system for biotreatment of refinery spent-sulfidic caustic.

The treatment system has three components: the bioreactor/settler, the pH control or acid-delivery system, and the nutrient storage and delivery component. The bioreactor/settler is basically a mixer/settler consisting of a sunken concrete basin. Mixing in the bioreactor is done by aeration. Sulfide oxidation to sulfate occurs in the bioreactor section, and settling of biomass for return to the bioreactor occurs in the settler. The hydraulic retention time and, therefore, the bioreactor effluent flow rate in the bioreactor were based on maintaining a steady-state sulfate concentration in the bioreactor of 0.2*M*. Sulfate concentrations >0.25*M* have been shown to be inhibitory to *T. denitrificans (5)*. Table 4 gives the sizes of the bioreactor and settler sections for the nine design cases. Table 5 gives calculations of theoretical air requirements for the three sulfide concentrations.

The pH control system consists of a pH meter/controller, a tank to store $H_2SO_4$ (chosen for cost), and a pump to deliver the acid as needed to the bioreactor. Acid-delivery rates for the nine cases are given in Table 6, as well as the tank capacity needed for a 30-d supply of acid in each case. The nutrient storage/delivery component consists of two 1000-gal fiberglass tanks, two pumps, and associated piping. A nutrient stock solution (35

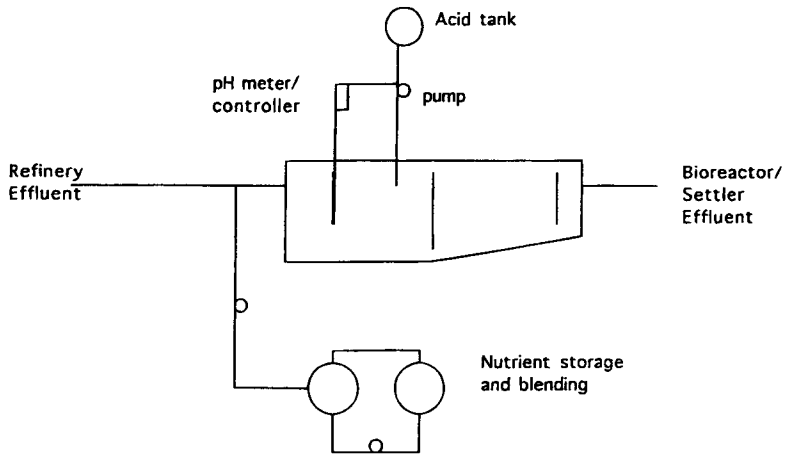


Fig. 1. Schematic diagram of a biotreatment system for refinery spent-sulfidic caustic.

Table 4
Bioreactor and Settler Volumes, 10-gpm Basis

Bioreactor

| [sulfide], M | Bioreactor Volume ($m^3$) |
|---|---|
| 0.2 | 114 |
| 0.6 | 341 |
| 1.0 | 568 |

Settler

Settler Volume ($m^3$)

| | [sulfide], M | | |
|---|---|---|---|
| $OH^-$ (N) | 0.2 | 0.6 | 1.0 |
| 1.0 | 82 | 109 | 136 |
| 2.0 | 150 | 177 | 204 |
| 3.0 | 216 | 245 | 272 |

wt% $NH_4NO_3$ + 6.3 wt% $P_2O_5$) can be prepared by adding the appropriate amount of $NH_4NO_3$ and $P_2O_5$ and water to one tank, and dissolving by circulating the suspension between the two tanks with a centrifigal pump, transferring the mixture to the second tank, and metering nutrient into the

Table 5
Theoretical Air Requirements, 10-gpm Basis

| [sulfide],(M) | molar sulfide feed rate (moles/hr) | Theoretical $O_2$ (moles/hr) | Theoretical Air (L/min) |
|---|---|---|---|
| 0.2 | 454 | 844 | 1630 |
| 0.6 | 1362 | 2533 | 4910 |
| 1.0 | 2270 | 4222 | 8190 |

Table 6
Acid-Utilization Rates and Acid Tank Capacity Required for 30-d Supply

Acid Utilization Rate (L/h)

| | [sulfide], M | | |
|---|---|---|---|
| $OH^-$ (N) | 0.2 | 0.6 | 1.0 |
| 1.0 | 101 | 50 | 0 |
| 2.0 | 227 | 177 | 126 |
| 3.0 | 353 | 303 | 252 |

Acid tank size

Tank Volume ($m^3$)

| | [sulfide], M | | |
|---|---|---|---|
| $OH^-$ (N) | 0.2 | 0.6 | 1.0 |
| 1.0 | 73 | 36 | 10 |
| 2.0 | 163 | 127 | 91 |
| 3.0 | 254 | 218 | 181 |

influent line of the bioreactor. The influent to the bioreactor consists of refinery effluent (assumed to be gravity-fed) plus the nutrient supplement. The nutrient metering rate and the operating capacity (in days)/1000 gal of nutrient tank volume are provided in Table 7.

Estimates of capital costs for a 10-gpm commercial system, including the bioreactor/settler, acid-storage and delivery system, aeration and nutrient storage, and delivery system for each of the nine design cases, were prepared by cost estimators from a major US oil company. These

Table 7
Nutrient Solution Metering Rate
and Tank (1000-gal) Capacity

| [sulfide],(M) | L/hr nutrient | Capacity (days) |
|---|---|---|
| 0.2 | 15.5 | 10.1 |
| 0.6 | 46.6 | 3.4 |
| 1.0 | 77.9 | 2.0 |

Table 8
Capital Costs for Biotreatment of Spent Caustic, 10 gal/min Basis ($000)

| | [sulfide], M | | |
|---|---|---|---|
| $OH^-$ (N) | 0.2 | 0.6 | 1.0 |
| 1.0 | 1452.8 | 1625.5 | 1822.9 |
| 2.0 | 1732.8 | 1907.5 | 2082.2 |
| 3.0 | 2011.6 | 2189.5 | 2361.8 |

capital costs are given in Table 8. These costs include a 25% contingency and 45% process development allowance. Therefore, these capital costs are heavily burdened with risk factors. Annual costs of acid and nutrients for the nine design cases are given in Tables 9 and 10, respectively. A bulk acid cost of $0.24/gal for 95% $H_2SO_4$ was assumed. Costs of nutrients were based on $4.13/40 lb bag of $NH_4NO_3$ and $5.51/40 lb bag of $P_2O_5$ *(9)*.

Table 11 gives the final cost (¢/gal) for treatment of refinery spent-sulfidic caustic for each of the nine design cases. These calculations were based on 365 d/yr, 24 h/d operation with capital costs annualized over 10 yr. Power, labor, and disposal costs for sulfate (if any) were not included. (These costs cannot be estimated accurately without more extensive pilot testing of the process; however, they are not anticipated to account for a significant fraction of the total operating cost.) Based on a proprietary analysis of alternative caustic treatment technologies by a major US oil company, the costs given in Table 11 show biotreatment of refinery spent-sulfidic caustic to be economically viable.

## CONCLUSIONS

Refinery spent-sulfidic caustics have been successfully biotreated on a bench and pilot scales, resulting in the neutralization and complete removal and oxidation of reactive sulfides using suspended cultures of

Table 9
Acid Costs for Biotreatment of Spent Caustic, 10 gal/min Basis ($000)

| | [sulfide], M | | |
|---|---|---|---|
| $OH^-$ (N) | 0.2 | 0.6 | 1.0 |
| 1.0 | 56.9 | 28.2 | 0 |
| 2.0 | 127.9 | 99.7 | 71.0 |
| 3.0 | 198.9 | 170.7 | 142.0 |

Table 10
Nutrient Costs for Biotreatment of Spent Caustic, 10 gal/min Basis ($000)

| | [sulfide], M | | |
|---|---|---|---|
| $OH^-$ (N) | 0.2 | 0.6 | 1.0 |
| 1.0 | 11.2 | 33.6 | 56.1 |
| 2.0 | 11.2 | 33.6 | 56.1 |
| 3.0 | 11.2 | 33.6 | 56.1 |

Table 11
Cost per gallon for Biotreatment of Spent Caustic, 10 gal/min Basis (¢/gal)[a,b,c]

| | [sulfide], M | | |
|---|---|---|---|
| $OH^-$ (N) | 0.2 | 0.6 | 1.0 |
| 1.0 | 4.0 | 4.3 | 4.5 |
| 2.0 | 5.9 | 6.2 | 6.4 |
| 3.0 | 7.8 | 8.1 | 8.3 |

[a]365 d/yr, 24 h/d operation.
[b]Capital cost annualized over 10 yr.
[c]Power and labor not included.

flocculated *T. denitrificans* strain F in stirred-tank reactors. Spent caustic could be fed to the bioreactor without prior neutralization. These observations suggest that biotreatment is a viable process concept for the treatment of these waste streams. An economic analysis shows that caustics can be biotreated for 4–8.3¢/gal.

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