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THE REMOVAL OF SULFATE AND METALS FROM MINE WATERS USING BACTERIAL SULFATE REDUCTION: PILOT PLANT RESULTS

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ABSTRACT

A treatment process that bacterially converts sulfate into elemental sulfur via a hydrogen sulfide intermediate was demonstrated at pilot scale for the treatment of three mine waters that contained metals and sulfate. Ethanol served as the bacterial carbon and energy source. The mine waters were treated at rates that ranged from 50-150 L day^{-1}. Contaminant concentrations up to 13 mg L^{-1} copper, 0.1 mg L^{-1} mercury, 0.04 mg L^{-1} cadmium, 3.5 mg L^{-1} zinc, 0.68 mg L^{-1} cobalt, 1.3 mg L^{-1} nickel, 49 mg L^{-1} iron, and 63 mg L^{-1} aluminum were removed to meet water quality effluent limits. Manganese removal was about 80% under normal operating conditions but increased to 96% when the process was optimized for manganese removal. The process was shown to be capable of decreasing sulfate concentrations from 1800 mg L^{-1} to less than 250 mg L^{-1}, nitrate from 100 mg L^{-1} to less than 1 mg L^{-1}, arsenic from 8 mg L^{-1} to less than 0.03 mg L^{-1}, and calcium from 310 mg L^{-1} to less than 100 mg L^{-1}. Acid mine waters were neutralized using bacterially-generated alkalinity; no external alkalinity source was needed.

Key words-- bacterial sulfate reduction, acid mine drainage, metal sulfide precipitation, bioreactor, water treatment, hazardous waste segregation, metal recovery.

INTRODUCTION

Contaminated water generated during the mining and processing of minerals often requires some degree of treatment before discharge or reuse. The traditional method of treating acidic mine water has been to add alkalinity, usually lime, to increase pH and induce the formation of metal hydroxide precipitates. These precipitates are then separated from the water by settling or, infrequently, by filtration. However, water treated in this manner cannot always meet metal effluent limits or the 500 mg L^{-1} limit for sulfate that has been proposed by the U.S Environmental Protection Agency (EPA) for the United States (Federal Register, 1995).

Lime addition can reduce sulfate concentrations from greater than 80,000 mg L^{-1} to 1500-1800 mg L^{-1} via gypsum ($CaSO_4 \cdot 2H_2O$) precipitation. However, treatment technologies that can further decrease sulfate concentrations to meet acceptable limits are few. Potential sulfate-removal methods include ion exchange, membrane treatment, chemical precipitation, and bacterial sulfate-reduction treatment (BSRT).

Ion exchange (Everett et al., 1994) and membrane treatments such as nanofiltration (Eriksson et al., 1996) are proven methods for reducing sulfate concentrations to less than 500 mg L^{-1}. However, neither ion exchange nor membrane treatments are stand-alone treatment technologies. Both require rigorous solids removal prior to treatment, and require a separate treatment for the concentrated waste streams that each produce. Although membrane treatment techniques can remove greater than 90% of most dissolved contaminants, supplemental treatment is still needed to meet metal effluent limits. Membranes have been prone to fouling and required frequent replacement; however, recent advances have extended membrane life and made membrane treatment techniques more cost effective.

The Walhalla Process® (Walhalla, Technologies Inc., 1994) is a sulfate-removal process that adds lime and a proprietary reagent to precipitate ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 3H_2O$) at pH 11.5. The ettringite precipitate is removed by settling, and carbon dioxide is then added to the supernatant to decrease the pH for discharge. The Walhalla Process is economically attractive because existing lime-treatment plants can easily be retrofitted to meet a 500 mg L^{-1} sulfate limit. However, operating costs may be high because the process requires relatively large amounts of both lime and the proprietary reagent.

BSRT uses bacterial processes to convert sulfate into elemental sulfur via a hydrogen sulfide intermediate. The BSRT process can meet the proposed 500 mg L^{-1} sulfate limit and the more restrictive 250 mg L^{-1} secondary drinking water standard. Moreover, BSRT can meet effluent limits for most metals without supplementary treatment. A 5000 m^3 d^{-1} BSRT plant has been operating at the Budelco zinc refinery in the Netherlands since May, 1992. The plant was designed and installed by Paques, Inc., for the removal of sulfate, zinc, and cadmium from contaminated groundwater. During four years of operation, zinc and cadmium removal has averaged 99.7%, and effluent sulfate concentrations have remained well below the discharge limit of 200 mg L^{-1} (Scheeren et al., 1993; DeVegt and Buisman, 1996).

In the current study, a pilot-scale BSRT plant was evaluated for the treatment of three mining-contaminated waters. The intent was to treat more severely contaminated waters than those treated at Budelco with a pilot plant that was functionally equivalent to the Budelco BSRT plant. Research goals were to optimize and demonstrate the treatment of each test water, and generate meaningful estimates of investment and operating costs.

BACTERIAL SULFATE-REDUCTION TREATMENT

The major components of the BSRT treatment system used in this study are shown in Fig. 1. The sulfate-reducing bioreactor was a 42.5 L Biopaq® upflow anaerobic sludge blanket reactor (UASB). Within the UASB, sulfate-reducing bacteria catalyzed the reduction of sulfate (electron acceptor) to hydrogen sulfide (H_2S) and bisulfide (HS^-), with the concurrent oxidation of ethanol (electron donor and biomass carbon source) to carbon dioxide, bicarbonate, and water.

$$4\ C_2H_5OH + 6\ SO_4^{2-} + 5\ H^+ \rightarrow 3\ H_2S + 3\ HS^- + 4\ CO_2 + 4\ HCO_3^- + 8\ H_2O$$

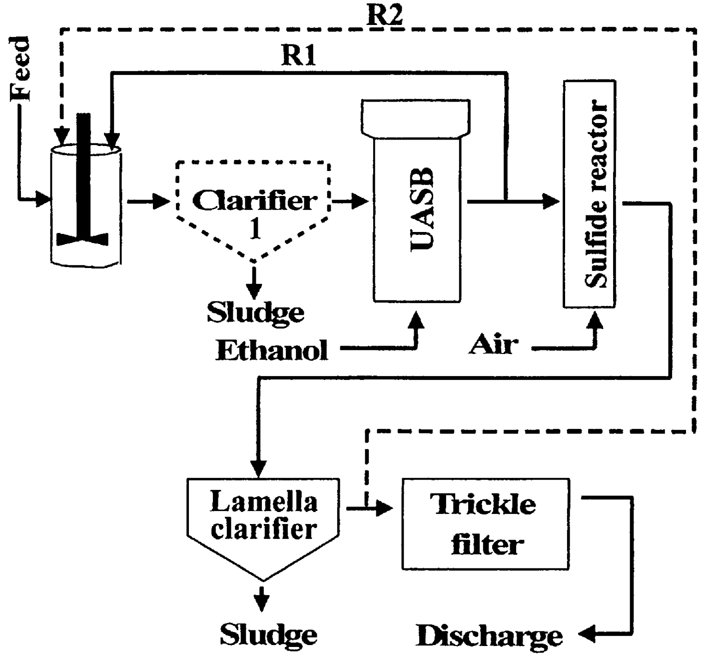

Figure 1. Flowsheet of the BSRT process used for this study. Clarifier 1 was used during the treatment of Arizona ground water and Nevada gold-mine water. Recirculation flow, R2, was only used during the treatment of Nevada gold-mine water.

Sulfate and acidity in the water were consumed by this reaction, and alkalinity in the form of bicarbonate was produced. Approximately equal amounts of H_2S and HS^- were formed when the UASB was maintained near pH 7. Both H_2S and HS^- quickly reacted with dissolved metals (Me^{2+}) present in the mix tank (via recirculation R1) and UASB to form insoluble metal sulfide precipitates (MeS).

$$Me^{2+} + H_2S \rightarrow MeS\downarrow + 2\,H^+$$
$$Me^{2+} + HS^- \rightarrow MeS\downarrow + H^+$$

Usually, the metal content of the water was insufficient to precipitate all available HS^- and H_2S. Excess HS^- and H_2S primarily exited the UASB in the liquid effluent. A minor amount of H_2S left the bioreactor with the biogas.

Hydrogen sulfide or HS^- that was not consumed by reaction with metals was converted into elemental sulfur in the Thiopaq® sulfide-oxidation reactor (sulfide reactor, Fig. 1), an 8-L fixed film bioreactor. When air was pumped into the base of the sulfide reactor, bacteria immobilized on the bioreactor support matrix catalyzed the oxidation of soluble sulfide species to form elemental sulfur. Alkalinity was also produced in this reaction:

$$2\ HS^- + O_2\ (aq) \rightarrow 2\ S^0\downarrow + 2OH^-$$

Prior to discharge, the treated effluent was pumped through an aerobic, trickling filter to remove minor amounts of nutrients (acetate and ammonia), and occasional traces of sulfide that were not completely consumed in the UASB or sulfide reactor. In a full-scale application, the trickling filter would likely be replaced by an aerobic wetland or an oxidation pond, or may not be needed due to better process control.

METHOD AND MATERIALS

Pilot Plant

The pilot plant, which included the mix tank, UASB, sulfide reactor, pumps, and control technology, was manufactured by Paques, Inc. Clarifiers were fabricated on site using transparent acrylic. Clarifier 1 was a partially filled, 30.5-cm diameter by 2.44-m column that contained 128 L. Clarifier 2 was a lamella clarifier with a capacity of 33.5 L.

Test Waters

The three waters treated in this study were chosen because they represent common treatment problems for the mining industry. Feed waters representing a mining-contaminated stream and ground water in Arizona were simulated (tables 1 and 4), based on analysis of the actual water. A gold mine water from Nevada (Table 5) was collected in plastic barrels from a tailings impoundment and used within two weeks without further preservation. These waters contain more sulfate and metals than the ground water treated at the Budelco BSRT plant.

Bacterial Inocula

The bacterial inoculum for the UASB was initially obtained from an anaerobic water-treatment plant at a paper manufacturing facility. The methane-forming activity in this inoculum predominated over the desired sulfate-reducing activity. Therefore, a second inoculum of predominantly sulfate-reducing bacteria from the Budelco BSRT plant was added approximately one month following pilot-plant startup. Activated sludge from a sewage treatment plant was used as the bacterial inoculum for the sulfide-oxidation reactor and the trickling filter.

Water Analysis

Water samples were filtered (0.45 μm), acidified with HCl (HCl was used instead of HNO_3 to prevent oxidation of sulfide), and analyzed for desired metals and sulfate (calculated from S content, assuming all S present as sulfate) using a Thermo Jarrell Ash inductively coupled plasma-emission spectrometer (ICP) and following standard protocol for sample handling and quality control (APHA, 1985). Samples that contained dissolved sulfide were boiled before analysis to drive off H_2S, and prevent the overestimation of the sulfate content. Periodically, sulfate determinations were made on unamended samples using ion chromatography to corroborate results obtained using the ICP method.

Samples collected for sulfide analysis were syringe-filtered (0.45 μm) with precautions to minimize air contact. These samples were analyzed within one hour using an Orion 940 millivolt meter with a silver-sulfide electrode.

Organic acids were determined from water samples that were filtered (0.45 μm), and acidified with 1N H_2SO_4. These samples were analyzed with a BAS 200 liquid chromatograph containing an OA 1000 column that was calibrated with acetate standards.

All pH and Eh values were read directly from the treatment system components using an Orion 290A meter with a triode pH electrode and a redox-combination electrode, respectively.

Gas Analysis

Gas samples were collected in vacutainers from the gas streams exiting the UASB and sulfide reactors. These samples were analyzed for H_2S, CH_4, CO_2, O_2, H_2, and N_2 using Hewlett Packard 5880 and 5890 gas chromatographs with Mole Sieve 5A and Porapak N columns, and thermal conductivity and flame ionization detectors.

ARIZONA STREAM WATER

Problem Description

Arizona stream water simulates an actual stream that has been impacted by decades of copper mining in the watershed. The stream is circumneutral in pH, and contains 1400-1700 mg L^{-1} SO_4^{2-} and 40-50 mg L^{-1} Mn (Table 1). Treatment goals are to reduce SO_4^{2-} and Mn concentrations to less than 500 mg L^{-1} and 0.2 mg L^{-1}, respectively.

Table 1. Untreated and treated water for Arizona stream water simulant. All concentrations are in mg L^{-1}; pH is in standard units.

	Untreated	Goal	Treated
pH	6.9	6-9	8.1
Mn	44	<0.2	8.0
SO_4^{2-}	1,400	<500	502

Treatment Strategy

The BSRT system configuration used to treat Arizona stream water is shown in Fig. 1. Feedwater was pumped into a stirred tank where it was mixed with about 50% of the effluent from the UASB. In this application, the purpose of UASB effluent recirculation was to increase residence time in the bioreactor. The mixed solution was then pumped into the UASB where ethanol was added, and sulfate was reduced to H_2S.

The UASB was operated at pH 7 so that about 50% of the H_2S dissociated into HS^- and the predominant carbonate species was HCO_3^-. Under these conditions, some Mn would be expected to react with dissolved sulfide or carbonate species to form MnS ($K_{sp} = 6 \times 10^{-16}$) or $MnCO_3$ ($K_{sp} = 8.8 \times 10^{-11}$) precipitates. The effluent from the UASB (minus the amount recirculated) flowed into the fixed-film bioreactor (sulfide reactor, Fig. 1) where air was added, and the remaining sulfide was oxidized to S^0. Traces of sulfides, organics, and ammonia were removed aerobically by the trickling filter (Fig. 1). Operating parameters for the pilot-scale BSRT plant during the treatment of Arizona stream water are provided in Table 2.

Table 2. Operating parameters of the BSRT pilot plant during the treatment of Arizona stream water, Arizona ground water, and Nevada gold-mine water.

Mix Tank

	Arizona stream	Arizona ground water	Nevada gold mine
pH	7.1	5.0	7.3
Temperature (°C)	29.8	28.9	27.6
Reactor volume (L)	18.8	18.8	18.8
Feed (L d^{-1})	148	108	54.5
Recirculation 1 (L d^{-1})	96	33	58
Recirculation 2 (L d^{-1})	--	--	33.5
Alkalinity addition	None	None	None
Hydraulic-retention time (h)	1.8	3.2	3.1

Clarifier 1

	Arizona stream	Arizona groundwater	Nevada gold mine
Volume (L)	--	128	128

Feed (L d^{-1})	--	141	146
Hydraulic-retention time (h)	--	21.8	21.0

UASB

	Arizona stream	Arizona ground water	Nevada gold mine
pH	6.8	6.8	7.0
Temperature (°C)	30.3	28.4	25.0
Bioreactor volume (L)	42.5	42.5	42.5
Bioreactor feed (L d^{-1})	244	141	146
Ethanol usage (mL d^{-1})	140	150	60
Hydraulic-retention time (h)	6.9	7.2	7.0
Sulfate-reduction rate (g-SO_4^{2-} L^{-1} d^{-1})	2.99	3.61	2.26
Ethanol-utilization efficiency (g-SO_4^{2-} mL^{-1}-ethanol)	0.91	1.02	1.60
Biogas production (L d^{-1})	38.1	28.5	6.55

Sulfide Reactor

	Arizona stream	Arizona ground water	Nevada gold mine
pH	8.1	8.3	8.3
Temperature (°C)	31.0	29.4	29.4
Bioreactor volume (L)	8.0	8.0	8.0
Feed (L d^{-1})	148	108	88

Hydraulic-retention time (h)	1.3	1.8	2.2
Sulfide-conversion rate (g-S^{2-} L^{-1} d^{-1})	5.12	3.35	3.20
Air flow (L d^{-1})	4900	Not determined	Not determined

Lamella clarifier

	Arizona stream	Arizona ground water	Nevada gold mine
Volume (L)	33.5	33.5	33.5
Flowrate (L d^{-1})	148	108	88
Hydraulic-retention time (h)	5.4	7.4	9.1

Results

Sulfate concentrations in Arizona stream water were decreased from about 1400 mg L^{-1} to 500 mg L^{-1} during pilot-scale testing (Fig. 2). The sulfide reactor removed dissolved sulfides from the UASB effluent, converting about 90% to S^0, and 10% to SO_4^{2-}. No H_2S was detected in gas samples taken from air exiting the sulfide reactor (Table 3). The SO_4^{2-} concentration goal of 500 mg L^{-1} was met with an ethanol consumption of 0.95 mL per liter of water treated. Manganese concentrations were reduced from 38 mg L^{-1} to about 8 mg L^{-1} (Fig. 3). Manganese discharge standards of 0.2 mg L^{-1} were not met.

Table 3. Percent composition of offgases from the UASB and sulfide bioreactors during the treatment of Arizona stream water and Arizona ground water.

	UASB	Sulfide reactor
Methane	80.24	0.04
Hydrogen sulfide	3.97	<0.001
Nitrogen	7.60	78.5

Carbon dioxide	7.84	0.38
Oxygen	0.19	20.13

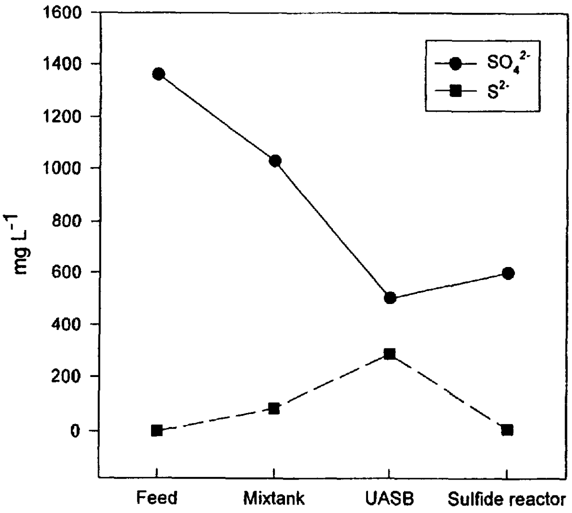

Figure 2. Sulfate and sulfide concentrations at different points in the BSRT process during the treatment of Arizona stream water.

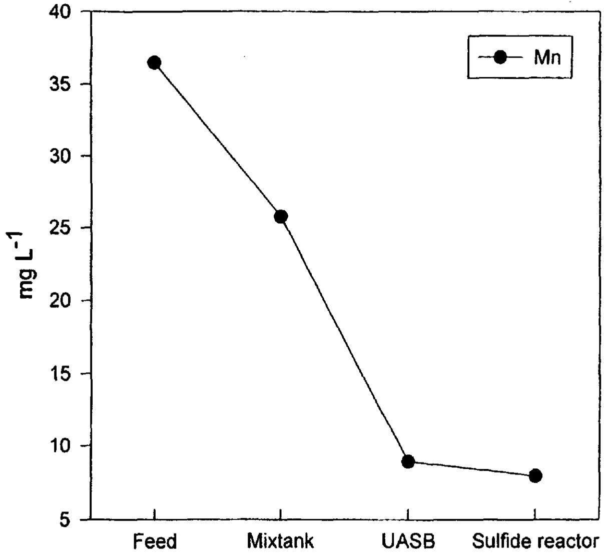

Figure 3. Manganese concentrations at different points in the BSRT process during the treatment of Arizona streamwater.

ARIZONA GROUND WATER

Problem Description

Contaminated ground water is being pumped from an alluvial aquifer in Arizona to arrest the movement of an acidic, metal-containing plume. This pH 3 ground water contains about 50 mg L^{-1} Fe, 21 mg L^{-1} Mn, 13 mg L^{-1} Cu, 8 mg L^{-1} Al, 3 mg L^{-1} Zn, and 1800 mg L^{-1} SO_4^{2-} (Table 4), and is currently treated with anhydrous NH_3 for use as process water at a nearby mine. The pump and treat option is an adequate solution to the problem as long as the mine is in operation. However, alternative treatment options are being considered to meet discharge standards after the mine closes. BSRT treatment goals (Table 4) for the Arizona ground water were to reduce all metal concentrations except Mn to less than 0.1 mg L^{-1}, reduce Mn concentrations to less than 0.2 mg L^{-1}, and reduce SO_4^{2-} concentrations to less than 500 mg L^{-1}.

Treatment Strategy

Copper and Zn are toxic to aquatic life at low concentrations (EPA, 1986). Therefore, Cu- and Zn-containing sludges should receive special handling and disposal to prevent the resolubilization of these metals. In this test, the basic BSRT process was modified slightly so that Cu and Zn could be recovered separately from other metals present in the Arizona ground water. Sufficient pH 7 effluent from the UASB was recirculated to the mix tank to raise the pH of the ground water to about 5. At this pH, Cu and Zn reacted with the dissolved sulfide in the UASB effluent to form CuS and ZnS precipitates, but Fe and Mn did not react. At pH 5, $Al(OH)_3$ was expected to form and be recovered with the CuS and ZnS solids in the underflow of Clarifier 1 (Fig. 1).

Table 4. Untreated and treated water quality for Arizona ground water simulant. All concentrations are in mg L^{-1} (X ± 1 standard deviation); pH is in standard units.

	Untreated	G Goal	Treated
pH	3.0	6-9	8.4
Fe	48.6 ± 6.2	<0.1	0.08 ± 0.01
Mn	21.5 ± 0.20	<0.2	4.72 ± 2.19
Cu	13.1 ± 0.10	<0.1	<0.01
Al	8.85 ± 0.10	<0.1	<0.1
Zn	3.23 ± 0.13	<0.1	0.01± 0.01
SO_4^{2-}	1,800 ± 6.4	<500	380 ± 140

Results

Sulfate concentrations were reduced to less than 500 mg L^{-1}, and all metals except Mn were reduced to less than 0.1 mg L^{-1} by the BSRT process (Table 4 and Fig. 4). Manganese concentrations were reduced to about 5 mg L^{-1}. More than 99% of the Cu and Zn, and 40% of the Al reported to the sludge from Clarifier 1. Iron, Mn, and Al were primarily removed from solution in the UASB, although significant Mn removal also took place in the sulfide reactor (Fig. 4). All Fe, Mn and S^0 solids, and 60% of the Al solids reported to the sludge from the lamella clarifier. Ethanol consumption was 1.4 mL L^{-1} of water treated (Table 2). No external source of alkalinity was added during this test.

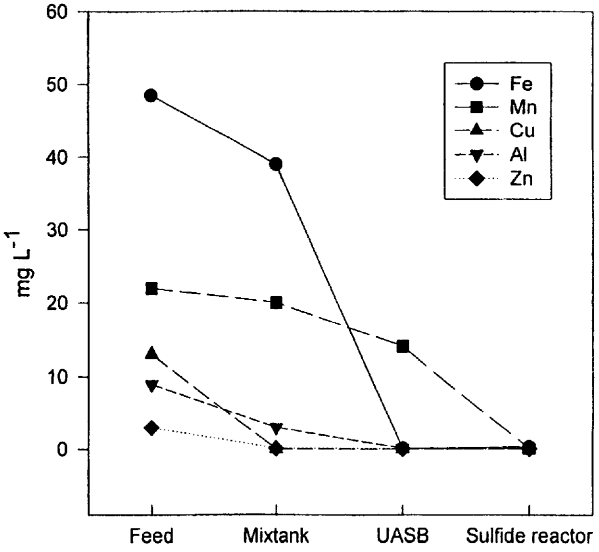

Figure 4. Metal concentrations at different points in the BSRT process during the treatment of Arizona groundwater.

NEVADA GOLD MINE WATER

Problem Description

Acidic water seeping from the base of sulfide-rich waste rock piles is pumped into a tailings impoundment. There, the acidity of the water is partially mitigated by lime addition and the alkalinity of the tailings. However, additional treatment is needed to remove SO_4^{2-}, NO_3^{2-}, and metals to meet local discharge standards. The chemical composition of the Nevada gold-mine water and treatment goals are shown in Table 5.

Treatment Strategy

Overall, the BSRT treatment of the Nevada gold-mine water was similar to that of the Arizona ground water. However, because the metal loading of the Nevada gold-mine water was low, there was no attempt to segregate hazardous and nonhazardous elements into different sludges. The mix tank (Fig. 1) was operated at pH 7.3 by recirculating pH 8.3 effluent from the lamella clarifier (R2, Fig. 1). Under these conditions, all regulated metals except Mn were expected to report to the sludge in Clarifier 1. Manganese removal was expected to be enhanced by operating the mix tank at a higher pH level.

Table 5. Untreated and treated water quality for Nevada gold-mine water. All concentrations are in mg L^{-1}; pH is in standard units.

	Untreated	Goal	Treated
pH	3.9	6-9	8.30
Fe	2.16 ± 0.13	<0.1	0.13 ± 0.14
Mn	6.65 ± 0.12	<0.1	0.29 ± 0.08
Cu	1.45 ± 0.11	<0.1	<0.01
Al	63.5 ± 2.09	<0.1	<0.1
Zn	3.55 ± 0.33	<0.1	0.06 ± 0.02
Cd	0.04	<0.01	<0.01
Co	0.68 ± 0.02	<0.1	<0.02
Ni	1.30 ± 0.03	<0.1	<0.02
Hg	0.10	<0.01	<0.01
Ca	312 ± 9.4	---	92.4 ± 10.7
NO_3^-	102 ± 7.73	<10.0	0.53 ± 0.28
SO_4^{2-}	1,770 ± 51.8	<250	248 ± 53.6

The Nevada gold-mine water contained 102 mg L^{-1} NO_3^- that had to be decreased to less than 10 mg L^{-1} to meet effluent limits. In anaerobic treatment systems, certain bacteria reduce NO_3^- to N_2 when provided with a suitable electron donor. We presumed that the biomass within the existing system was capable of reducing NO_3^-, and that ethanol was a suitable electron donor. Therefore, no changes were made to the basic BSRT process specifically for NO_3^- removal.

Results

The treatment goals for all Nevada gold-mine water contaminants were met except for

Mn. Manganese concentrations were reduced to 0.3 mg L^{-1}, the best result obtained thus far using this BSRT pilot plant. The 250 mg L^{-1} secondary drinking water standard for SO_4^{2-} and our goal of less than 10 mg L^{-1} NO_3^- were also attained. Nitrate removal (Fig. 5) and metal precipitation primarily occurred in the mix tank. Calcium (Fig. 5) and Mn (Fig. 6) were removed in the UASB and the sulfide reactor. The apparent removal of Ca and Mn in the mix tank was due to dilution of the feedwater by the recirculation of Ca- and Mn-depleted water. Ethanol consumption was 1.1 mL per L of water treated (Table 2). No external source of alkalinity was added during this test.

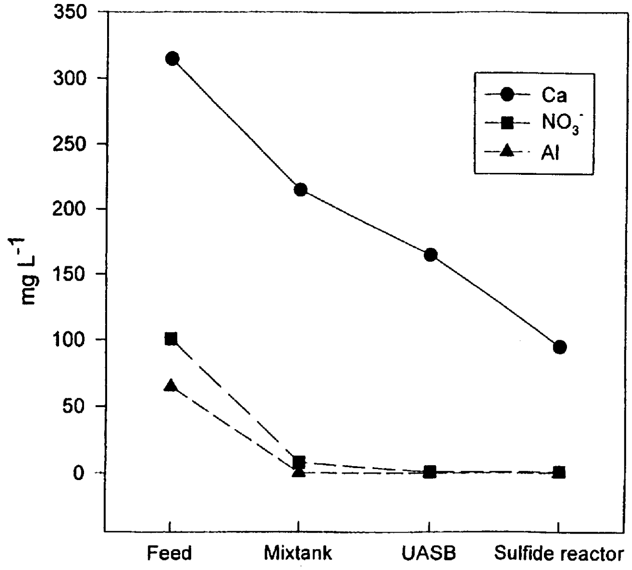

Figure 5. Concentrations of nitrate, calcium, and aluminum at different points in the BSRT process during the treatment of Nevada gold-mine water.

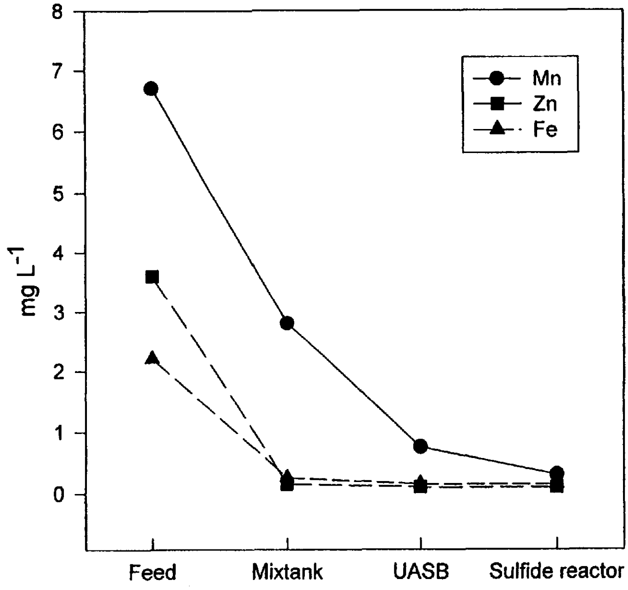

Figure 6. Concentrations of manganese, iron, and zinc at different points in the BSRT process during the treatment of Nevada gold-mine water.

DISCUSSION

UASB Operation

The Arizona stream water was the first water treated by the pilot plant following startup, and the biomass in the UASB had less than one month to adapt to the high-sulfate environment. and ethanol substrate. Therefore, the low-ethanol-utilization efficiency (EUE) of 0.9 g $SO_4{}^{2-}$ mL^{-1}-ethanol (Table 2) was expected. Approximately one month later, when the Arizona ground water was tested, the EUE had increased to 1.0 g-$SO_4{}^{2-}$ mL^{-1}-ethanol, and during the treatment of the Nevada gold-mine water about nine months later, the EUE had increased to 1.6 g-$SO_4{}^{2-}$ mL^{-1}-ethanol although sulfate in the UASB effluent was less than 30 mg L^{-1}. The best EUE observed with the current UASB pilot plant was 2.0 g-$SO_4{}^{2-}$ mL^{-1}-ethanol, which was attained six months after startup under non-sulfate limited conditions (Hammack et al., in press). The EUE for the full-scale BSRT plant at Budelco also averages about 2.0 g-SO_4^{2-} mL^{-1}-ethanol (DeVegt and Buisman, 1996). A maximum EUE of 2.8 g-SO_4^{2-} mL^{-1}-ethanol is theoretically possible if ethanol is completely used for SO_4^{2-} reduction. Therefore, in these tests, about 70% of the supplied ethanol resulted in sulfate reduction. Most of the remaining ethanol was needed for the growth of sulfate-reducing biomass. However, some ethanol exited the bioreactor unused or was nonproductively metabolized by methane-forming bacteria.

The UASB produced 38 L d^{-1} of biogas during the treatment of Arizona stream water, but less than 7 L d^{-1} during the treatment of Nevada gold mine water. The drop in biogas production was the result of decreased methane formation, the primary component of the biogas.

The conversion of ethanol to hydrogen and acetate by acetogenic bacteria is rapid (Shuler and Kargi, 1992) and assumed to be complete within the UASB. Hydrogen and acetate are then used by sulfate-reducing and methane-forming bacteria for bacterial respiration or cell growth. The presence of hydrogen in the biogas or acetate in the liquid effluent would indicate incomplete utilization of these substrates. Hydrogen was not detected. However, acetate concentrations in the UASB effluent were about 300 mg L^{-1} when the Arizona stream water was tested, but decreased to less than 50 mg L^{-1} during the treatment of the Nevada gold-mine water.

These results indicate that biomass adaptation improved the ability of the biomass to use acetate and increased sulfate-reduction activity at the expense of methane production. Improvement in bioreactor performance attributable to biomass adaptation was most apparent during the first four months of operation.

The UASB bioreactor loading was about 3 g SO_4^{2-} L^{-1} d^{-1} during the treatment of the three tested waters. This was significantly less than the 10 g-SO_4^{2-} L^{-1} d^{-1} loading of the full-scale UASB at the Budelco treatment plant (DeVegt and Buisman, 1966). However, with an adapted biomass and without sulfate limitations, the pilot UASB used in these tests has had sustained loadings of 10 g-SO_4^{2-} L^{-1} d^{-1} (Hammack et al., in press) and for brief periods (two to three days), has dealt with loadings in excess of 12 g-SO_4^{2-} L^{-1} d^{-1}.

Sulfide-Reactor Operation

Following inoculation, the sulfide-oxidizing activity of this bioreactor was rapidly established. Airflow regulation was used to control the redox within the bioreactor and optimize the conversion of sulfide to S^0. Under optimum conditions, the sulfide reactor converted more than 90% of dissolved sulfide to S^0, and less than 10% to SO_4^{2-}. Alkalinity generated by this conversion increased pH by about one unit. This pH increase may have contributed to the Mn and Ca removal that occurred in the sulfide reactor.

Acetate was also removed in the sulfide reactor, presumably by heterotrophic bacteria present in the aerobic consortium. No acetate was detected in the sulfide-reactor effluent.

Sulfate Removal

Sulfate-discharge goals were met during the treatment of all three waters tested. However, because the Arizona stream water and the Arizona ground water were treated using an immature anaerobic biomass, the volume of ethanol consumed per gram of sulfate reduced was inordinately large. The Nevada gold-mine water was treated using an adapted biomass and, although sulfate concentrations were limiting, ethanol-utilization efficiency was close to that of the full-scale Budelco BSRT plant.

Metal Removal

These tests demonstrated the ability of the BSRT process to effectively remove metals from solution. Treatment goals were met for Hg, Cu, Cd, Zn, Co, Ni, Fe, and Al. However, treatment goals for Mn were not met. The Mn effluent limit at the Nevada gold mine was 0.1 mg L^{-1}. In an attempt to meet this low Mn limit, the UASB and sulfide reactors were operated at a higher pH than normal. Using this strategy, Mn concentrations were reduced to 0.3 mg L^{-1} , which was not adequate at this mine site, but would meet many less stringent discharge limits.

The high pH conditions that were maintained to enhance Mn removal also improved Ca removal. During the treatment of Nevada gold-mine water, the BSRT process decreased Ca concentrations from 312 mg L^{-1} to 92 mg L^{-1} probably by the precipitation of $CaCO_3$. Although Ca is not a commonly regulated parameter, reducing Ca concentrations would reduce total dissolve solids (TDS) values, which are often regulated.

Separation of Toxic and Nontoxic Sludges

The pilot-scale treatment of Arizona ground water demonstrated the ability of the BSRT process to separate sludges containing potentially hazardous metals from sludges that contain only innocuous elements. This capability can reduce disposal costs by minimizing the volume of sludge considered to be hazardous waste. During the treatment of Arizona ground water, the potentially toxic elements Cu and Zn reported to the Clarifier 1 sludge. At this site, the least expensive disposal option would be to send Cu- and Zn-containing sludge to a nearby Cu smelter where Cu would be recovered, and Zn would be converted into an inert slag. A second sludge that contained S^0, Fe, and Mn was collected from the underflow of the lamella clarifier. This sludge was nontoxic, and could be inexpensively landfilled. Aluminum was recovered in both sludges, although it would have been desirable to recover all Al in the nontoxic lamella clarifier sludge. Reducing the mix tank pH from five to four (by reducing recirculation flow) would have reduced the amount of Al reporting to Clarifier 1 (hazardous) sludge, but may have resulted in incomplete Zn removal.

Nitrate Removal

Pilot scale tests with the Nevada gold-mine water demonstrated the effectiveness of the BSRT process for NO_3^- removal. Nitrate was removed in the mix tank, presumably by bacterial reduction to N_2. Dissolved sulfide and acetate from the recirculated UASB effluent provided the anaerobic environment and carbon source needed for bacterial NO_3^- reduction. It is economically important that NO_3^- treatment was achieved without modifications to the basic BSRT process.

CAPITAL AND OPERATING COSTS

The capital and operating costs for a BSRT plant are linked to the amount of sulfate that must be removed. Even if no sulfate standard must be met, sulfate must be reduced to provide sulfide for metal precipitation, and generate alkalinity to neutralize acidic water.

UASB treatment systems use substances such as ethanol as the electron donor, or alternatively, one can specify gas-lift bioreactors that use H_2 as the electron donor. In general, the UASB systems are more cost-effective in applications where less than 10 tons of sulfate are reduced per day while the gas-lift, H_2 reactor is preferable for applications with higher sulfate loadings. Figure 7 provides an indication of the investment cost for a BSRT plant based on sulfate removal capacity. Because the number of separation steps as well as the degree of liquid recirculation is different for each application, a range of investment costs is presented. These are based on a system using a gas lift, sulfate-reducing bioreactor with H_2 as the electron donor.

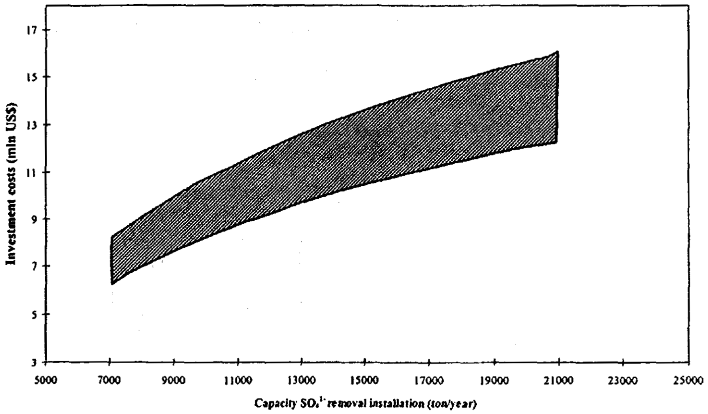

Figure 7. Range of investment costs for a BSRT plant (H_2 electron donor) based on sulfate-removal capacity.

The total treatment costs for a BSRT plant depend on the characteristics of the stream to be treated and discharge criteria. For example, the estimated treatment costs (chemicals, energy, labor, and depreciation (15 percent annuity)) of a treatment system reducing 10,000 tons of sulfate per year are approximately $330 (1997 dollars) per ton of sulfate removed. Depending on the nature of the water being treated, these costs can largely be offset by metal values recovered by shipping copper and/or zinc to a smelter (Hammack et al., in press).

CONCLUSIONS

This study provided the opportunity to monitor the gradual transformation of a predominantly methane-forming biomass to a sulfate-reducing biomass in a sulfate-rich environment. During this adaptation period, the ability of the sulfate-reducing biomass to use acetate as an electron donor also increased. The overall result was that the utilization of the ethanol substrate for sulfate reduction improved from 0.9 to 1.6 g-SO_4^{2-} mL^{-1}-ethanol.

These pilot-scale tests with mining-impacted waters demonstrated that the BSRT process can:

1. meet proposed SO_4^{2-} standards by converting SO_4^{2-} to S^0 via an H_2S intermediate,
2. meet discharge standards for all metals except Mn (can meet all but the most restrictive Mn standards),
3. meet NO_3^- standards by biologically reducing NO_3^- to N_2,
4. decrease Ca concentrations to less than 100 mg L^{-1} via $CaCO_3$ precipitation,
5. limit sludge-disposal costs by segregating hazardous and nonhazardous elements, and
6. neutralize acidic waters with biologically generated alkalinity.

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