



TREATMENT OF WATER FROM AN OPEN-PIT COPPER MINE USING BIOGENIC SULFIDE AND LIMESTONE: A FEASIBILITY STUDY

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(First received April 1993; accepted in revised form February 1994)

Abstract—A bench-scale biogenic sulfide and limestone treatment system was used to treat acidic metal-contaminated water from the Berkeley Pit, an abandoned open-pit copper mine in Butte, Montana. Hydrogen sulfide was generated in a sulfate reduction bioreactor and was used to precipitate metal sulfides from the mine water in a separate reactor. The metal-depleted, sulfate-rich mine water then passed through a limestone-filled reactor to raise its pH before entering the bioreactor. The treatment process removed more than 99% of the initial concentrations of Fe, Cu, Zn, and Al (620, 178, 530, and 278 mg l⁻¹, respectively) in the mine water. The process also removed 91% of the initial Mn concentration (191 mg l⁻¹). Copper and Zn concentrates were selectively recovered from the mine water based on the pH-dependent dissociation of the added H₂S. The limestone used to raise the pH was eventually passivated, possibly by the precipitation of gypsum, silica, clay minerals, and aluminum hydroxide. A modification of this biogenic sulfide/limestone treatment system has the potential to treat Berkeley Pit water to within discharge standards, and could generate saleable metal sulfide concentrates to partially offset treatment costs.

Key words—bacterial sulfate reduction, acid mine drainage, metal sulfide precipitation, limestone neutralization, bioreactor, water treatment, Berkeley Pit, Montana

INTRODUCTION

The discovery of vast Cu, Pb, and Zn deposits at Butte, Montana in the 1880's led to the development of one of the world's most important mining complexes, often referred to as "the richest hill on earth". Open pit mining occurred there from 1953 until 1982, creating the most dramatic remnant of this mining activity, the Berkeley Pit. During its excavation, over 300 million m³ of rock were removed and the pit reached a depth of 542 m, making it one of the largest mine pits in the United States.

Water is now filling the 77 ha Berkeley Pit at the rate of approximately 23 million l day⁻¹ from ground and surface water sources. The water level is rising at a rate of approximately 8 m per year, and is expected to reach the level of the adjacent alluvial aquifer by 2012 (Canonie Environmental, 1992). The water in the Berkeley Pit is a moderately-oxidizing, acidic, Ca-Fe sulfate solution, containing high concentrations of Al, As, Cd, Cu, Fe, Mn, and Zn (Davis and Ashenberg, 1989). The threat of groundwater contamination from the rising pit water makes it essential that a water treatment system be established, and a number of different options are being considered.

Acidic, metal-contaminated mine drainage is commonly treated by adding quicklime (CaO), hydrated lime [Ca(OH)₂], or caustic soda (NaOH) to precipitate metals from solution as hydroxides. Soda ash (Na₂CO₃) is sometimes used to precipitate metals such as Cd and Ni as insoluble carbonates (Lanouette, 1977). Metals can also be precipitated from wastewater as insoluble sulfides. In most existing sulfide treatment systems, an alkaline agent such as lime is first added to the water to raise its pH between 6 and 8. Sulfide is then added in either a soluble (Na₂S, NaHS), slightly soluble (BaS, FeS) or gaseous (H₂S) form (Bhattacharyya *et al.*, 1979; Peters and Ku, 1985; Streeter, 1970), and one or more metal sulfide precipitates form.

Sulfide precipitation has several potential advantages over hydroxide precipitation. Metal sulfides are generally less soluble than their corresponding metal hydroxides, allowing more complete precipitation of contaminant metal ions, even at low pH (Fig. 1; Peters and Ku, 1985). Hexavalent Cr can be reduced to the trivalent form during sulfide treatment and subsequently be precipitated as a hydroxide using lime or caustic (Lanouette, 1977). Metals complexed with ammonia or cyanide are often more readily precipitated as sulfides than as hydroxides (Lanouette, 1977). Metal sulfides are also more compact, have faster settling velocities, and exhibit better thickening and dewatering characteristics than corre-

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sponding hydroxide sludges (Whang *et al.*, 1982; Peters *et al.*, 1985; Peters and Shem, 1993).

The potential disadvantages of sulfide precipitation systems also need to be considered. If the amount of sulfide reagent added to a solution differs from the stoichiometric amount required to precipitate metal sulfides, either excess metals will remain in solution or excess H_2S will be present. The objectionable odor and toxicity of H_2S may require that process tanks be enclosed and vacuum-evacuated (Peters and Ku, 1985). Although Whang *et al.* (1982) reported that a metal sulfide sludge containing Cu, Ni, Pb, Cd, and Zn was three times less susceptible to leaching at pH 5 than an equivalent metal hydroxide sludge, the potential for metal sulfide sludge oxidation and resolubilization in landfills must be evaluated carefully. Finally, the increased cost of chemical sulfide reagents over lime, caustic, and soda ash (Lanouette, 1977), may preclude the choice of this treatment method.

The cost of sulfide treatment can potentially be lowered in several ways. Instead of using commercial sulfide reagents, sulfide might be generated less expensively by sulfate-reducing bacteria acting on waste organic materials and sulfate from the mine water. Limestone can be substituted for more expensive alkaline reagents to achieve final neutral pH values (Dean *et al.*, 1972) because most heavy metal sulfides can be precipitated at a pH below 6 (Fig. 1). Lastly, if metal concentrations are high enough, and appropriate control is exerted over the physical properties and chemical composition of the metal sulfide sludges produced, the sulfide precipitates can be processed by existing smelters for metal recovery (Bhattacharyya *et al.*, 1981; Hammack *et al.*, 1993). Metal recovery

also partially eliminates the need for sludge disposal. In this paper, we report on the feasibility of treating Berkeley Pit water using a bench-scale biogenic sulfide/limestone treatment system that employs several of these cost-saving methods.

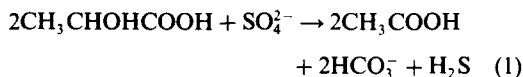
SYSTEM DESIGN

A schematic diagram of the bench-scale sulfide treatment system is shown in Fig. 2. The system consisted of three components: (1) a sulfate reduction bioreactor (*bioreactor*) to produce H_2S ; (2) a counter-current metal sulfide precipitator (*precipitator*) to bring metal-contaminated water in contact with H_2S ; and (3) a limestone neutralization reactor to raise the pH of the water before it entered the bioreactor. A recirculating gas stream was used to sparge H_2S from the bioreactor and carry it into the sulfide precipitator. Berkeley Pit water was pumped into the precipitator, where heavy metals reacted with H_2S in the recirculating carrier gas to form metal sulfide precipitates. Effluent water from the precipitator flowed through the limestone neutralization reactor, where the pH increased to approximately 6. The water then flowed into the bioreactor. Sodium lactate was injected directly into the bioreactor to provide a carbon source for sulfate-reducing bacteria. The medium in the bioreactor was therefore depleted in heavy metals, contained relatively high concentrations of sulfate and sodium lactate, and had an optimal pH for bacterial sulfate reduction activity. Final effluent from the treatment system left through a U-shaped gas trap at the top of the bioreactor.

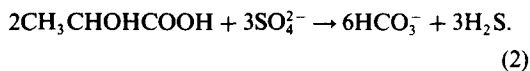
The three components of the treatment system were constructed from 5 cm i.d. transparent PVC cylinders. The lengths, volumes, and operational residence times of each component and the entire system are shown in Table 1.

Sulfate reduction bioreactor ("Bioreactor")

An anaerobic bioreactor served as the H_2S source for all tests. Sodium lactate was degraded in the bioreactor by a mixed culture of unidentified sulfate-reducing and other anaerobic bacteria originally isolated from spent mushroom compost. No solid bacterial support matrix was used in the bioreactor. Metabolism of the lactate by sulfate-reducing bacteria would be expected to result in its partial oxidation to acetate:



as well as its complete mineralization,



Continual sparging of the bioreactor medium with inert gas prevented H_2S from accumulating to concentrations that could be toxic to sulfate-reducing

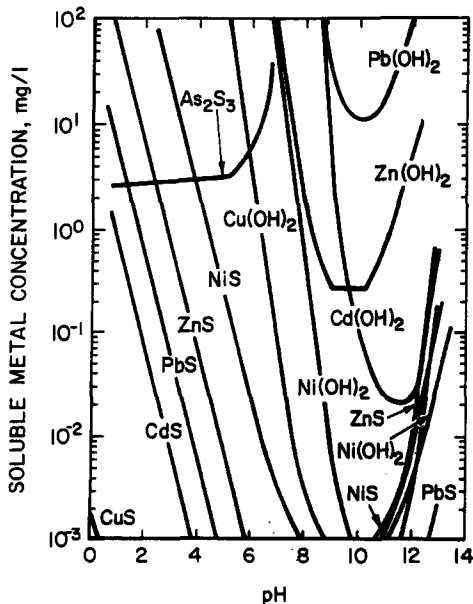


Fig. 1. Metal sulfide and hydroxide solubilities as a function of pH (after Peters and Ku, 1985).

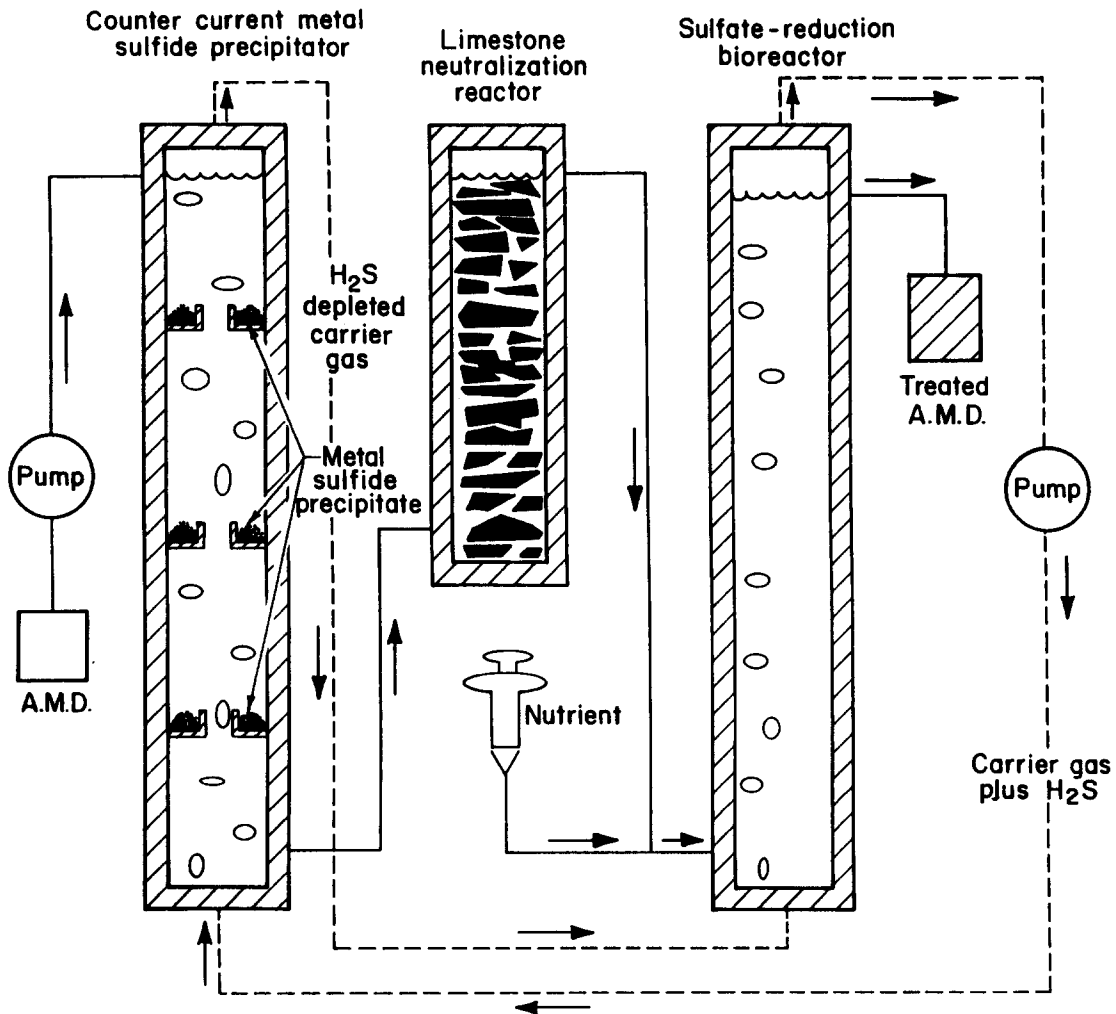


Fig. 2. Schematic of the biogenic sulfide/limestone treatment system for metal-contaminated acid mine drainage. See text for operational details. Dashed lines indicate the path of gas flow; solid lines indicate the path of liquid flow. For clarity, only 4 of the 9 reaction chambers in the counter-current precipitator are shown and the holes between chambers are exaggerated in size.

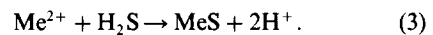
bacteria (Reis *et al.*, 1991). Other gases, such as CO_2 , H_2 , and CH_4 , would also be expected to form in the reactor due to the metabolic activity of other anaerobic bacteria (Widdel, 1988). However, sulfate reduction would be expected to be the dominant form of bacterial respiration under anaerobic conditions where sulfate and lactate concentrations are not limiting.

Table 1. Size, volume, and residence time specifications for the bench-scale sulfate reduction/limestone treatment system

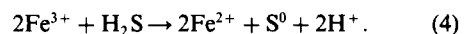
System component	Length (cm)	Void vol (ml)	Hydraulic residence time (days)
Precipitator	145	2950	4.1
Neutralizer	31	280	0.4
Bioreactor	145	2950	4.1
Entire system	—	6180	8.6

Counter-current metal sulfide precipitator ("Precipitator")

In this reactor, H_2S reacted with dissolved metals (Me) in the mine water to form insoluble metal sulfides



The precipitator was designed to serve two purposes: (1) to remove Cu and Zn, which are present in Berkeley Pit water in concentrations reported to be inhibitory to sulfate-reducing bacteria (Booth and Mercer, 1963; Römer and Schwartz, 1965), and (2) to reduce ferric iron to ferrous iron



This reaction was considered necessary to prevent ferric iron from coating the limestone surfaces in the limestone neutralization reactor. Alternatively, Fe

Table 2. Water quality of the Berkeley Pit influent feed and effluent from the sulfate reduction/limestone treatment system

Sample	pH	Concentration (mg l ⁻¹)				
		Cu	Zn	Fe	Mn	Al
Influent	2.3	178	530	620	191	278
Effluent						
Day 15	7.9	<0.1	<0.1	1.0	17.4	<0.1
Day 16	8.1	<0.1	<0.1	0.9	17.2	<0.1
Day 20	7.7	<0.1	<0.1	1.2	37.5	<0.1
Day 21	6.5	<0.1	<0.1	143	130	<0.1

could have been removed by some other treatment method, such as ion exchange, but this was not considered for economic reasons. In addition, it was necessary to supply the sulfate-reducing bacteria in the bioreactor with some iron to support their metabolic activity (Postgate, 1984).

The precipitator consisted of 9 separate reaction chambers, each 5 cm wide × 15 cm long (only four are shown in Fig. 2). Each chamber was connected to the next by a 1 cm hole to allow the passage of both water and gas. A piece of Tygon tubing extended 4 cm upwards into each overlying chamber to prevent the downward migration of metal precipitates within the precipitator. Water exited the bottom of the precipitator from the side of reaction chamber 9; this chamber was thus constructed differently from the other chambers and was not included in the data analysis. At the end of the experiment, the precipitates were collected from the remaining 8 chambers and were analyzed to determine whether the counter-current flow of water and gas had resulted in the selective precipitation of metals along the length of the column. This hypothesis was based on the expectation that the opposing concentration gradients of metals and H₂S would cause the solubility products for Cu and Zn sulfides to be exceeded in different segments of the column. Limestone chips (1 × 3 cm) were placed in the uppermost chamber (chamber 1) in an attempt to passively increase the pH of the incoming untreated water to a value greater than 3, where the precipitation of both Cu and Zn sulfides would be expected.

Limestone neutralization reactor

In this reactor, the pH of the effluent from the precipitator (about pH 1.7) was raised to within the pH range of 5 to 9.5 reported to be tolerated by sulfate-reducing bacteria (Postgate, 1984). The reactor was filled with 1 × 3 cm size fraction limestone chips.

EXPERIMENTAL

Test water

The water treated was a pooled sample collected in 1991 from approximately 1 m and 70 m depths in the Berkeley Pit. The sample was not preserved following collection, so the test water may differ from the initially collected sample. The chemical characteristics of the water used in the laboratory tests are shown in Table 2. Some metals (Al, Mn, and

Zn) exceeded maximum concentrations reported by Davis and Ashenberg (1989).

Treatment system operation

During system startup, Postgate's medium B (1984) was pumped into the bioreactor to encourage the growth and activity of sulfate-reducing bacteria. When a stable H₂S production rate was obtained, Berkeley Pit water was introduced into the system. No effluent samples were collected until almost 2 volumes of Berkeley Pit water had passed through the system (15 days) to be certain that most of the growth medium salts had been washed from the system.

Following startup, Berkeley Pit water was pumped through the system at a flow rate of 30 ml h⁻¹. Sodium lactate syrup (60% wt/wt) was injected into the bioreactor as a carbon source for the sulfate-reducing bacteria at a rate of 0.16 ml h⁻¹. All experiments were carried out at room temperature (24–30°C). Carrier gas, consisting initially of N₂, recirculated between the bioreactor and precipitator at a rate of 75–100 cm³ min⁻¹. Upon completion of the continuous treatment test, the metal sulfide precipitates were removed from the eight uppermost reaction chambers of the precipitator for subsequent analysis.

Analysis of water and metal sulfide precipitates

All water samples were filtered (0.45 µm), acidified with HCl, and analyzed for Cu, Zn, Al, Fe, and Mn using inductively-coupled argon plasma emission spectroscopy (ICP) and following standard protocol for sample handling and quality control (APHA, 1985). All pH determinations were made on unfiltered samples immediately after their collection using an Orion SA230 pH meter with a combination pH electrode. Samples of the metal sulfide precipitates were dried, weighed, and digested using the nitric acid digestion method (Method 302 D; APHA, 1985), substituting aqua regia for concentrated nitric acid. The resulting solutions were filtered and analyzed for metals by ICP as described previously.

Evaluation of bioreactor performance

Hydrogen sulfide production rates were measured by installing a series of gas traps in the effluent gas stream from the bioreactor. Each gas trap contained 20 ml of a 0.03 M zinc acetate solution that reacted with H₂S to form a ZnS precipitate. After a given period of time at a known flow rate, the gas trap contents were filtered and the filtrate was analyzed for Zn by ICP spectroscopy. The H₂S production rate and P_{H_2S} were calculated from the rate of Zn loss from the gas trap solution.

Batch treatment tests

Sodium hydroxide was used to adjust the pH of Berkeley Pit water to nine values between pH 2.3 (raw water) and pH 4.0. The pH-adjusted water was filtered to remove ferric iron precipitates and was placed in 30 ml gas traps. Hydrogen sulfide was sparged from the treatment system bioreactor with N₂, and bubbled through each gas trap until no further precipitation occurred (at least 16 h). The contents of the gas traps were then filtered and the filtrate was analyzed for metals by ICP spectroscopy.

Limestone passivation study

Raw Berkeley Pit water was contacted for 24 h in Fisher–Milligan gas washers with biogenic H₂S sparged from the bioreactor. The contents of the gas washer were then filtered (0.45 µm) to remove the dark brown precipitate that formed (CuS + S⁰), and the water was returned to the gas washer. Biogenic H₂S was bubbled through the water for an additional 30 min, and the solution was then examined visually. If any additional precipitates had formed, the water was treated with biogenic H₂S for an additional 6 h and

refiltered. This procedure was repeated until no additional precipitates were detected.

A 200 ml aliquot of the pretreated Berkeley Pit water was saturated with biogenic H_2S and transferred to a 500 ml round-bottom flask that contained 100 g of limestone chips (1×3 -cm size fraction). The headspace of the flask was purged with N_2 to prevent the oxidation of ferrous iron and the flask was sealed.

The limestone was then allowed to equilibrate with the water for 24 h. After that time, the water was replaced with a fresh 200 ml aliquot of pretreated Berkeley Pit water. The 100 g limestone sample was contacted with five separate volumes of pretreated Berkeley Pit water before the experiment was concluded.

Samples of the pretreated Berkeley Pit water were collected before and after contacting the limestone. The pH of each sample was determined, and the sample was filtered ($0.45 \mu m$), acidified with HCl, and analyzed by ICP spectroscopy as described previously. When the passivation experiments were completed, the limestone surfaces were examined using a Leica Stereoscan 360 scanning electron microscope (SEM) integrated with a Fisons Delta energy dispersive X-ray spectrometer (EDS) with a 1 atmosphere, thin-window detector.

RESULTS

Bioreactor performance

The ability of the sulfate reduction bioreactor to provide a sustained H_2S yield was determined for 6 weeks before and during the treatment tests. The H_2S content of the bioreactor effluent gas averaged $0.30 \pm 0.11\%$ H_2S (vol/vol), and the H_2S production rate of the bioreactor averaged $4.3 \pm 1.6 \text{ mmol l}^{-1} \text{ d}^{-1}$ ($x \pm SD$, $n = 33$). This compares with reported rates of sulfate reduction for other bioreactors ranging from 1.25 (Ueki *et al.*, 1988) to $2229 \text{ mmol l}^{-1} \text{ d}^{-1}$ (Nielsen, 1987).

Continuous tests

A light-brown precipitate formed immediately in the precipitator when Berkeley Pit water was first contacted with effluent gas from the bioreactor. This precipitate continued to form and accumulate in the precipitator until the test concluded. As expected, elemental sulfur and sulfide sulfur [equations (3) and (4)] were the major components of the precipitate (Table 3). Copper comprised 11 to 22% of the precipitate collected from the reaction chambers

Table 3. Weight and composition of precipitates that accumulated in the reaction chambers of the countercurrent metal sulfide precipitator

Chamber ^a	Dry wt (mg)					
	S	Cu	Zn	Fe	Mn	Total
1	346	65	31	3	0.5	445.5
2	400	117	18	2	0.5	537.5
3	241	69	6	0.5	0.3	316.8
4	417	91	10	1	0.5	519.5
5	344	62	4	1	0.3	411.3
6	412	92	5	1.5	0.5	511
7	584	111	3	2.5	0.4	700.9
8	373	48	1	2	0.3	424.3

^aReaction chambers in the precipitator were labeled 1 (top; liquid inflow/gas outflow) through 9 (bottom; liquid outflow/gas inflow). Chamber 9 was not sampled.

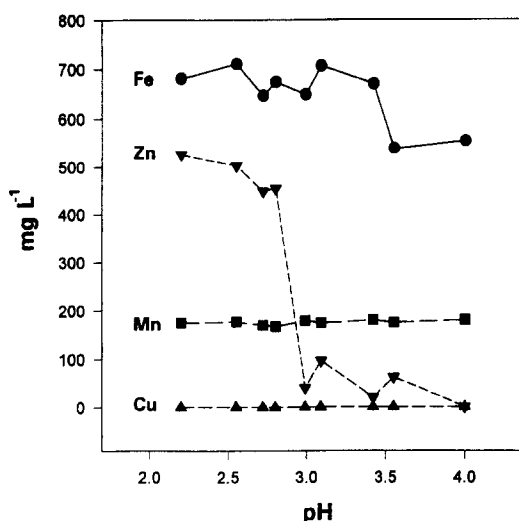


Fig. 3. Solubility of Cu, Zn, and Fe in Berkeley Pit water treated in batch tests with biogenic H_2S as a function of pH. Initial concentrations: Cu = 180 mg l^{-1} , Zn = 530 mg l^{-1} , Mn = 190 mg l^{-1} and Fe = 680 mg l^{-1} .

within the precipitator (Fig. 2). The highest Zn content (6.9%) was found in the precipitate in chamber 1, which was nearest to the inflow port for the mine drainage and contained limestone chips. The Zn content of precipitates from chambers 2 through 8 decreased with increasing distance from the inflow port. Copper, Zn, and S made up greater than 99% of the precipitate collected from each chamber.

The limestone neutralization reactor initially raised the pH of the precipitator effluent from 1.7 to about 6, but after 22 days the limestone surfaces became less reactive and were visibly coated with patches of white and black precipitate. This decrease in the acid neutralization capability of the limestone allowed low pH water to flow into the bioreactor and inhibit bacterial activity.

Analyses of the final effluent from the biogenic sulfide/limestone treatment system are shown in Table 2. Copper, Zn, and Al concentrations were always below detection limits ($<0.1 \text{ mg l}^{-1}$) in the effluent. Iron removal efficiency decreased from 99.9% early in the experiment to less than 77% after 21 days (Table 2). Similarly, Mn removal efficiency decreased from 92 to 32%, and the pH of the treated effluent decreased from approximately pH 8 early in the experiment to less than pH 5 over the same time. This decrease in system performance corresponded to the coating of limestone surfaces in the limestone neutralization reactor.

Batch tests

Batch tests were used to determine the best pH values for the selective recovery of Cu and Zn sulfide concentrates from Berkeley Pit water. Only Cu sulfide precipitated upon the addition of biogenic H_2S at the pH of raw Berkeley Pit water (Fig. 3). Significant

amounts of ZnS precipitated only when the pH was raised above 3. Likewise, some iron precipitated when the pH was greater than 3, presumably as ferric hydroxide ($\text{Fe}(\text{OH})_3$). No Mn compounds precipitated in the pH range 2.3 to 4.0.

Limestone passivation study

The conditions that existed within the neutralization reactor during continuous tests were simulated in a separate experiment to investigate the processes responsible for the passivation of the limestone surfaces. Initially, when Berkeley Pit water pretreated with biogenic H_2S was allowed to equilibrate with limestone for 24 h, its pH increased from 1.8 to 5.8 (Fig. 4, test 1). The equilibrium pH was lower in each subsequent test until the study was concluded. In the final test (test 5), the equilibrium pH was only 2.5 following 24 h of limestone contact.

Changes in dissolved Ca, Al, Si, and sulfate concentrations in Berkeley Pit water resulting from limestone contact are shown in Fig. 4. In this figure, increases in dissolved ion concentrations are shown as positive values and decreases are shown as negative values, while the zero line indicates no change. As expected, increases in Ca concentration were noted in all tests, although the amount of the Ca increase decreased in each successive test. Concentrations of dissolved Fe, Zn, and Mn remained unchanged throughout the experiment (data not shown). Sulfate was removed from solution throughout the test series, presumably via gypsum precipitation, but the quantity of sulfate removed decreased with each successive

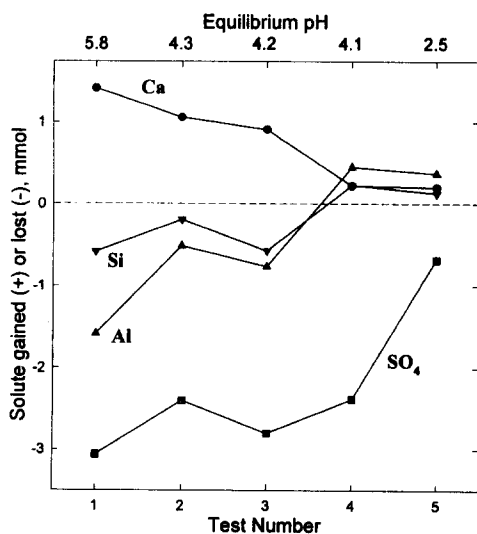


Fig. 4. Changes in the concentrations of Ca^{2+} , Al^{3+} , SiO_4^{+} and SO_4^{2-} in Berkeley Pit water treated with biogenic sulfide when contacted with limestone. For each test, a fresh 200 ml aliquot of water was allowed to equilibrate for 24 h with the same 100 g sample of limestone. Positive values represent net addition of solute to the solution; negative values indicate net loss from solution. The equilibrium pHs shown at the top of the graph indicate the final values at the completion of each test.

test. Aluminum and Si were removed from solution in tests 1 through 3, but were partly resolubilized in tests 4 and 5 as the equilibrium pH of the solution decreased (Fig. 4).

Geochemical modeling software (PC MINTQA2 V 3.10; Allison *et al.*, 1991) was used to determine the saturation indices for minerals that may have formed when the pretreated Berkeley Pit water reacted with limestone. The limestone-contacted water was found to be supersaturated with respect to $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum), CaSO_4 (anhydrite), SiO_2 (amorphous silica, quartz, chalcedony, and cristobalite), and AlOHSO_4 in all five tests. When the equilibrium pH was greater than 4 (tests 1–4, Fig. 4), the water was also found to be supersaturated with respect to $\text{AlO}(\text{OH})$ (boehmite and diaspore), $\text{Si}_2\text{O}_5\text{OH}$ (pyrophyllite), $\text{Al}_2\text{Si}_2\text{O}_5\text{OH}_4 \cdot 2\text{H}_2\text{O}$ (halloysite), $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ (kaolinite), and $\text{Ca}_2\text{Al}_4\text{Si}_8\text{O}_{24} \cdot 7\text{H}_2\text{O}$ (leonhardtite).

SEM and EDS analysis revealed that limestone surfaces contacted by pretreated Berkeley Pit water were enriched in Si, S, O, and Al compared to the untreated limestone. Distinct, but discontinuous patches of euhedral monoclinic gypsum crystals were observed in secondary electron images of the limestone surfaces. No other effort was made to determine the mineralogy of the passivated limestone surfaces.

DISCUSSION

In 1970, Pugsley *et al.* suggested that biogenic sulfide could be used to selectively recover valuable metals from mine drainage. Although conceptual schematics were drawn, this idea was apparently never tested. Later, Jenke and Diebold (1983) examined the pH-controlled dissociation of H_2S as a way to selectively recover different metal sulfides from contaminated mine waters. In their calculations, they assumed that undiluted H_2S gas would be used in the process. Assuming $P_{\text{H}_2\text{S}} \approx 1$ atm, the concentration of dissolved H_2S in solution was calculated using the following expression (Jenke and Diebold, 1983):

$$[\text{H}_2\text{S}(\text{aq})] = P_{\text{H}_2\text{S}} \beta / 22.414, \quad (5)$$

where $P_{\text{H}_2\text{S}}$ is the partial pressure of H_2S in atm and β is the Bunsen absorption coefficient (2.582 at 20°C). At $P_{\text{H}_2\text{S}} = 1$ atm, $[\text{H}_2\text{S}(\text{aq})] = 0.115$ M at saturation.

The sulfide concentration $[\text{S}^{2-}]$ at different pH values can then be determined by substituting for $[\text{H}_2\text{S}(\text{aq})]$ and $[\text{H}^+]$ in the following expression:

$$[\text{S}^{2-}] = 2.2 \times 10^{-22} [\text{H}_2\text{S}(\text{aq})] / [\text{H}^+]^2. \quad (6)$$

For a pH 2.3 mine water treated with undiluted H_2S , $[\text{S}^{2-}] = 1 \times 10^{-18}$ M. At this sulfide concentration, the treated water would be supersaturated with respect to Cu and Zn sulfides, and a combined Cu–Zn sulfide solid phase would form. Therefore, Jenke and Diebold believed that pH control would not be an effective way to precipitate Cu and Zn sulfides separ-

ately. However, they also stated that the separate precipitation of Cu and Zn sulfides might be possible if an efficient mechanism for introducing a closely controlled amount of sulfide ion could be developed. Treatment with biogenic H_2S offers such a mechanism.

The H_2S content of the bioreactor offgas used in this study was about 0.3% by volume ($P_{H_2S} = 0.003$ atm). Berkeley Pit water contacted with this gas would contain 3.4×10^{-4} M H_2S (aq), which corresponds to 3×10^{-21} M S^{2-} at pH 2.3. At this sulfide concentration, the Berkeley Pit water becomes supersaturated with respect to Cu sulfides, but remains undersaturated with respect to ZnS, FeS, and MnS (Fig. 3). Likewise, once Cu has been removed from solution and the pH has been raised to 3.5, the H_2S -treated water becomes supersaturated with respect to ZnS, but remains undersaturated with respect to MnS (Fig. 3).

The precipitation of iron in Berkeley Pit water bubbled with biogenic H_2S occurred at a lower pH than would be expected if FeS was being formed (Fig. 3). Our calculations [equation (6)] indicate that FeS saturation should not occur until the pH has reached approximately 4.9. In our experiments, the Fe was probably precipitating as ferric hydroxide in response to the pH adjustment step in the experiment, rather than as FeS. Ferric iron could conceivably be eliminated from the mine water by increasing the duration of sulfide treatment at a pH < 3 to achieve complete reduction of ferric iron to ferrous iron before ZnS precipitation.

The selective recovery of metals using a continuous, biogenic sulfide treatment process required that a separate precipitator be placed upstream from the bioreactor (Fig. 2). We originally thought that both Cu and Zn sulfides might form in this precipitator, and that the countercurrent flow of mine water and H_2S -laden gas would spatially fractionate the precipitation of the Cu and Zn sulfides. Copper and Zn sulfides did form in the precipitator, and there is some evidence that fractionation did occur (Table 3). However, the fractionation was more likely due to the pH dependent-dissociation of H_2S rather than the concentration gradients of H_2S and metals that we had hoped to establish in the precipitator. Because the pH within the precipitator was not measured, we can only speculate on its variation between the different reaction chambers. The influent pH was 2.3 and the pH probably increased when the mine water flowed over the limestone chips in the first reaction chamber. Because ZnS was found in the uppermost chambers of the precipitator (Table 3) and the mine water was not supersaturated with respect to ZnS at a pH < 2.7, the pH was probably at least 2.7 in the upper part of the precipitator. Downstream from chamber 1, the pH of the mine water would be expected to decrease as metal sulfides formed and ferric iron was reduced [equations (3) and (4)]. These reactions would lower the pH below 2.7 and prevent the formation of ZnS

in the lower chambers of the precipitator. However, the mine water was supersaturated with respect to Cu sulfides at all pH values in the precipitator, and Cu sulfide precipitates were recovered from all of the reaction chambers.

A major problem with the biogenic sulfide/limestone treatment system design was the gradual passivation of the limestone in the neutralization reactor. After this occurred, acidic water entered the bioreactor, eventually overcame the alkalinity produced by bacterial sulfate reduction, and lowered the pH in the bioreactor below the range in which sulfate reduction occurs (Postgate, 1984). Our results suggest that a number of mineral species could have contributed to the passivation of limestone surfaces. EDS analysis showed that the passivated limestone surfaces were enriched with Si, S, O, and Al, which corresponded to the Si, Al, and SO_4 missing from the Berkeley Pit water after contacting the limestone. After a 24 h equilibration with limestone, Berkeley Pit water was found to be supersaturated with respect to many Si, Al, and SO_4 -containing minerals, any of which could have been responsible for the observed passivation. Gypsum was the only mineral positively identified on the limestone surface. However, as it only occurred as discontinuous patches of euhedral crystals, it seems unlikely that gypsum was solely responsible for the observed limestone passivation.

Manganese concentrations were not expected to be lowered significantly by biogenic sulfide/limestone treatment because of the relatively high solubility of MnS. However, 91% of the Mn was removed when the effluent pH was 8. Although it is possible that some MnS may have formed, the high alkalinity of the water makes it more likely that the solution was supersaturated with respect to rhodochrosite ($MnCO_3$; Krauskopf, 1979).

The economic viability of the current approach depends on a number of variables, such as the volume of water to be treated, the volume of sludge to be disposed, the proximity of the site to hazardous waste landfills, and the availability and cost of organic substrates for bacterial sulfate reduction. Substrates other than sodium lactate, such as molasses (Maree and Strydom, 1987) and ethanol (Scheeren *et al.*, 1992), have been used successfully as carbon sources for sulfate reduction bioreactors. Certain agricultural and food processing wastes may serve as less expensive substitutes for these materials. Preliminary research indicates that materials such as spent yeast from beer breweries, dairy whey, and peach processing waste all compare well with lactate in terms of the total amount of H_2S produced by a mixed culture of sulfate-reducing bacteria (data not shown).

Another promising organic carbon source is primary sewage sludge, which is abundant and widely available. The anaerobic digestion of sewage involves the hydrolysis of insoluble organic compounds and the fermentation of some soluble organics, followed by the formation of gases by anaerobic bacteria such

as methanogens. Anaerobic digestion can generate about 20 l of biogas for every liter of sewage sludge treated (Knivett, 1960). This biogas typically consists of about 70% CH₄ and 30% CO₂, and is often burned to maintain the digester temperature between 29 and 35°C (Bailey and Ollis, 1986). Several studies indicate that the anaerobic digestion of sewage sludge is just as effective when carried out by sulfate-reducing bacteria in the presence of sulfate as it is in conventional methanogenic systems (Pipes, 1960; Burgess and Wood 1961; Knivett, 1960). Reported H₂S production rates from an inert gas-sparged digester containing sulfate and sewage sludge ranged from 25 to 78 mmol H₂S l⁻¹ day⁻¹ (Butlin *et al.*, 1956); each liter of sewage sludge used in that study could produce about 500 mmol H₂S during a 10 day residence time in an anaerobic digester.

The methane generated by anaerobic digesters is often used to maintain digesters in their optimal temperature range and provide auxiliary power for pumps. Although sulfate reduction and methanogenesis are often considered to be mutually exclusive processes, methane concentrations in gas streams from sulfate reduction-based sewage treatment systems are relatively high (Butlin *et al.*, 1956; Hilton and Archer, 1988), possibly due to the adaptation of methanogens to high concentrations of sulfide (Isa *et al.*, 1986). The observation that sludge gas from conventional anaerobic digesters is an ideal sweeping gas for H₂S (Knivett, 1960) suggests that a treatment system for mine water and sewage sludge may need to include both conventional and sulfate reduction-based sludge digesters.

For mine sites located near municipalities, it may be possible to link mine water treatment with the treatment of sewage sludge. For example, the Berkeley Pit is adjacent to the city of Butte, Montana, where the sewage treatment system serves a population of approximately 38,000 people. If the material currently processed by the Butte municipal sewage treatment plant was used solely to generate H₂S for removing Cu and Zn from the pit water, almost 7.6 million liters of Berkeley Pit water could be processed each day. The value of the Cu and Zn sulfide concentrates collected each day would total almost \$5000 at current market value, which would partially offset operating costs.

SUMMARY

The results of this feasibility study indicate that a biogenic sulfide treatment system can be used to treat water from the Berkeley Pit, given a sufficient residence time and an effective source of alkalinity. The treatment process removed more than 99% of the initial concentrations of Fe, Cu, Zn, and Al, and 91% of the initial Mn in the mine water. Copper and Zn concentrates were selectively recovered from the mine water based on the pH-dependent dissociation of the added H₂S. However, as applied in this study, lime-

stone was not an effective long-term source of alkalinity. Although limestone dissolution in the neutralization reactor initially increased the pH of the water entering the bioreactor to about 6, a passivating coating gradually formed on the limestone. The pH of the water entering the bioreactor then dropped below the optimal pH range for the activity of sulfate-reducing bacteria, decreasing the overall effectiveness of the treatment system.

Although not all aspects of this treatment system were successful, the study provided practical information that has since been incorporated into the design of systems used to treat other mine waters. For example, variation of the pH within the precipitator was found to be more effective in controlling the selective formation of different metal sulfides than was variation of the P_{H_2S} . Since this study was conducted, pH control has been used in a multi-staged precipitation process to selectively recover separate Cu and Zn sulfide concentrates from effluents of the Iron Mountain (California) and Rio Tinto (Nevada) copper mines (Hammack *et al.*, 1993; Hammack *et al.*, 1994). Limestone may still be a suitable source of alkalinity for biogenic sulfide treatment systems if it can be applied as a slurry or used in a fluidized reactor, where continual abrasion may prevent the formation of a passivating coating.

Acknowledgements—James Noll provided excellent technical assistance and generated many useful ideas during the course of this research. Don Martello (U.S. Department of Energy, Pittsburgh Energy Technology Center) did the SEM and EDS analyses of the passivated limestone.

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