THE BIOSULFIDE PROCESS: INTEGRATED BIOLOGICAL/CHEMICAL ACID MINE DRAINAGE TREATMENT - RESULTS OF LABORATORY PILOTING[1]

Michael V. Rowley, Douglas D. Warkentin, Vita T. Yan, and Beverly M. Piroshco[2]

Abstract: The need for an economically viable treatment alternative to lime neutralization of acid mine drainage (AMD) has led to the investigation of many processes, including those utilizing biological sulfate reduction. Realization of the limitations imposed by conventional sulfate reduction motivated the development of the Biosulfide process over the last six years. The Biosulfide process separates the chemical precipitation of sulfides from the biological conversion of sulfate to sulfide. Metals can be removed selectively and separately, allowing for the recovery of saleable products and the isolation of hazardous sludges. This paper concerns the evaluation of the process in a 75 hour continuous pilot run of a 100 L system at the Triton Development Corporation laboratory. The objective of this demonstration was to operate and evaluate a continuous, integrated chemical/biological AMD treatment system depending solely on microbially-generated products for stream treatment. Results are included that demonstrate the effectiveness of the process in treating a strong AMD sample (pH 2.45, 20 g/L $SO_4^{=}$, 4 g/L total metals) to strict discharge requirements while isolating metal co-products. In addition to being an effective AMD treatment method, the Biosulfide process has also demonstrated exceptional reliability and ease of operation through more than a year of uninterrupted bioreactor operation, and ten months of semi-continuous and continuous chemical stage operation in the 100 L pilot system.

Additional Key Words: acid mine drainage treatment, sulfate reduction, resource recovery, sulfide precipitation.

Introduction

In the mining industry, there is an increasing need for an economically viable and environmentally sound method of managing acid mine drainage and other sulfate-laden waste streams. This need is the result of the short-comings of the lime treatment process and the increasing trend toward more stringent, government-imposed discharge guidelines.

Conventional AMD treatment with lime produces large volumes of unstable metal hydroxides mixed with gypsum. The sludges are voluminous and costly to dispose of, especially when toxic metals content classifies it as a hazardous waste.

The application of sulfate reducing bacteria (SRB) to sulfate-containing wastes has been studied for many years in substantial detail (Barnes et al 1991, Dvorak et al 1991, Gyure et al 1990, Hammack et al 1993 and 1994, Maree et al 1986 and 1987, and Tuttle et al 1969). Conventional sulfate reduction utilizes a bioreactor where SRB grow on some form of solid support or in a sludge bed. Sulfate is metabolized according to equation 1, below. Hydrogen sulfide generated by the SRB contacts metal cations, forming insoluble metal sulfides which precipitate in the bioreactor, according to equation 2.

$$SO_4^{=} + \text{Nutrients} + H_2O \rightarrow H_2S + HCO_3^{-} \quad (1)$$

$$M^{++} + S^{=} \rightarrow MS_{(s)} \quad (2)$$

---

[1]Paper presented at the International Land Reclamation and Mine Drainage Conference and the Third International Conference on the Abatement of Acidic Drainage, Pittsburgh, PA, April 24-29, 1994.

[2]Michael V. Rowley, Process Microbiologist, Douglas D. Warkentin, Process Engineer, Vita T. Yan, Chemical Engineer, and Beverly M. Piroshco, Research Associate, Triton Development Corporation, Vancouver, BC, Canada.

Proceedings America Society of Mining and Reclamation, 1993 pp 205-213
DOI: 10.21000/JASMR94010205

Conventional sulfate reduction processes treat the entire stream in a bioreactor, resulting in significant limitations in terms of both application and effectiveness in treatment. The sensitivity of the bacterial population to low pH and high metal loading necessitates prohibitively long retention times for the treatment of highly contaminated streams. In addition, because the entire AMD stream enters biological treatment, the bioreactor is subjected to widely varying conditions of flow and feed stream strength with seasonal fluctuations, making it difficult to maintain the chemostat conditions necessary for optimum bioreactor performance. The sludge produced by conventional sulfate reduction processes also presents some problems. Firstly, sulfide sludge is precipitated in the bioreactor, which may cause problems of plugging, abrasion, and toxicity. Secondly, the sludge contains a mix of metals. Metals of concern are mixed with those of lesser concern, creating a greater volume of sludge to be classified as toxic, and incurring a greater disposal expense. The sludge also contains biomass (lost from the bioreactor) which further increases the volume of sludge for disposal. Conventional sulfate reduction processes are, however, well suited to certain specific applications, particularly those concerning the treatment of streams with low metals concentrations (Barnes et al, 1992).

Attempts to overcome the limitations inherent in conventional sulfate reduction treatment of AMD resulted in the development of the Biosulfide Process and the subsequent design, construction, and operation of a 100 L laboratory-scale pilot system. Developed over the last six years, the Biosulfide process differs from conventional sulfate reduction by the combination of the following features: 1) the biological component of the process is separated from the chemical precipitation/neutralization stage; 2) only a fraction of the stream volume, as determined by sulfide and/or alkalinity requirements, enters the bioreactors; 3) AMD treatment to discharge quality is achieved entirely with bacterially generated products, and; 4) metal concentrates, metal sludge, and biomass can be produced separately for sale or disposal.

The Biosulfide process completely separates the chemical precipitation of sulfides from the biological conversion of sulfate to hydrogen sulfide. Raw AMD enters the chemical circuit and is contacted with hydrogen sulfide generated in the biological circuit. Some fraction of the volume of treated AMD enters the biological circuit for the biologically catalyzed conversion of sulfate to sulfide. In this manner, the sulfide sludges are isolated in the chemical circuit, eliminating the problems experienced due to their build-up in the bioreactor and effectively separating them from the biomass. In addition, by operating a multi-stage chemical precipitation circuit the Biosulfide process permits metals to be removed and isolated selectively. Selective separation is achieved by pH manipulation in the reactors, as specific metals begin to precipitate as sulfides at different pH ranges. Alkalinity requirements for the stepwise pH manipulations are supplied by the biological circuit. Alkalinity is produced simultaneously in the biological conversion of sulfate to sulfide in the form of carbonate (equation 1).

The precipitation of metals as sulfides has many advantages over hydroxide precipitation. Sulfides form more rapidly, create a denser sludge, are more stable, and are less soluble than hydroxides (Bhattacharyya et al 1981, and Kim 1981). These benefits are shared by conventional sulfate reduction processes. However, by isolating the toxic fraction of the AMD stream in a sulfide sludge separate from the biomass sludge and from the metals deemed valuable, the Biosulfide process can significantly reduce the volume of sludge requiring expensive disposal. In addition, the cost of treatment can be offset or eliminated in streams with significant recoverable metals through the sale of metal sulfide concentrates to smelters. Metals readily removed as sulfides include copper, cadmium, zinc, arsenic, nickel, iron, lead, and antimony, among others. Molybdenum can also be removed in this manner, although the reaction kinetics are slower. Aluminum, which does not form a sulfide can be precipitated as an hydroxide at a pH of 4 to 4.5.

This paper summarizes the methods of Biosulfide process piloting conducted since August 1992. Piloting was conducted in a 100 L, fully integrated biological/chemical system that has been operated extensively with five different AMD samples and sulfate sources to date. In order to demonstrate and evaluate the Biosulfide process prior to on-site demonstration, the 100 L system was operated for a 75 hour continuous run treating a strong AMD sample (table 1). The objective of the 75 hour run was to treat the AMD to discharge quality using only bacterially-generated products in a stand-alone laboratory pilot system. To do this, all pH adjustment was done

with bioreactor products, and all precipitation was done with bioreactor off-gas. Data included here is from the 75 hour demonstration. Discharge requirements are listed in table 2.

Table 1. Head analysis of AMD treated.

Parameter	Units	Assay	Parameter	Units	Assay	Parameter	Units	Assay
pH	-	2.45	sulfate	mg/L	20000	Al	mg/L	1200
As	mg/L	12	Ca	mg/L	400	Cd	mg/L	2
Co	mg/L	8	Cu	mg/L	190	Fe	mg/L	2300
Mg	mg/L	1500	Mn	mg/L	313	Ni	mg/L	18
Zn	mg/L	273						

Table 2. Discharge requirements.

Parameter	Units	Value	Parameter	Units	Value	Parameter	Units	Value
pH	-	> 5.5	Cu	mg/L	< 0.05	Zn	mg/L	< 0.2

Methods and Materials

Description of Apparatus -100 L Pilot System

Overview. A Biosulfide process schematic is shown in figure 1.

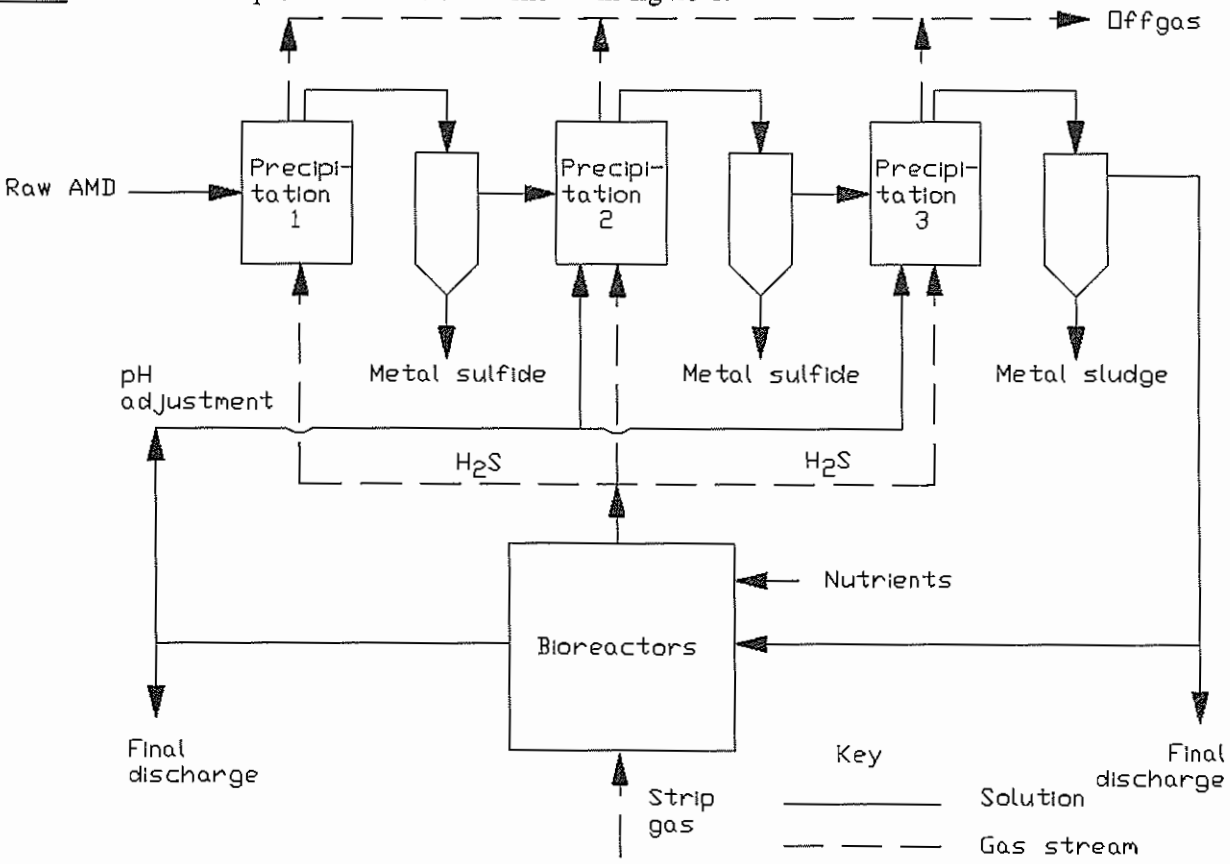

Figure 1. Biosulfide process schematic.

Chemical Stage. The chemical precipitation circuit consisted of three series-configured acrylic reactors of 6 L, 5 L, and 6 L, respectively. Each of these vessels was agitated by a magnetic stirring plate, and was followed in the circuit by a 1.5 L cylindrical glass settling vessel (thickener) with a conical base. The first precipitation reactor was pH-monitored, whereas the final two were pH-controlled at desired values. Peristaltic pumps transferred the AMD through the circuit for contacting with bioreactor off-gas.

Biological Stage. The biological stage of the pilot system consisted of two 40 L polyvinylchloride (PVC) anaerobic bioreactors developed specifically for the Biosulfide process during bioreactor comparison tests in 1990 and 1992. Solution exiting the chemical precipitation stage was mixed with nutrients (table 3) in batches of 20 to 50 L to be fed to the bioreactors. A single peristaltic pump moved solution through the series-configured bioreactor stage. Nitrogen gas travelled through the system to carry the product hydrogen sulfide to the chemical precipitation circuit. Bioreactors were maintained at 30°C with submersible heaters.

The mixed bacterial culture used throughout Biosulfide process development and piloting was originally obtained from bog water in 1988. This culture has been utilized continuously in Biosulfide development research for over six years, and has been adapted to a variety of specific operating conditions.

Table 3. Nutrient additions used in testwork.

Nutrient	Source	Addition
N	NH_4Cl	0.35 g/L
P, K	KH_2PO_4	0.06 g/L
C, H	90/10 Ethanol/Methanol	1g/g $SO_4^=$

Analyses

Dissolved sulfate was determined by turbidimetric analysis with a spectrophotometer at an absorption wavelength of 420 nm, following barium sulfate precipitation at low pH. Bioreactor off-gas analyses were performed using an SRI 8610 Gas Chromatograph equipped with a nine foot long, 1/8" O.D. teflon column packed with 100/120 mesh Hayesep D material, and a Thermal Conductivity Detector. Solid and solution samples were analyzed by ICP for trace metal concentration analysis, and by Atomic Absorption Spectrophotometry for particular metals present in high concentrations.

Results

In this section, figures and tables are presented that demonstrate the effectiveness of the Biosulfide process at AMD treatment. All results were obtained during the 75 hour continuous, integrated pilot run.

Prior to the commencement of the 75 hour continuous run the system had been operated extensively with different AMD samples and sulfate streams. The two bioreactors had been operated continuously for seven months and four months, respectively, while the precipitation circuit had been operated for shorter periods over a four month period to determine the optimum system configuration. In the week preceding the 75 hour run the bioreactors began treating pure (non-diluted) chemical stage discharge solution, and the chemical stage completed multiple shorter runs sufficient to ensure a complete change-over from previous AMD testing.

The system performed well throughout the

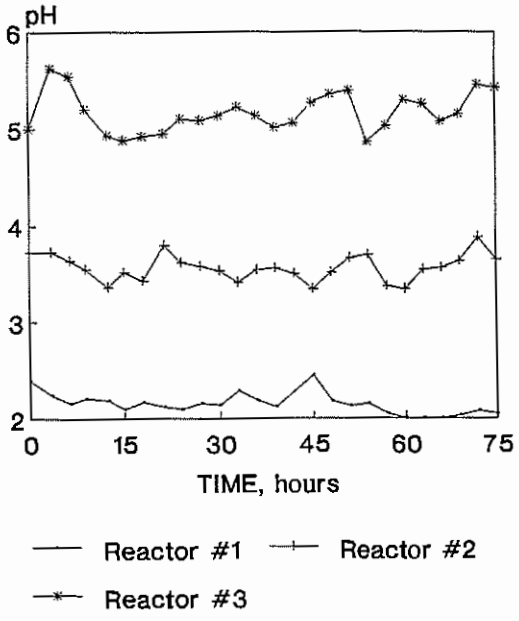

Figure 2. Chemical stage pH values during 75 hour continuous AMD treatment.

demonstration, experiencing no mechanical upsets or failures, and meeting the strict discharge requirements for the duration utilizing only microbially-generated products. As shown in figure 2, chemical stage pH values were held near the target values of 2.0, 3.5, and 5.2 in reactors one, two, and three, respectively. It is important to note that the pH of third precipitation reactor does not need to meet the discharge requirement of greater than 5.5. As shown in the process schematic (fig. 1), remaining bioreactor product solution and treated AMD are mixed to form the final discharge of the process. With this addition, the pH of Biosulfide process final discharge solution during the pilot run was consistently greater than 5.5.

Chemical stage copper, zinc, and iron concentrations are shown for the duration of the pilot run (fig. 3, 4, and 5). Together these graphs demonstrate the precipitation trends within the three-reactor chemical stage.

Prior to hour 60 of operation the formation of copper sulfide was occurring primarily in the second and third reactors, not in the first reactor as intended (fig. 3). Similarly, zinc sulfide was forming primarily in the third reactor and not in the second, as intended (fig. 4). On hour 60 the flow rate of AMD through the chemical stage was decreased (table 4). Following this change a substantial improvement in the selective precipitation of copper and zinc can be noted, with copper sulfide forming in the first precipitation reactor, and zinc sulfide in the second. Iron precipitated primarily in the third reactor for the duration of the demonstration (fig. 5). Aluminum hydroxide also precipitated primarily in the third reactor, as evidenced by the product concentrate/sludge analyses (table 5).

The composition of the final discharge solution is determined by the third precipitation reactor, as this solution forms the greatest fraction of the ultimate discharge solution. As shown in figure 1, third precipitation reactor solution is diluted with bioreactor product solution, which contains no metals.

Table 4 shows a summary of the pilot run, presenting the volumes and flow rates of AMD treated, as well as the volume of bioreactor product solution added to meet the alkalinity requirements of AMD neutralization in the chemical stage.

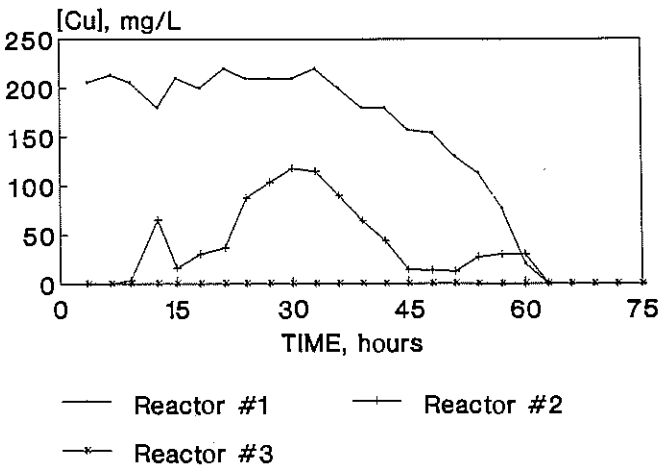

Figure 3. Chemical stage dissolved copper levels during 75 hour continuous AMD treatment.

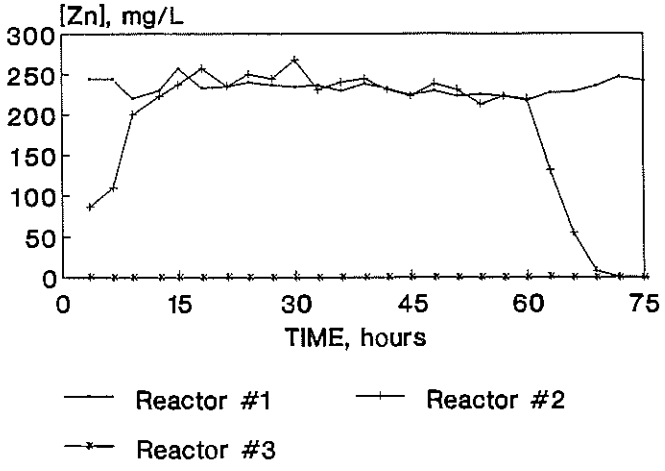

Figure 4. Chemical stage dissolved zinc levels during 75 hour continuous AMD treatment.

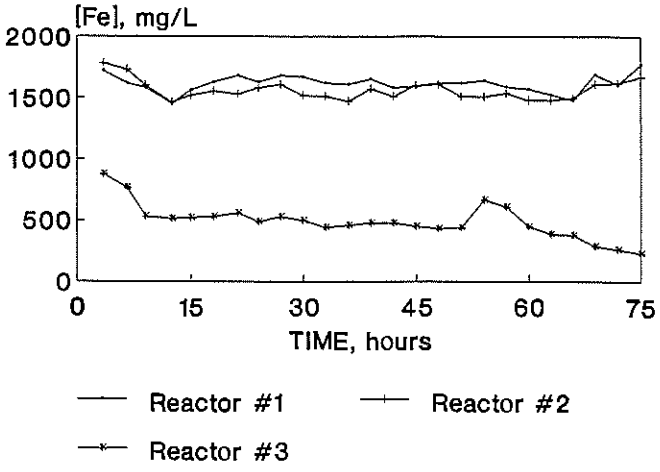

Figure 5. Chemical stage dissolved iron levels during 75 hour continuous AMD treatment.

Product precipitate grades from the final (optimum) 15 hours of operation are presented in table 5. The formation of isolated copper and zinc concentrates for sale, along with a mixed (aluminum and iron) waste sludge for disposal, is demonstrated.

As shown in table 6, bioreactor performance was reliable and consistent throughout the pilot run, maintaining an average sulfate reduction of 85 % at retention times of approximately 40 hours each. Biological data is presented from the time at which the bioreactors began feeding pure (non-diluted) chemical stage discharge on day 245 to day 255. The 75 hour run spanned days 252 to 255. Bioreactor percent sulfate reduction values presented in table 6 consider the influent and effluent sulfate of each bioreactor only and are therefore not cumulative. Overall sulfate reduction is presented in the product data section of table 6.

Table 4. Summary of 75 hour continuous operation.

Parameter, units	Hour 0 to 60	Hour 60 to 75
AMD treated, L	44.30	7.30
AMD feed rate, L/hr	0.74	0.49
Chemical stage retention, hrs	22.30	33.70
Bioreactor solution added, L	63.60	13.90
Recirculating load, %	144	190

Table 5. Precipitate analyses in %.

Residue	Al	Cu	Fe	S	Zn
Precipitation #1	-	10.0	0.24	89.8	0.06
Precipitation #2	2.5	13.1	10.70	25.8	6.18
Precipitation #3	8.5	0.3	8.95	24.9	2.11

Table 6. Biological operating data prior to and during the 75 hour pilot run.

		Days 245 to 251			Days 252 to 255		
Parameter	Units	High	Low	Average	High	Low	Average
Feed							
pH	-	6.40	6.00	6.13	6.21	6.04	6.14
rate	L/d	24.5	22.0	23.3	24.7	21.5	23.2
sulfate	mg/L	8271	6810	7482	7364	5780	6597
First bioreactor							
pH	-	5.89	5.14	5.42	5.36	5.17	5.27
sulfate	mg/L	4560	4105	4294	4830	3462	4239
sulfate reduction	%	50.4	33.0	42.0	46.6	24.2	35.5
sulfate reduction rate	mg/L/d	2457	1269	1850	2175	889	1415
retention time	hrs	42.5	38.2	40.2	43.5	37.8	40.5
Second bioreactor							
pH	-	8.30	7.67	7.94	7.84	7.44	7.63
sulfate	mg/L	1385	1167	1289	1380	268	933
sulfate reduction	%	74.4	67.2	69.8	92.3	69.5	78.6
sulfate reduction rate	mg/L/d	2085	1789	1889	2577	1890	2137
retention time	hrs	39.1	35.5	36.9	40.0	34.7	37.2
Product data							
pH	-	8.46	7.90	8.15	8.39	7.88	8.16
sulfate	mg/L	1170	757	995	1700	337	1024
overall sulfate reduction	%	90.8	84.1	86.5	94.2	75.3	84.9
off-gas hydrogen sulfide	%	4.8	1.2	3.0	3.1	2.0	2.6

Discussion

The biological stage of the system performed well throughout the duration of continuous testing, providing a reliable source of hydrogen sulfide and alkalinity for use in the chemical stage. In fact, one of the two bioreactors in the 100 L Biosulfide pilot system has been operating continuously at retention times of 21 to 44 hours for 14 months without interruption or a decline in performance. The dependability of the biological stage is a result of both the bioreactor design and the configuration of the Biosulfide process. By placing the chemical stage prior to the biological stage, the bioreactors receive an almost metal-free solution, and sulfate loading can be controlled to maintain optimum bioreactor performance.

Like the biological stage, the chemical stage performed reliably throughout the pilot run. However, it was only with a substantial reduction of chemical stage feed rate that the precipitation of sulfides occurred in the desired vessel. While not altering the effectiveness of the treatment in terms of meeting discharge requirements, the precipitation of all metals in one reactor detracted from the potential for metal recovery. Due to the rapid formation of metal sulfides observed in batch tests conducted since 1988 (Warkentin et al, 1992), it was suggested that inadequate hydrogen sulfide/AMD contacting resulted in the slowed reaction kinetics observed in the pilot run. Improvements in precipitation reactor design have been incorporated since that should bring a substantial increase in the rate of sulfide formation as well as in the efficiency of sulfide utilization.

Three product sludges were isolated from the AMD. The first two, copper and zinc sulfide concentrates, are intended to be sold to smelters to offset treatment costs during commercial-scale operation. A third sludge, intended for disposal, consisted primarily of iron, aluminum, and sulfur. A substantial reduction in disposal sludge volume is achieved by the combination of recoverable metals isolation with the benefits of sulfide precipitation over lime precipitation. The result is a higher density sludge that contains fewer of the metals present in the AMD. All sludges produced have the additional benefit that sulfides are much less prone to re-dissolution than their hydroxide counterparts, resulting in increased long-term sludge stability.

The copper and zinc grade of the product concentrates were not as high as previous batch testwork has demonstrated to be possible. This was due primarily to dilution of the precipitates by the formation of large quantities of elemental sulfur. Sulfur was formed by the reaction of sulfide and ferric iron, as shown in equation 3. In addition to diluting and increasing the volume of the product sludges, the reaction also incurs substantial losses of sulfide, placing greater demand on the bioreactors.

$$S^{=} + 2Fe^{+++} \rightarrow S^{0}_{(s)} + 2Fe^{++} \qquad (3)$$

The occurrence of this reaction was verified by the presence of ferrous iron and elemental sulfur in the precipitates. This problem could be addressed in part by utilizing 'fresh' AMD. The sample tested had been stored for approximately two months, permitting the slow, ongoing oxidation of ferrous iron to ferric to become significant. Substantial quantities of ferric hydroxide were noted in the storage drums as a result of this oxidation followed by precipitation at the pH of the AMD sample (2.45). Utilization of 'fresh' AMD (with a more favourable Fe^{++}:Fe^{+++}) would reduce sulfide losses to this reaction. Also, an additional precipitation reactor added to precede the copper precipitation reactor would convert ferric iron to ferrous prior to copper sulfide precipitation to permit the production of a higher grade copper concentrate. The additional precipitation reactor would produce a high sulfur sludge, and would necessitate the production of greater amounts of hydrogen sulfide.

Conclusions

The results of continuous Biosulfide process piloting in a 100 L system demonstrate the process to be a potential alternative to conventional AMD treatment, particularly lime treatment. A strong AMD (2.45, 20 g/L $SO_4^{=}$, 4 g/L dissolved metals) sample was treated to discharge requirements utilizing only bacterially-generated reagents in a reliable, consistent manner. Dissolved metal levels were reduced to below discharge requirements

for the duration of the run. Furthermore, metal concentrations in Biosulfide process discharge were consistently far below those of conventional lime treatment because metal sulfides are much less soluble than their hydroxide counterparts, most often by several orders of magnitude. The treatment was also successful in meeting discharge pH requirements throughout the run.

In addition to treating the stream successfully, copper and zinc sulfide concentrates were isolated to demonstrate the potential for the process to offset or eliminate operating costs through production of saleable co-products.

Throughout nearly a year of operation the 100 L Biosulfide pilot system has demonstrated remarkable reliability and consistency of performance while treating five different AMD samples and sulfate sources to date. This stability results from the two-stage nature of the treatment. The biological stage is able to maintain optimum and chemostat conditions due to separation of the bioreactors from the raw AMD. Similarly, the chemical stage is able to precipitate metals from and neutralize the stream independent of the specific operating requirements of the biological stage. With the successful conclusion of laboratory pilot demonstration, design work is underway for a 3 m^3 on-site demonstration system scheduled to commence operation in mid-1994.

Literature Cited

Barnes, L. J., F. J. Janssen, J. Sherren, J. H. Versteegh, R. O. Koch, and P. J. H. Scheeren. 1991. A new process for the microbial recovery of sulphate and heavy metals from contaminated waters extracted by a geohydrological control system. Chemical Engineering Research and Design 69:184-186.

Barnes, L. J., F. J. Janssen, P. J. H. Scheeren, J. H. Versteegh, and R. O. Koch. 1992. Simultaneous microbial removal of sulphate and heavy metals from waste water. Transactions of the Institution of Mining and Metallurgy 101:C183-C199.

Bhattacharyya, D., G. Sun, C. Sund-Hagelberg, and K. Schwitzgebel. 1981. Precipitation of heavy metals with sodium sulfide: Bench-scale and full-scale experimental results. AIChE Symposium Series 77(209):31-38.

Dvorak, D. H., H. M. Edenborn, R. S. Hedin, and P. E. McIntire. 1991. Treatment of metal-contaminated water using bacterial sulfate reduction: results from pilot-scale reactors. In Proceedings of the 1991 SME Annual Meeting. (Denver, CO, February 25-28,1991).

Gyure, R. A., A. Konopka, A. Brooks, and W. Doemel. 1990. Microbial sulfate reduction in acidic (pH 3) strip-mine lakes. FEMS Microbiology Ecology 73:193-202.
http://dx.doi.org/10.1111/j.1574-6968.1990.tb03941.x

Hammack, R. W., D. H. Dvorak, and H. M. Edenborn. 1993. The use of biogenic hydrogen sulphide to selectively recover copper and zinc from severely contaminated mine drainage. Biohydrometallurgical Technologies, Proceedings of the International Biohydrometallurgy Symposium, Jackson Hole, WY. Edited by A. E. Torma, J. E. Way, The Minerals, Metals and Materials Society. p. 631-639.

Hammack, R. W., D. H. Dvorak, and H. M. Edenborn. 1994. Selective metal recovery using biogenic hydrogen sulfide: Rio Tinto mine, Nevada. In Proceedings of the International land Reclamation and Mine Drainage Conference and the Third International Conference on the Abatement of Acidic Mine Drainage. (Pittsburgh, PA, April 24-29, 1994).

Kim, B. M. 1981. Treatment of metal containing wastewater with calcium sulfide. AIChE Symposium Series 77(209):39-48.

Maree, J. P., A. Gerber, and W. F. Strydon. 1986. A biological process for sulphate removal from industrial

effluents. Water SA 12(3):139-144.

Maree, J. P., G. Hulse, D. Dods, and C. E. Schutte. 1987. An integrated process for biological treatment of sulfate-containing industrial effluents. Journal Water Pollution Control Federation. 59 (12): 1069-1074.

Tuttle, J. H., P. R. Dugan, and C. I. Randles. 1969. Microbial sulfate reduction and its potential utility as an acid mine water pollution abatement procedure. Applied Microbiology 17(2):297-302.

Warkentin, D. D., M. V. Rowley, P. E. Elson, and P. B. Marchant. 1992. Development of the Biosulphide Process. In Proceedings of the 31st C.I.M. Conference of Metallurgists, Edmonton, Alberta, August 1992.