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USE OF SULFATE REDUCING BACTERIA IN ACID MINE DRAINAGE TREATMENT

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INTRODUCTION

The environmental impacts caused by Acid Mine Drainage (AMD) were first recorded in 1556 by Georgius Agricola. In the United States 10,000 miles of streams and 29,000 surface acres of impoundments are estimated to be seriously affected by AMD. Abandoned surface mines are estimated to contribute about 15% of the drainage, while active mines (40%) and shaft and drift mines (45%) contribute the remainder.

AMD results when metal sulfide minerals, particularly pyrite (FeS_2), come in contact with oxygen and water. Acid generation occurs when metal sulfide minerals are oxidized according to the Initiator Reaction:

$$FeS_2(\text{pyrite}) + 3\tfrac{1}{2}O_2 + H_2O \dashrightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$$

Figure 1 illustrates the pyrite oxidation cycle. This reaction is one of many that results in increased metal mobility and increased acidity (lowered pH) of the mine water. Figure 2 puts forth the oxidation of Iron Sulfides. The oxidation of ferrous sulfate is accelerated by bacterial action of Thiobacillus ferrooxidans, a naturally occurring bacterium that at pH 3.5 or less, can rapidly accelerate the conversion of dissolved Fe^{2+} (ferrous iron) to Fe^{3+} (ferric iron), and can act as an oxidant for the oxidation of pyrite. Ferric ions, as well as other metal ions, and the sulfuric acid have a deleterious influence on the biota of streams receiving AMD.

The Lilly/Orphan Boy Mine, located in the Elliston Mining District of Powell County, Montana, was selected as the Sulfate Reducing Bacteria (SRB) technology demonstration site. The mine is situated on a patented claim on Deerlodge National Forest Land about 11 miles south of Elliston, Montana. This abandoned mining operation consists of a 250-foot shaft, four horizontal workings, and some stoping. The shaft is flooded with AMD to the 74-foot level and is discharging about 3 gallons per minute (gpm) at a pH of 3.0 from the adit associated with this level. The total aluminum, arsenic cadmium, copper, manganese, iron, and zinc concentrations of the Lilly/Orphan Boy Mine Water are shown in Table 1. The pH range observed in the mine water is also presented.

METHODOLOGY

The main objective of conducting laboratory-scale tests was to determine the effectiveness of bacterial sulfate reduction in the reduction of metal concentrations at the ambient shaft water pH of 3.0 and temperature of 8°C. The temperature of the shaft water ranged from 6°C, at the portal, to 11°C, in the shaft, over a one-year period (5/93 to 7/94) during which time samples were collected from the site. This objective was facilitated by monitoring the laboratory-scale system over a period of 60 days through the collection and analysis of multiple samples, principally metals concentration in the influent and effluent waters. The sulfur cycle was observed throughout Phase 1 and Phase 2 of the pilot plant SRB experiment (Figure 3).

The experimental design of the laboratory-scale testing allowed for the comparison of two different bacterial preparation methods and three different substrate layering methods. The testing was performed at a typical shaft water temperature (8°C) and with influent water obtained from the shaft of Lilly Orphan Boy Mine one week prior to start up.

$$FeS_2(\text{pyrite}) + 3\tfrac{1}{2}O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$$

Initiator reaction

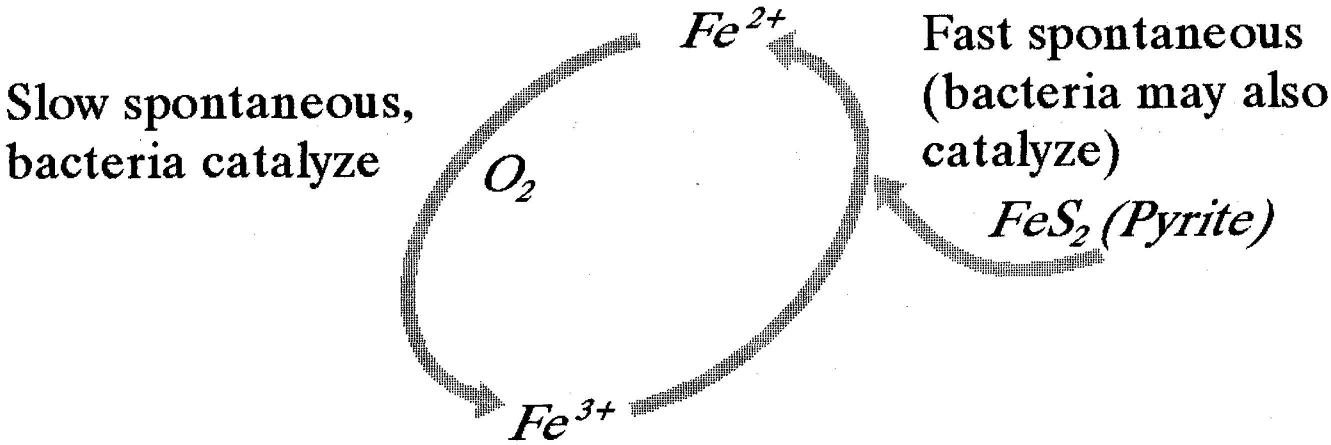

Figure 1. The Pyrite Oxidation Cycle

FERROUS SULFATE BY NON-BIOTIC OXIDATION :

$$2\,FeS_2 + 2\,H_2O + 7\,O_2 \rightarrow 2\,FeSO_4 + 2\,H_2SO_4$$

BACTERIAL OXIDATION OF FERROUS SULFATE BY Thiobacillus ferrooxidans:

$$4\,FeSO_4 + O_2 + 2H_2SO_4 \rightarrow 2\,Fe_2(SO_4)_3 + 2\,H_2O$$

FERRIC SULFATE IS REDUCED AND PYRITE OXIDIZED BY CHEMICAL REACTION :

$$Fe2(SO_4)_3 + FeS_2 \rightarrow 3\,FeSO_4 + 2\,S$$

$$2\,S + 6\,Fe_2(SO_4)_3 + 8\,H_2O \rightarrow 12\,FeSO_4 + 8\,H_2SO_4$$

ELEMENTAL SULFUR OXIDATION BY Thiobacillus thiooxidans:

$$2\,S + 3\,O_2 + 2\,H_2O \rightarrow 2\,H_2SO_4$$

Figure 2. The Oxidation of Iron Sulfides

Pilot scale testing was conducted in eight packed-bed reactors (4 foot, vertical, plexiglass columns) operated in up-flow configurations. This design was selected to closely model the actual conditions of the hydrogeologic flow of water entering the shaft via groundwater up-flowing to the adit level, and leaving the shaft through the mine adit. Eight tests were conducted in parallel. Four reactors had diameters of 14 inches while the remaining four reactors were 18 inches in diameter. The reactors were housed in a wooden, insulated, air-conditioned enclosure during the entire testing period to help maintain a temperature representative of the shaft water, nominally 8°C.

Mud from the Lilly/Orphan Boy Mine was used as a source of Sulfate Reducing Bacteria (SRB) for the pilot-scale testing. Approximately three cubic feet of mud was obtained from the portal area of the mine. In order to maintain the SRB in an anaerobic environment, the mud was placed in plastic bags within five gallon buckets until it was mixed with cow manure and decomposed woodchips to make the organic substrate that was packed into the reactors.

RESULTS

Seven of the eight pilot SRB reactors were very effective in reducing all metal concentrations from the Lilly/Orphan Boy Mine shaft water. The one reactor (using a fishnet containment system) allowed the untreated water to by-pass the substrate reactor. Water sampled in the shaft of the Lilly/Orphan Boy Mine was characterized and typical results are shown in Table 1. The Project Goals are also included in Table 1.

Table 2 shows no data for arsenic. This is because Sulfate Reducing Bacteria (SRB) were collected from mud outside the adit of the Lilly/Orphan Boy Mine. This mud contained high levels of arsenic that, when mixed with the manure, solubilized. Therefore, the data collected from the effluent were considered to be invalid measurements of the capabilities of the process in arsenic removal.

TABLE 1. LILLY/ORPHAN BOY SHAFT WATER CHEMISTRY (MG/L)

Fe	Mn	Cu	Zn	Al	Cd	As	Soluble Sulfide	SO_4^{-2}	pH
29.0	6.28	0.24	25.6	8.09	0.24	1.02	0.75	277	2.8-3.0
			GOALS:	LILLY ORPHAN BOY PILOT MINE PROJECT					
1.0	2.0	0.1	4.0	1.0	0.1	0.03	---	---	6-8

LABORATORY-SCALE TESTING

The main objective of conducting laboratory-scale tests was to determine the effectiveness of bacterial sulfate reduction in the mitigation of metal concentrations at the ambient shaft water pH (Table 1) and temperature (Nominally 8°C). The temperature of the shaft water ranged on average from 6°C, at the portal, to 11°C, in the shaft, over a one-year period (5/93 to 7/94) during which samples were collected from the site. This objective was facilitated by monitoring the laboratory-scale system over a period of 60 days through the collection and analysis of multiple samples, principally metals concentration in the influent and effluent waters.

The experimental design of the laboratory-scale testing allowed for the comparison of two different bacterial preparation methods and three different substrate layering methods. The testing was performed at a typical shaft water temperature (8°C) and with influent water having a representative pH (3.0) of the ambient shaft water.

TABLE 2. SRB TECHNOLOGY RESULTS

Measurement	Effluent (mg/L)	Change
Iron (Fe)[1]	0.17	99% reduction
Manganese (Mn)[2]	1.84	71% reduction
Copper (Cu)[3]	0.0069U	97% reduction
Zinc (Zn)[3]	0.172	99% reduction
Aluminum (Al)[1]	0.03U	99% reduction
Cadmium (Cd)[3]	0.0047U	98% reduction
Soluble Sulfide	3.12	416% increase
Sulfate (SO_4^{-2})	257	8% reduction
pH	7.6	Approximately 4.6 pH unit increase

[1]Reduction probably due to hydroxide precipitation resulting from pH increase.

[2]Reduction probably due to either carbonate precipitation or absorption.

[3]Reduction due to sulfide precipitation.

U = non-detect (the number before the "U" is the instrument detection limit).

FIELD TESTING

The field testing of the 50 ton *in situ* bioreactor is in progress and will continue until at least December 1995. The final reporting is scheduled for April 1996. The field demonstration of sulfate-reducing-bacteria technology required the placement of an organic Substrate containing the SRB at positions in the two vertical shafts and horizontal tunnel (ADIT) of the mine where the natural flow of shaft water must pass through the substrate (Figure 4). The biological action of the SRB and subsequent chemical reactions 1) reduce the amount of sulfate in the water, 2) form soluble hydrogen sulfide, 3) form metal sulfides from a reaction of the metallic ions with the hydrogen sulfide, 4) precipitate the metal sulfides within the substrate and 5) increase the pH of the effluent discharge to 7.6+.

CONCLUSIONS

Sulfate reduction was accomplished by sulfate reducing anaerobic bacteria. Sulfate-reducing bacteria decompose simple organic compounds (substrate) using sulfate as a terminal electron acceptor, thus producing soluble hydrogen sulfide and bicarbonate as metabolic products. The hydrogen sulfide reacts with dissolved heavy metals in the water to form insoluble metal sulfides. The bicarbonate has the effect of increasing pH. These two processes have the potential to greatly reduce or eliminate the problems associated with some rural remote abandoned acid generating mine sites.

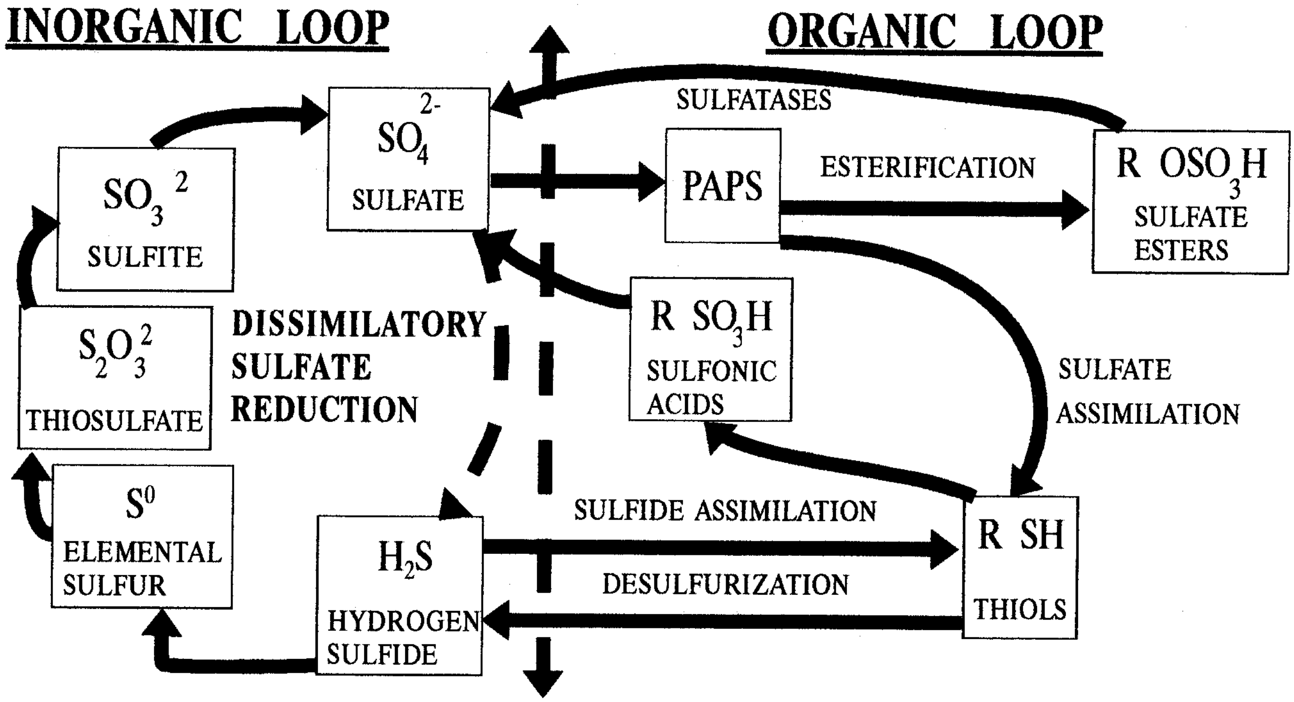

Figure 3. The Sulfur Cycle

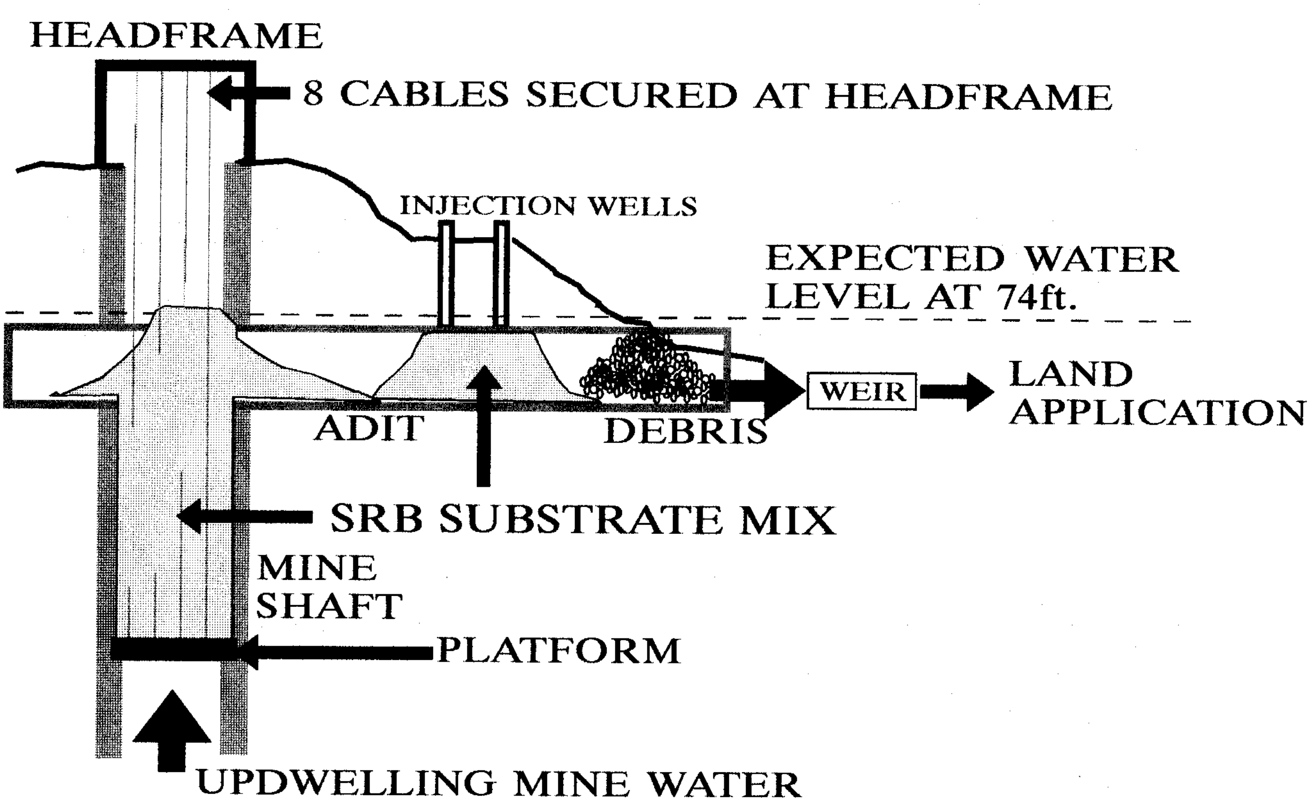

Figure 4. Lilly Orphan Boy Mine Profile

The Phase 1 (laboratory pilot plant) was successful in demonstrating the Sulfate-Reducing Bacteria (SRB) process. Metals were reduced by 90+% and the effluent discharge levels in milligrams per liter were within the project's goals in seven of the eight column reactors used in the laboratory experiment. The process worked at 8°C with a retention time of approximately 4-1/2 days.

The Phase 2 (Field demonstration of the SRB technology) required the placement of an organic substrate containing the Sulfate Reducing Bacteria (SRB) at positions in the vertical shafts and the horizontal adit of the Lilly Orphan Boy Mine where the natural flow of water was forced through the substrate. The effluent discharge criteria appears to have been met using the current data available.

REFERENCES

1. MSE, Inc. Laboratory Report for the Sulfate-Reducing Bacteria Laboratory Demonstration, Mine Waste Technology Pilot Program, Activity III, Project 3. MSE, Inc., Butte, Montana, October 1994.

2. Odom, J.M. and Singleton, R. The Sulfate-Reducing Bacteria: Contemporary Perspectives. ISBN 0-387-97865-8; ISBN 3-540-97865-8; QR92, S8585, Pages 211-249), 1992.

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