EFFECT OF BACTERICIDE TREATMENTS ON METALLIFEROUS ORE TAILINGS[1]

by

Andrew A. Sobek[2], Vijay Rastogi[3], and Mark A. Shellhorn[4]

Abstract. Three bactericides were used to treat uranium, nickel and copper tailings to determine the potential of using bactericides to control acid production in tailing piles. Ten gram samples were treated in beakers and placed in an incubation chamber set at 31°C and 98% humidity to optimize conditions for the activity of acidophilic Thiobacillus. Induced leachates taken at 14 day intervals were analyzed for total hot acidity for a period of 56 days. The initial and final leachates were analyzed for concentrations of copper, zinc, cobalt, nickel and uranium. Initial leachates from untreated samples used for controls were tested qualitatively for acidophilic Thiobacillus and developed strong positive responses. Bactericide treatments of copper tailings produced reductions in cumulative acidity by as much as 33%. Correlative decreases were witnessed in all trace metals. This study indicates similarities between biogeochemical reactions of ore tailing materials and coal waste materials; therefore, bactericidal control of acid production in ore tailing piles should be effective.

Additional Key Words: Bactericides, acid production, metalliferous ore tailings, trace metals solubility.

Introduction

Increasing quantities of tailings from ore processing, and the concern for the adverse impacts of disposal, have focused attention on the development of a safe, economical and environmentally acceptable means for disposal. Reclamation of tailing piles are severely limited by heavy metals in soil solution associated with the acidic waste, and represent potential hazards to both surface and ground-water systems (Yamamoto, 1982; Nielson and Peterson, 1972). Hydrometallurgical processes enhanced by bacterial mechanisms have allowed extraction of metals from low-grade ores, thereby increasing the amount of available mineral resources and the volume of waste associated with it (Carnahan and Lucas, 1982).

Bacterial Leaching

The iron-oxidizing bacterium, *Thiobacillus ferrooxidans*, was initially discovered in coal mine drainage where its energy for growth is derived from the oxidation of ferrous iron.

$$2FeSO_4 + 1/2\ O_2 + H_2SO_4 \longrightarrow Fe(SO_4)_3 + H_2O \qquad (1)$$

Ferric sulfate subsequently can react with metallic sulfide minerals by the general reaction

$$MS + 2Fe^{3+} \longrightarrow M^{2+} + 2Fe^{2+} + S^0 \qquad (2)$$

and in the presence of sulfate produced by metal sulfide oxidation

$$MS + 8Fe^{3+} + 4H_2O \longrightarrow M^{2+} + SO_4^{2-} + 8H^+ + 8Fe^{3+}. \qquad (3)$$

Chemical oxidation of ferrous iron is kinetically limited, but the rate can be accelerated as much as 500,000 times in the presence of iron oxidizing bacteriumn permitting the resulting ferric iron to directly oxidize metal sulfides, producing more ferrous iron (Krauskopf, 1967).

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[2]Andrew A. Sobek, Technical Manager, ProMac® Systems, The BFGoodrich Company, Brecksville, OH 44141

[3]Vijay Rastogi, Business Manager, ProMac® Systems, The BFGoodrich Company, Akron, OH 44318

[4]Mark Shellhorn, Geologist, ProMac® Systems, The BFGoodrich Company, Brecksville, OH 44141

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Increased acid concentration generated by these reactions has created an environment conducive to bacterial catalyzed metal dissolution. Bactericidal control of acid formation, recently noted in the coal industry, has prompted this investigation concerning the potential use on tailings of mineral ores. Similarities in geomicrobiology existing between coal and mineral ore waste indicate effective control of sulfuric acid production and associated trace metal solubilities could be obtained.

Copper

Copper minerals commonly found in porphry deposits consist chiefly of chalcopyrite ($CuFeS_2$) and chalcocite (Cu_2S). As these minerals are subject to chemical attack by ferric iron, associated pyritic minerals are likely to be the prime source. Reactions governing pyrite dissolutions and enhanced by bacterial mechanisms result in product necessary to establish equation 1. Oxidation of copper compounds by ferric iron producing Cu^{2+} result in competitive solubility systems where

$$14Cu^{2+} + 5FeS_2 + 12H_2O \longrightarrow 7Cu_2S + 5Fe^{2+} + 3SO_4{}^{2-} + 24H^+ \quad (4)$$

Acidity generated by both systems improved the activity of chemoautotrophic thiobacilli promoting a continuation of the cycle dependent on the oxidation of ferrous iron.

Uranium

Low temperature uranium minerals found in podiform and roll front deposits occur in a hexavalent state. Oxidized uranium (VI) transported by ground waters and precipitated as either coffinite ($USiO_4.nH_2O$) or pitch blend (uranite, UO_2) can be solubilized by ferric iron.

$$UO_2 + Fe_2(SO_4)_3 \longrightarrow UO_2SO_4 + 2FeSO_4 \quad (5)$$

Bacterial activity accelerating the production of ferric iron can directly cycle this reaction through both pyritic supplied ferrous iron and ferrous iron generated by the competitive solubility system established in equation 5.

Nickel

Nickel sulfide minerals occur in greatest concentration in ultramafic rocks and to a lesser extent as laterite deposits. In either type of deposit, iron is a common associate providing a system of oxidation and bacterial catalyzation similar to that described for copper. In mineral form, it commonly occurs as pentlandite $(Fe, Ni)_9S_8$.

Methods

Samples of tailings from copper, uranium and nickel mineral ores were obtained to test the potential use of bacterial inhibitors. Each sample was submitted for sulfur fraction determination, a qualitative bacterial assessment in 9K media, and batch incubation testing (Lacey and Lawson, 1970). Qualitative bacterial assessments were made using leachates from 2:1 dilutions. Remaining portions of these leachates were concentrated by evaporation and analyzed for trace metals by x-ray fluorescence (XRF).

Batch incubation testing was done using ten-gram samples of each material. Control and treated samples were placed in an incubation chamber set at 30°C and 98% humidity to optimize bacterial activity. Samples taken at 14-day intervals and extracted with 100ml of distilled and deionized water, were analyzed for total hot acidity and trace metals (Shellhorn and Rastogi, 1984). The study was continued for a period of 56 days. Trace metals of initial and final leachates were determined using atomic absorption spectroscopy.

Results

Sulfur fraction determinations were performed on all three materials to assess the potential available pyritic sulfur and resultant ferrous iron. Table I illustrates the level of various sulfur forms for each material in which the levels of pyritic sulfur by decreasing amounts are copper, nickel and uranium, respectively.

TABLE I: Sulfur Fraction Determinations

Sample	Pyritic Sulfur %	Sulfate Sulfur %	Organic Sulfur %	Total Sulfur %
Copper	47.500	0.400	0.810	48.700
Nickel	5.430	2.310	3.160	10.900
Uranium	0.321	0.992	0.017	1.330

Ore tailings were extracted with water in 1:1 ratio and qualitative bacterial assessments were established by using 1:10::leachate:9K media (a ferrous iron rich medium) dilutions. Five replicates of each sample were tested, resulting in positive scores for copper and uranium leachates only. Visual observations indicated a much stronger positive response for the copper leachates compared to the uranium sample.

Five-hundred mililiters of leachate derived from a 1:1::water:soil extraction of each sample were evaporated, producing a solid residue that was analyzed by XRF for a total metal scan. Table II shows the results of this scan and delineates those metals to be monitored in batch incubation testing for each material.

Figures 1-3 represent acidity data obtained from eight weeks of incubation testing for tailing samples of copper, uranium and nickel ores, respectively. As the data represent separate samples from each incubation period,

TABLE II: XRF Metal Scan on Leachates of Mineral Ore Tailings

Tailings	Metals
Copper	Ba, Cd, Sr, As, Zn, Ni, Cu,Co, Fe, Mn, Ti, Ca, Sn, K, Cl, La, S, Si, Al, Mg, Na, F
Nickel	Zr, Br, Ti, Cu, Fe, Ni, Ca, K, Cl, S, Ba
Uranium	Sb, Mo, U, La, Zr, Se, As, Zn, Cu, Ni, Fe, Mn, V, Ce, Ti, Cs, Ca, K, Cl, S, Si, Al, Mg, Na

the results are cumulative and should be compensated for by adjusting to a time zero baseline.

Data trends established in Figure 1 indicate that subsequent to four weeks of incubation, acid production was minimal. A final reduction in acidity at week eight of >50% averaged for the treated samples was obtained.

Induced leachates from uranium tailings (Figure 2) suggested an immediate response to the bactericides was obtained, evidenced by 70% reduction in acid production at the second week of incubation. However, trends established through week eight indicate a return towards control level acidity values. In contrast, results on nickel tailings (Figure 3) indicate no reductions in acid production by any of the treatments were obtained during the test period.

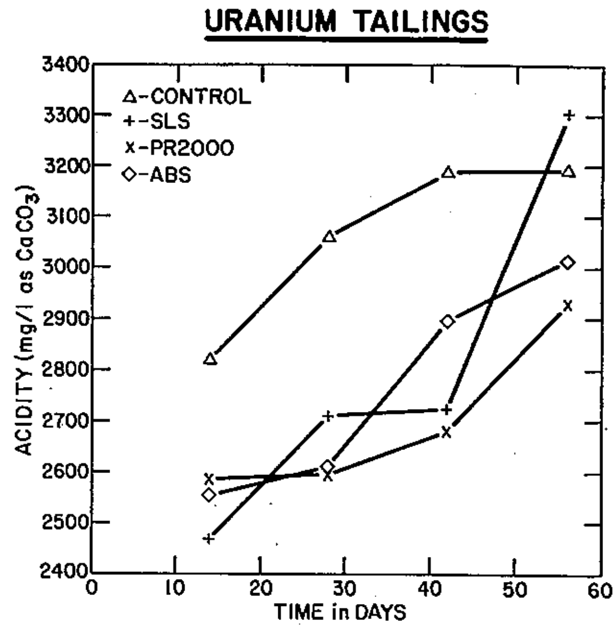

Figure 2. Eight-week acidity determination from incubation testing of uranium tailings. Data points represent average of three analyses of each treatment each incubation period.

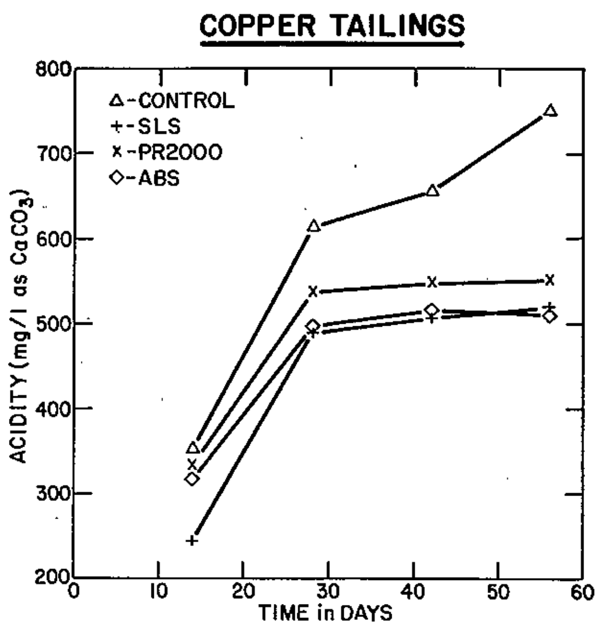

Figure 1. Eight-week acidity determination from incubation testing of copper tailings. Data points represent averages of three analyses of each treatment each incubation period.

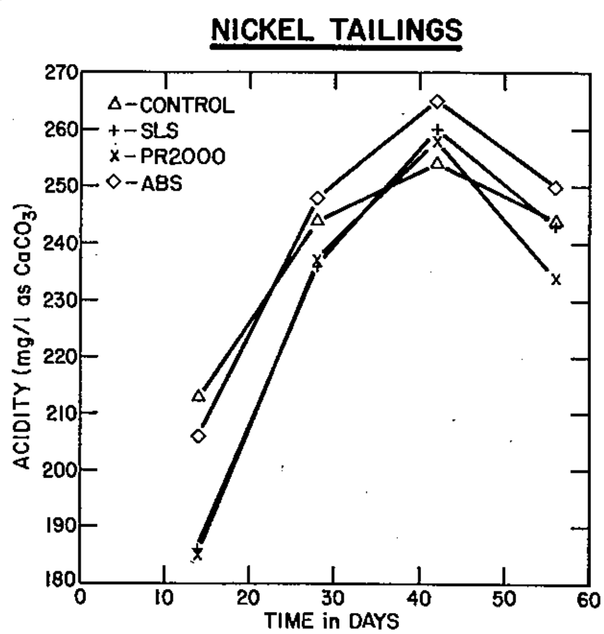

Figure 3. Eight-week acidity determination from incubation testing of nickel tailings. Data points represent average of three analyses of each treatment each incubation period.

Trace Metals

Determination of trace metals outlined in Table II were made at the last incubation period to compare treatments against controls. Results indicate that treatments on copper tailings alone produced significant reductions in trace metals. Table III illustrates trace element concentrations determined after 56 days of incubation.

TABLE III: Mean Metal Concentration for Copper Tailing Leachates

Sample	Cu mg/L	Zn mg/L	Co mg/L	Ca mg/L
Control	15	196	43	159
SLS	7	117	37	152
PR2000	3	114	33	135
ABS	3	110	8	144

Results obtained on uranium and nickel leachates contrast those determined for copper in that little or no significant variations were established.

Discussion

Acidified ferric ion solutions are effective lixiviants for many metals of sulfide and oxide ores. On this basis, the copper ore tailings possessing the highest pyritic sulfur level would be expected to produce the most acidity. Data presented in Figures 1-3 contradict this prediction, showing a significantly higher level of acidity for uranium ore samples. Nickel tailing leachates produced acidity levels at rates relative to uranium and copper tailings in agreement with pyritic sulfur analysis.

Batch incubation data by itself shows that significant inhibition of iron-oxidation and subsequent pyrite oxidation and acid formation were witnessed only for copper ore tailings. The lack of a positive bacterial response for nickel leachates suggests that inorganic kinetics were governing the pyritic oxidation. However, uranium tailing leachates exhibiting strong positive bacterial responses produced minimal levels of acid inhibition during interim incubation periods. High baseline acidities for this material may generate potential acid hydrolysis of the bactericide solutions producing limited effects. Trace metal determinations support the conclusions drawn from acidity data showing that significant ferrous-ferric solutions enhanced by acidophillic thiobacillus are prominent only in the copper and uranium tailings. Preliminary column leaching tests on uranium tailings indicate that sequential flushing removed a stored mass of oxidation products. Bactericide treated columns respond as expected showing acid production inhibited as much as 50% with a control level intermediate to that produced in copper and nickel columns. The initial results from this work are consistent with that predicted from sulfur fraction data with exception to nickel tailings. It appears that the nickel materials have not acidified to a level favorable for bacterial activity.

Conclusions

Direct and indirect leaching of pyrite by bacterial mechanisms and the resultant impact on the solubility of trace metals has been utilized throughout the history of metal sulfide ore mining. Bactericidal control of acidophilic thiobacillus was demonstrated to be effective by reducing acid production in ore tailings where bacterial mechanisms played a significant role. Associated trace metals were reduced non-uniformly to the levels of acid inhibition. Copper tailing incubation data and preliminary uranium column leaching results indicate that bactericidal control of acid production is feasible and should have a positive impact in tailing reclamation and the quality of discharge water.

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