THE USE OF MICROENCAPSULATION TO PREVENT ACID ROCK DRAINAGE[1]

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Abstract: Two commercial microencapsulation products were tested for their ability to coat unoxidized pyrite and prevent oxidation. EcoBond-ARD™, a phosphate based compound and KEECO KB-SEA™, a silica based product, were each applied to an unoxidized acid generating rock. Each company selected three application rates; low, optimum and high. Humidity cell testing has been conducted for 318 weeks. Untreated rock (controls) produced drainage below pH 6.0 after 1 week and pH stabilized at about 3.3 after 60 weeks. EcoBond-ARD™ delayed the onset of acidification but was not successful in preventing acid drainage; pH decreased to below 6 after 12-16 weeks. These cells were terminated after 59 weeks when the pH was essentially the same as the controls. KB-SEA™ initially prevented acid drainage at all levels of treatment, but pH was around 12. Although pH decreased, the pH in the 5% treatment was consistently above 9 for about 75 weeks. Sulfide oxidation rate was about 10% of the controls. The pH for the low application rate (1%) declined below 6.5 at 168 weeks and treatment essentially stopped after about 200 weeks when pH dropped below 5. The pH in the 3 and 5% treatments remain neutral at 7.5 and 7.8 respectively. The treatment mechanism has not yet been determined. Possible explanations include: high pH, due to the presence of lime in the product, cementation of the material, resulting in a macro encapsulation of the rock grains, and microencapsulation of the surfaces with silica. Microscopic evaluation of samples did not clearly identify a mechanism. Silica was generally present along the edge of the pyrite crystals but oxygen penetration had still occurred. These cells are being continued to assess long-term treatment effectiveness. The treatment will be considered effective as long as the pH remains above 6.0. Additional work to determine the mechanism and cost should be conducted.

Introduction

Successful management of the environmental impacts of mine waste has become a major issue in new mine development and is an essential element of procuring both a ‘legal’ and ‘social’ license to operate. Accordingly, operational and reclamation plans must include provisions to prevent, control or treat any poor quality water that could be produced at the site.

In mining, as with most industries, not all the raw material ends up as saleable product. “Average" figures for Canadian metal mines indicate that 42% of mined material is rejected as waste rock, a further 52% leaves the mill as tailings and 4% exits the smelter as slag; the valuable product represents just 2% of the originally mined tonnage (Boldt, 1967; Godin, 1991). Consequently, many operations are as much about waste disposal as they are about resource extraction.

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Waste disposal results in direct physical impacts on the disposal site but the presence of potentially harmful contaminants in the waste influences the spatial extent and duration of overall environmental impacts. Contaminants can disperse into and degrade surface and groundwater, spread via windblown dusts and cause ecosystem impacts on land and in the water environment. A well-documented example of a mine waste-related impact with significant spatial and duration aspects is acid rock drainage (ARD).

ARD results when pyrite (FeS_2), marcasite (FeS_2) and pyrrhotite (FeS_{1-x}) – common mine waste contaminants at non-ferrous mines – are exposed to oxygen and water, generating sulfuric acid, ferrous iron (Fe^{2+}) and ferric iron (Fe^{3+}), often in the presence of catalyzing bacteria. Ferric iron is a powerful oxidizing agent, and oxidizes insoluble metal sulfides (also often present in mine waste) to water-soluble sulfates, which may then disperse in the acidic water. Other minerals present in the ore may also dissolve on contact with the ARD, further increasing the concentration of potentially harmful metals. Once acid generation begins, it may continue for hundreds of years. Despite extensive waste characterization and modeling to predict the potential for ARD generation, unexpected and uncontrolled releases do still occur.

In general, "end-of-pipe" (remedial) approaches dominate the management of mine waste, such as the use of cover materials, underwater disposal and long-term collection and treatment. The first two options rely on the long-term prevention of contact between water and / or oxygen and the sulfide bearing mine waste at a macro-scale during operation and following closure. This requires a long-term commitment from the mine operator or other responsible party. Failure to meet this commitment may result in the costly third option – long-term collection and treatment of ARD. Consequently, the current methods of dealing with mine waste are not 'walk-away' solutions.

New proactive methods of preventing acid generation are needed to complement the existing approaches and enhance the mining industry's capacity to meet the various expectations of its large (and vocal) stakeholder community. One promising approach changes the focus from the 'macro-level' to the 'micro-level', by coating reactive mine waste particles and isolating them from the oxidizing agents (i.e. O_2, Fe^{3+}) that cause ARD. This process is often called microencapsulation and reasonably successful coatings were reported in laboratory studies using phosphates (Evangelou, 1994; Georgopoulou et al., 1995; Roy and Worral, 1999), silicates (Zhang and Evangelou, 1998; Fytas *et al.*, 1999), and various organic materials (Adams *et al.*, 1994; Moskalyk, 1995)).

Rather than focus on fundamental research, this study examined the performance of two proprietary products that were commercially available at the outset of the project. These were a silica-based compound originally produced by Klean Earth Environmental Company (KEECO[4]), and a phosphate-based compound produced by Metals Treatment Technologies, LLC (MT2[5]).

Objectives

The investigation was designed to undertake a long-term evaluation of the two compounds' ability to prevent acid generation from mine waste and to evaluate different application rates and treatment lifetime. To date the investigation has been running for 318 weeks (just over 6 years) and monitoring is ongoing.

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[4] KEECO became bankrupt in 2003.

[5] See www.metalsst.com for further information on the company.

Approach

In order to determine the effectiveness of the microencapsulation products to prevent acid drainage, a laboratory investigation using humidity cells was conducted. In consultation with KEECO and MT2 staff, three appropriate chemical application rates were defined, comprising ‘low’, ‘recommended optimum’ and ‘high’ rates. This spread of rates enabled dose-response trends to be determined and the consequences of under- or over-dosing to be assessed.

Methods

Materials

The unoxidized mine waste was rock from the Archean metavolcanics and metasedimentary formations, or greenstone belts, collected at Soudan State Park in northern Minnesota. The sample was crushed using a stage crushing process to a target size range of 0.021-0.64 cm (smaller than typical waste rock generated during mining due to the limited laboratory humidity cell size). The proprietary compounds were KB-SEA^{TM} (KEECO) and EcoBond-ARD^{TM} (MT2).

Solid Phase Analyses

Rock samples were analyzed for total sulfur, sulfate, and sulfide (determined by difference) and evolved carbon dioxide, using ASTM E-1915-97 (ASTM, 2000). A 10% hydrochloric acid solution was used to solubilize the carbonate minerals; carbonate was defined as total carbon in the initial sample minus that in the residue. Whole rock constituents were determined using a lithium tetraborate fusion modified from ASTM E886-94 (ASTM, 2000) and analysis by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Concentrations of Ag, Cd, Cu, Ni, Pb, Zn, and Bi were determined using a total digestion modified from Crock *et al*. (1983), with analysis by ICP-AES.

Experimental Procedure

Humidity cells were filled with 1000 g of rock, added in increments of approximately 250 g. The solids were rinsed daily for 3 days to remove any oxidation products generated between crushing and the beginning of the experiment. The outlet port was then closed and 500 mL of distilled water was slowly added to each cell, allowed to sit for ten minutes and then drained. Drainage samples were weighed and analyzed for pH and specific conductance, then filtered for determination of sulfate and metals. A sixty-eight parameter ICP-MS scan was conducted on a composite of the three initial rinses for each cell.

Applications (by weight) for the microencapsulation chemicals were 1% (‘low’), 3% (‘recommended’) and 5% (‘high’) for KB-SEA^{TM} and 1.5% (‘low’), 3.0% (‘recommended’) and 4.5% (‘high’) for the MT2 product. The encapsulation products were added to each cell by closing the outlet and flooding with water containing the appropriate amount of the proprietary chemical. After 10 minutes, the outlet on each cell was opened and the treatment solution drained. Two cells were left untreated as controls against which the performance of the proprietary products could be measured. The cells were then placed in a constant temperature and humidity room for a week before the start of the experiment

Drainage Quality Sampling

The cells were rinsed weekly using the initial rinse procedure with the exception that the rinse water was added as a slow drip. Effluent samples were collected and analyzed for pH, specific conductance and alkalinity. Samples were analyzed at weeks 1, 2, 3, 4, 6, 8, 10, 12, 14, 16, 18, 20 and 24, and at 4-week intervals thereafter. Through week 8, effluents were analyzed for sulfate, Ca, Mg, Na, K, Fe, Cu, Ni, Co and Zn. Subsequently; the effluents were analyzed for SO_4, Ca, Mg and Fe by MDA. Additional selected samples for EcoBond-ARD^{TM} treated cells were analyzed for total phosphate, orthophosphate and arsenic. A sixty-eight parameter ICP-MS scan was also conducted on the week 1 samples.

Between rinses the samples were retained in the cells to oxidize. The cells were stored at a controlled temperature and humidity. Temperature was 22.2-27.5^{o}C (average 24.5^{o}C; standard deviation (SD) 1.2^{o}C) and relative humidity was 51.3-63.5% (average 57.3; SD 1.8%).

Microscope Observations

An unleached cell treated with 3% KB-SEA^{TM} (the 'recommended' dose) was dismantled to provide samples for microscopic evaluation. During this process, samples were examined with an optical microscope and analyses were undertaken with a JEOL Electron Probe Microanalyzer. Sulfide mineral grains were handpicked from samples, and embedded in an epoxy mount, polished and carbon coated.

A number of sulfide mineral grains were analyzed to show the compositional variation at the outer edge of the grain. For each sulfide grain analyzed, a backscattered electron image was used to document the location of analysis points. A line analysis was made from the inner portion of the sulfide grain, across its outer edge and into the surrounding epoxy. Elements analyzed included Fe, S and the known components of the commercial products. The purpose of these line profiles was to show the degree of oxidation at the interface, and the degree to which the commercial product was still coating the surface.

Results

Solid-Phase Analyses

Total sulfur averaged 2.04% and ranged from 1.55-2.45%. About 98% of the sulfur was present as sulfide. Evolved CO_2 measurements were very low and indicated the near total absence of carbonate (values ranged from <0.05% to 0.11%). The major elements in the mine waste were silica (73.4% SiO_2), aluminum (8.7% Al_2O_3) and iron (8.6% Fe_2O_3). Although detailed mineralogy was not conducted, mineralogical analyses of other samples from the area have shown that the major minerals present are quartz (SiO_2), sericite ($KAl_2Si_3O_{10}(OH_2)$) and chlorite (a complex Mg, Al, Fe silicate) (Lapakko *et al.*, 2002). Since this material was not associated with any ore body, the trace metal content was low. Chromium was present in the highest concentration (226 mg kg^{-1}), followed by Zn (102 mg kg^{-1}). Acid production potential (APP) was calculated from the average sulfide content (2%) to be 62.5 kg $CaCO_3$ equivalents per metric ton. The average neutralization potential (determined using the Sobek procedure and back titrating to an endpoint of 8.3) was 5.5 kg $CaCO_3$ per metric ton.

EcoBond-ARD^{TM} dissolved completely and was very easy to apply. There was no evidence of preferential flow or uneven application following draining of the cells. KB-SEA^{TM} was applied with more difficulty as a slurry. Although the material in the cell appeared to wet completely, the solid portion of the treatment chemical was not evenly distributed. Material accumulated on the top and in layers in various parts of the cells. Visible material increased with increased application rate.

Drainage Quality

Results from the beginning of the experiment through week 318 are presented for the controls and the cells treated with KB-SEA^{TM}. Cells treated with EcoBond-ARD^{TM} were stopped after 60 weeks since the product failed to prevent the generation of acid drainage.

pH

The initial pH in the control cells varied from 5.6-6.54 but decreased quickly and was <4 after 10 weeks and stabilized at about 3.3 after 19 weeks time (Figure 1). The initial pH from all the cells treated with KB-SEA^{TM} was 12 or greater. The pH declined slowly and the rate of decrease was related to the application rate. In the cells treated with 1%, pH declined to below 10 after 5 weeks, while in cells treated with 5%, the pH did not remain consistently below 10 until week 34. The pH continued to decrease in all the KB-SEA^{TM} reactors. By week 140, the pH in the reactors treated with 1% KB-SEA^{TM} dropped to <7 and continued to decrease to the present value of around 4. While somewhat higher than the drainage pH for the control cells, the 1% treatment failed to control sulfidic oxidation and the generation of acidity. The pH was higher in the reactors treated with 3% and 5% KB-SEA^{TM}. In the reactor treated with 3%, the pH leveled out at about 8 at week 80 and has remained around that level through week 318 (Figure 1). It took about 75 weeks for the pH from the reactors treated with 5% product to decrease to <9. The pH stabilized at around 8 after week 200 (marginally higher than drainage from the 3% cells).

Initial pH from the cells treated with EcoBond-ARD^{TM} ranged from 8.4 to 9.06. The pH decreased in all treated cells with time and the decrease was independent of application rate. The pH dropped to <6 after 12-13 weeks, and was generally <4 after 27-31 weeks. At week 60, when the cells were stopped, the pH in all the treated cells was within about 0.2 pH units of the untreated controls (Figure 1).

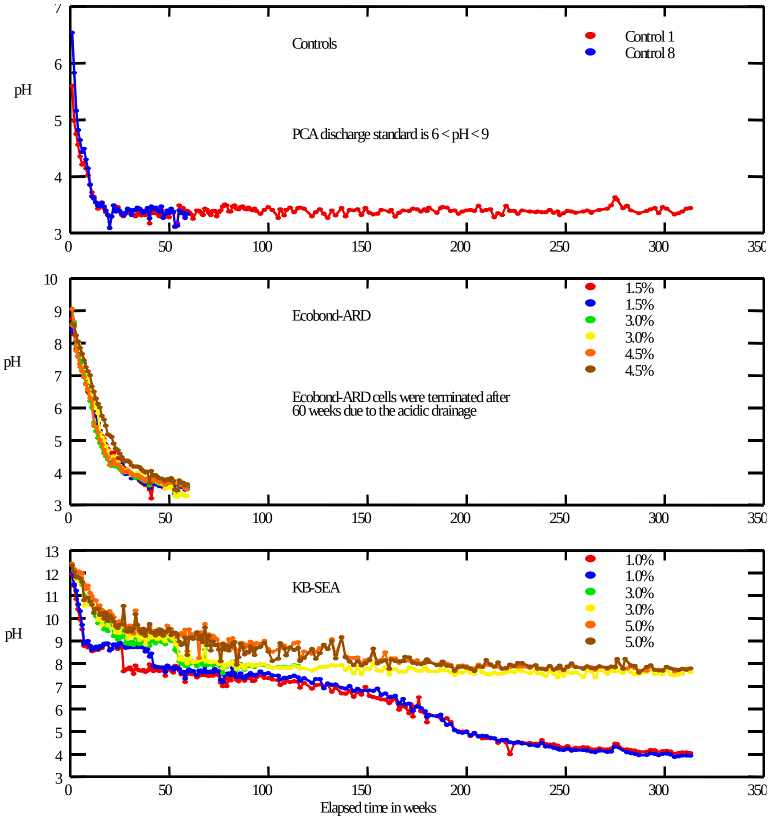

Figure 1: Drainage quality- pH vs. time

Sulfate

Sulfate concentrations in the control cells decreased after the initial rinse to around 60 mg L^{-1} but increased sharply after week 10, when the pH dropped below 4. Concentrations peaked between 180-200 mg L^{-1} during weeks 12-14, and then decreased to about 130 mg L^{-1}. Concentrations slowly decreased to around 100 mg L^{-1} at week 60, and continued to decrease with time until it stabilized at around 70 mg L^{-1} at week 168 (Figure 2).

Cells treated with KB-SEA^{TM} produced drainage with sulfate concentrations lower than the controls, and sulfate concentrations tended to decrease with increasing application rates, particularly during the first 12 weeks. In the 1% cells, sulfate concentrations ranged from 36-108 mg L^{-1}, but dropped to <10 mg L^{-1} after week 20. At week 60, sulfate concentrations were around 7 mg L^{-1}. Concentrations have continued to increase slightly since week 60, to above 25-30 mg L^{-1} by week 318. At the higher application rates, the initial concentrations were lower but decreased less quickly than the 1% cells. At week 60, the sulfate concentration in these cells was around 10 mg L^{-1}, and concentrations continued to slowly decrease (Figure 2). At week 160, concentrations ranged from around 2.5 mg L^{-1} for the 3% treatment to about 6 mg L^{-1} for the 5% treatment (Figure 2). By week 318 the difference between sulfate concentrations for 3% and 5% treatments was marginal, with concentrations typically <5 mg L^{-1}.

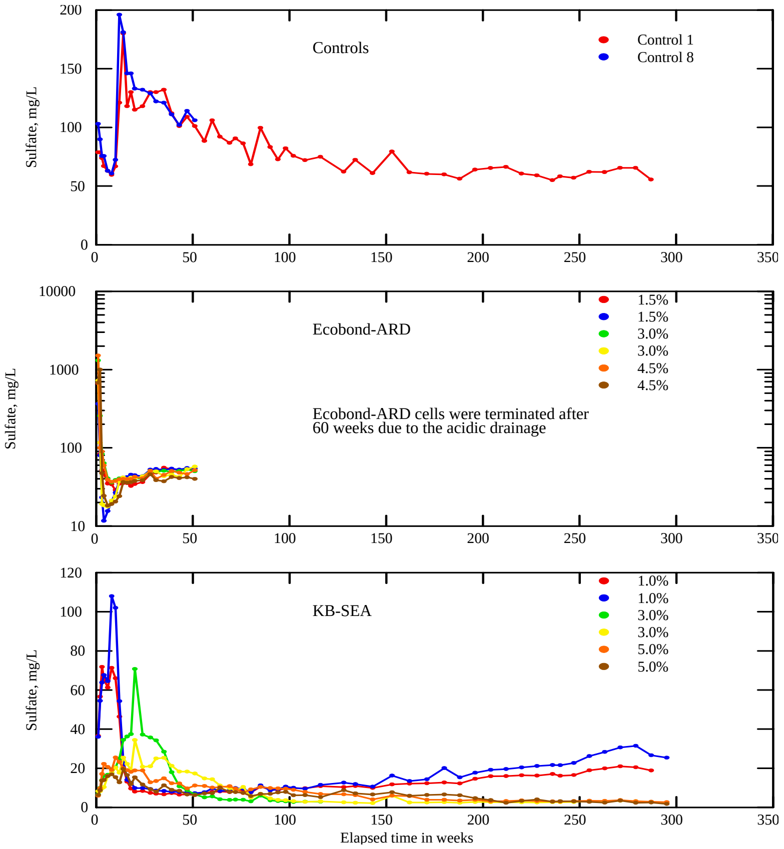

Figure 2: Drainage quality-sulfate vs. time

In the cells treated with EcoBond-ARD™ the sulfate concentrations varied by a factor of two between duplicate cells, with concentration increasing with application rate. The maximum concentration of 1510 mg L^{-1} occurred at the experiment's beginning, and then dropped rapidly, with sulfate in all cells decreasing to around 40 mg L^{-1} by week 14. Sulfate remained relatively constant throughout the remainder of the experiment. Average sulfate concentrations ranged from 41 to 52 mg L^{-1} in weeks 20-59, less than half that in the control.

Other Parameters

Trace metals were analyzed during the first ten weeks of the experiment. Concentrations in the treated cells were generally low and tended to decrease with time (Eger *et al*, 2004). Arsenic and phosphorus were elevated in the initial samples from the cells treated with EcoBond-ARD™. Arsenic was elevated in all cells and ranged from about 0.4 to 0.8 mg $L^{-1}$and did not drop below 0.05 mg L^{-1}until after week 4. By week 4 the other trace metals had decreased to below the detection limit of 0.002 mg L^{-1}. Phosphorus concentrations in the control were very low, initially ranging from 0.01-0.02 mg L^{-1} and dropping below the detection limit (0.01 mg L^{-1}) by week 10. In cells treated with EcoBond-ARD™, phosphorus concentrations were elevated during the initial part of the experiment with almost all of the phosphorus in the ortho (biologically available) form. Initial phosphorus concentrations were extremely high and ranged from around 1300 to 3900 mg L^{-1}. Although phosphorus concentration decreased rapidly, concentrations did not decrease below 0.03 mg L^{-1} until after week 14.

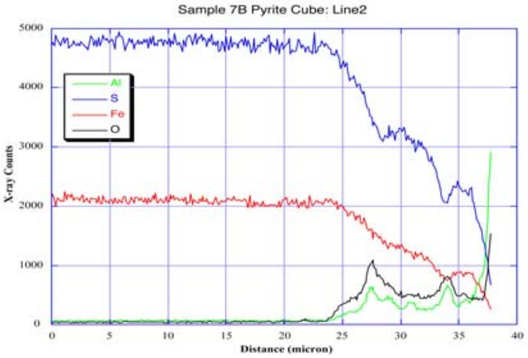

Figure 3: Microprobe results, pyrite crystal, unleached KB-SEA reactor

Microscope Evaluation

Unleached Samples – KB-SEA™

A rock fragment with a visible coating of KB-SEA™ was selected to determine the general properties of the product. The coating contained a rounded "bead-like" structure (mostly Si, Al, and Ca), angular mineral fragments (quartz grains), and acicular (needle-like) grains (a Si, Al, Ca phase).

Several pyrite cubes were examined to determine the action of KB-SEA^{TM} at the sulfide surface. The first surface had product "beads" on the outside of the surface and a "transitional zone" at the surface of the pyrite. In the transition zone (~ 15 microns), Ca and Si were mixed with S (Figures 3, 4).

Additional analyses of other surfaces did not show this type of transition zone. Although chemical product was observed on most surfaces, possible interaction zones were much smaller (2-3 microns).

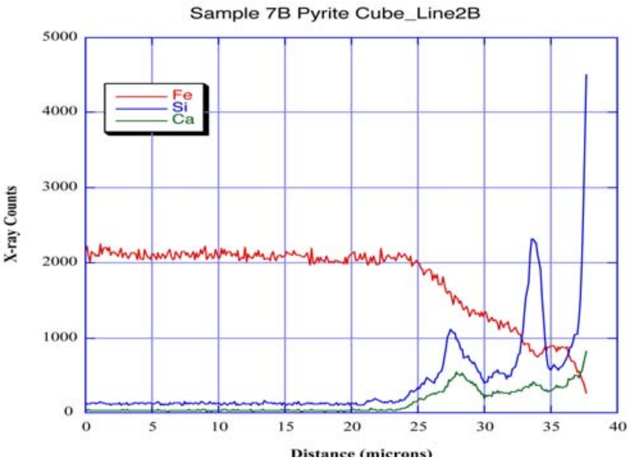

Figure 4: Microprobe results, pyrite crystal, unleached KB-SEA^{TM} reactor

The product was also observed as a coating on other rock fragments including quartz mineral grains. This indicated that the product had coated other mineral phases, even though it may not have actually chemically reacted with them.

Leached Samples – KB-SEA^{TM}

Several sites on five different pyrite grains were selected for microprobe analyses. Some of the sites had obvious zones of oxidation, while others had none. On oxidized grains, analysis revealed that oxygen had diffused into the pyrite to a depth of about 2-15 microns. Some surfaces contained an abundance of S in this oxidized zone (Figures 5,6); others contained only minimal amounts. Silica was generally present along the edge of the crystal indicating the presence of the KB-SEA^{TM} coating. However, oxygen penetration and reaction zone thickness did not appear to be correlated with the presence of silica on the pyrite surface. The immediate presence or absence of KB-SEA^{TM} did not appear to control whether an oxide layer developed on the pyrite grain surface; other micro-chemical environmental changes must also play a role.

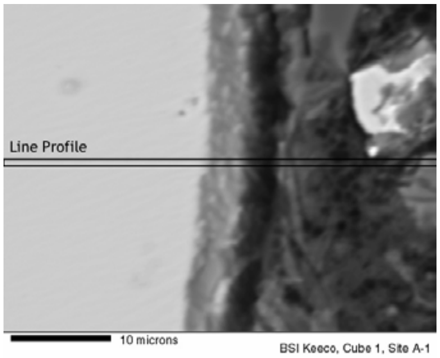

Figure 5: Pyrite crystal- microprobe line

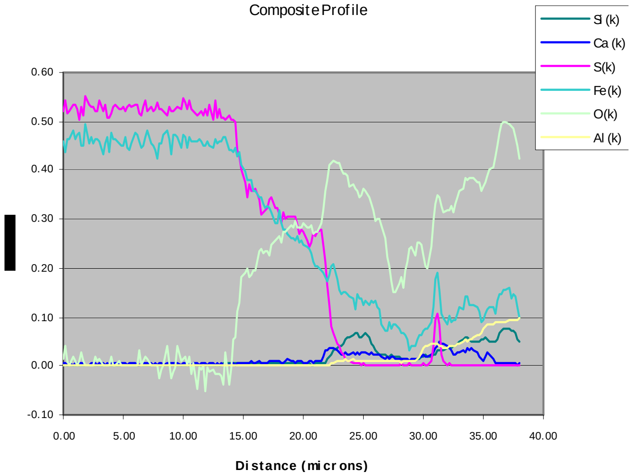

Figure 6: Elemental analyses-leached reactor

Unleached Samples – EcoBond-ARD™

The EcoBond-ARD™ was applied as a clear liquid; therefore there was no residual material visible in the reactor (as observed for KB-SEA™). The pyrite grains from the unleached reactors did not appear to contain significant coatings of the treatment chemical. Electron microprobe analyses did show that many grains had a thin coating of K and P indicating the presence of the EcoBond product (Figure 7). In some cases the K and P concentrations are offset from the actual edge of the pyrite grain by about 5 to 7 microns (Figure 10). This offset is due to shrinkage within the epoxy.

As the mounting epoxy cures, it tends to shrink a small amount and can pull away from the pyrite grain, leaving a gap. This gap can be seen on many of the backscattered electron images. The fact that the K and P coating were easily pulled away from the pyrite grain indicated that it was a simple coating on the grain and was not chemically bonded to it. There is no evidence of P or K intermixing with the pyrite components.

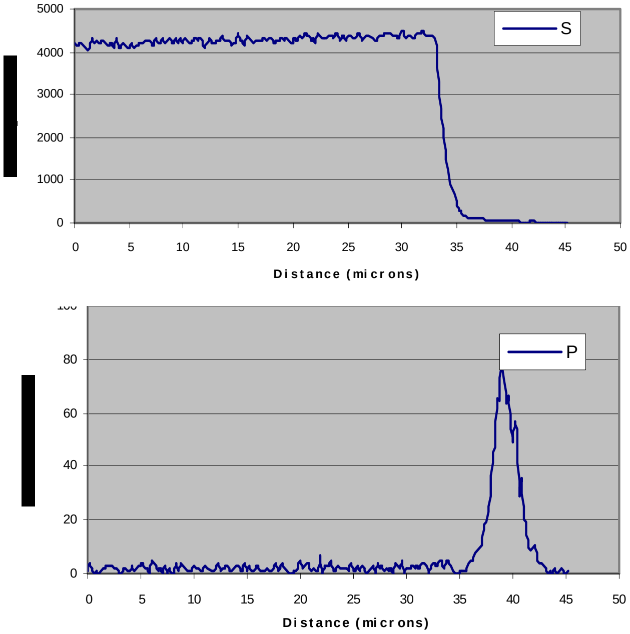

Figure 7: Microprobe results, pyrite, unleached *EcoBond-ARD™* reactor

Leached Samples – EcoBond-ARD™

The pyrite cubes from the EcoBond-ARD*™* reactors have visible oxidation and contained an oxidized "rind" typically 5-10 microns thick. In some cases, the oxidized layer had been pulled away from the crystal face by the epoxy while in other samples the oxidized layer adhered to the crystal face. The position of the layer was a measure of the tensile strength of the oxide layer. Those coatings with poor tensile strength may be secondary oxide coatings, while those that are strongly bonded to the crystals may represent early stages of oxidation of the pyrite crystal itself.

Low to trace amounts of P and K were present near the crystal edge; these appeared to be generally associated with the oxidized iron layers. Silica was also observed in several of the oxidized areas suggesting the formation of iron-silica-hydroxide. There was no obvious decrease in S within the pyrite, but oxygen penetration had occurred and ranged in depth from 2-8 microns.

Discussion

Controls

The ratio of acid production potential to the neutralization potential was 11.4, and as expected, the control cells produced acid drainage. Since the greenstone material contained almost no carbonates, the neutralization potential was very low. Only minor amounts of siderite ($FeCO_3$) have been observed in mineralogical analyses of greenstone samples from this area (Lapakko *et al.*, 2002).

EcoBond-ARD™

Although the cells treated with EcoBond-ARD™ initially maintained pH above 6.0, treatment was ultimately not effective in preventing the formation of ARD. Although the specific nature of EcoBond-ARD™ is proprietary, the product contains phosphate and was developed based on the reaction of phosphate with Fe^{3+} to form an insoluble iron phosphate compound. Ideally this compound would form on the surface of the iron sulfide minerals and render the remaining surface unreactive.

Phosphate application has been shown to reduce sulfide oxidation (Evangelou, 1995; 2001). Evangelou used hydrogen peroxide to oxidize pyrite to produce ferric iron ions that combined with phosphate in solution to form an insoluble $FePO_4$ over a period of 3-4 days. The pyrite oxidized in material treated with phosphate was more than an order of magnitude less reactive than the control and about 99% of the iron released was retained in the test column (Evangelou, 2001). SEM photos confirmed the presence of an iron phosphate coating on the pyrite surface (Evangelou, 1995). Although the phosphate coating was initially successful in decreasing the rate of sulfide oxidation, the effect of the coating decreased as pH decreased, probably as a result of the dissolution of the ferric phosphate coating at low pH (pH <4; Evangelou, 1995). Once the coating dissolved, the rate of sulfide oxidation was essentially equal to the untreated control.

Since the objective of this study was to determine if the microencapsulation chemicals could prevent ARD from unoxidized material, only small amounts of Fe^{3+} were present initially. To compensate for the potential lack of Fe^{3+}, the product contains an oxidizing agent that is designed to attack unreacted sulfide surfaces and generate Fe^{2+}. MT2 initially requested that the cells be saturated with their product for 24-48 hours. However, it was considered that this would not reflect the reality of a field application to a large waste rock stockpile and a much shorter saturation time (10 minutes) was chosen to simulate spraying of treatment chemical on to the waste pile surface, in which there would be very few saturated areas.

Microscope evaluation of unleached pyrite cubes treated with EcoBond-ARD™ showed P along the crystal edge, but there was no evidence of interaction with the pyrite. The presence of product along the edge may be an artifact of experimental conditions. Cells were flooded with product and then drained; no rinsing was done to remove residual solution. As interstitial water originally present evaporated during storage, product was therefore left on all surfaces. For some of the pyrite samples a crack developed as the epoxy pulled away from the crystal during drying and in several of the images the P peak was separated from the crystal, suggesting that the P was a residue from evaporation of the product solution.

Oxidation was visible on the pyrite cubes from leached reactors, which was expected since the EcoBond-ARD™ reactors had produced ARD. In general, there was evidence of product at the edge of the pyrite in the leached samples, but oxygen had penetrated into the pyrite, from about 2-15 microns. In some samples the S in the pyrite decreased but in most the S remained unchanged, suggesting minimal reaction.

This was the first trial of EcoBond-ARD™ in preventing sulfide oxidation. Previous trials used oxidized mine waste containing elevated concentrations of $Fe^{3+}$and other trace metals; treatment generated insoluble iron and phosphate compounds that controlled metal release decreased (Gobla *et al.*, 2000). The most likely explanation for the failure of EcoBond-ARD™ in this case is the absence of Fe^{3+} in the unoxidized material. The short application time was not long enough to produce sufficient $Fe^{3+}$to react with the phosphate present in the treatment product.

Additionally, there were several other potential water quality issues. Initial drainage samples contained elevated levels of As and P. Arsenic concentrations were about two orders of magnitude higher than the controls and ranged from 400-800 $\mu g\ L^{-1}$, well above the current federal drinking water standard of 50 $\mu g\ L^{-1}$ and proposed drinking water standard of 10 $\mu g\ L^{-1}$. Arsenic remained above 100 $\mu g\ L^{-1}$ for the first 3-

4 weeks and did not decrease to 10-20 µg L^{-1} until 8 weeks. Phosphorus concentrations were elevated during the initial part of the experiment with almost all of the phosphorus in the biologically available ortho form. Phosphorus is the limiting nutrient in aquatic systems and concentrations above 0.03 mg L^{-1} are generally believed to lead to excessive algal growth and eutrophication. Although phosphorus concentrations decreased rapidly, concentrations did not decrease below 0.03 mg L^{-1} until after week 14. The elevated concentrations of arsenic and phosphorus would require that the initial drainage be collected and reused or treated.

KB-SEA^{TM}

All cells treated with KB-SEA^{TM} were initially successful in preventing acid drainage and reducing sulfide oxidation. The 1% treatment failed (i.e. the discharge pH fell below 6) at about week 175, but the 3% and 5% treatments are both successfully, maintaining pH at around 8 more than 6 years into the study. Evangelou (2001) demonstrated that silica treatments could effectively reduce sulfide oxidation and proposed a model whereby initially the silicate reacts with hydroxyl groups to form a silica polymer on the hydroxide surface that has formed on the pyrite. Once the surface is coated, additional condensation of silica occurs to produce a surface silica film. The theory was tested by treating coated pyrite with different acids; treating with 4 M hydrochloric acid increased the rate of sulfide oxidation, but to only about half that of the control. Treatment with 4 M hydrofluoric acid removed all the silica and the rate of oxidation was essentially the same as the control (Evangelou, 2001).

The treatment effect with KB-SEA^{TM} may be related to several factors in addition to coating the surface with silica. KB-SEA^{TM} contains 30-50% lime (CaO). At current release rates, it would take about 9 years to remove all the residual calcium (Eger *et al*, 2004). The product also cemented some of the material resulting in a macroencapsulation of the rock grains. When the unleached cell treated with 3% KB-SEA^{TM} was dismantled and examined, about 50% of the rock grains were cemented together. Many of the areas – particularly those with coarser rock grains – were so solid that water flow was obstructed, effectively reducing the total area of sulfides exposed in the cell.

Although there was little visible sulfide oxidation in the treated cells after 60 weeks, oxidation has increased with time. The amount of visible oxidation decreased as the rate of application increased. Microscope evaluation of the unleached and leached reactors did not clearly identify a mechanism or explain the success of KB-SEA^{TM}, although there was evidence for some interaction between the product and the pyrite. However, in most images the product was on the outside of the crystal and had not prevented oxygen migration. The microscope evaluation examined large pyrite crystals and although easier to analyze, have relatively little surface area and tend to be significantly less reactive than finer grained framboidal pyrite. Analyzing fine-grained material was difficult due to the similarity between the original material and secondary reaction products. A more controlled experiment with pyrite crystals might provide a better model to determine the interaction of KB-SEA^{TM} with the pyrite.

In a field application, drainage from an area treated with KB-SEA^{TM} would have to be collected in the immediate period following treatment due to elevated pH.

Conclusions

Although EcoBond-ARD^{TM} delayed the onset of ARD generation, it did not prevent it. Additionally, treatment with EcoBond-ARD^{TM} resulted in elevated levels of P and As in the drainage. Concentrations remained above concern levels for around 8 weeks for arsenic and 30 weeks for phosphorus. KB-SEA^{TM} (3 and 5%) continue to successfully prevent acid drainage after 6 years and pH appears to have stabilized around 8. The rate of sulfide oxidation was about 10% of the rate measured in the untreated controls. However, the pH from all cells treated with this product were initially around 12 and although pH has decreased in all cells, the cells treated with 5% had pH values consistently above 9 for about 75 weeks. Microscopic evaluation of pyrite crystals from one of the reactors treated with 3% KB-SEA^{TM} found that although some silica was generally present on the surface of the pyrite crystals, oxygen had penetrated into the pyrite. For the moment, the exact mechanism for the success of this product has not yet been determined, but there is certainly sufficient data now to justify a more detailed examination.

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