ACID ROCK DRAINAGE PREVENTION AND TREATMENT WITH THIOCYANATE AND PHOSPHATE-CONTAINING MATERIALS[1]

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Abstract. Stopping the weathering of sulfide minerals causing acid rock drainage (ARD) involves control of both biological and chemical oxidation processes. We are developing a technology for ARD prevention and control that combines thiocyanate and phosphate treatments of sulfidic materials. The technology extends to overburden, tailings, waste rock, and spent heap leach ore. Thiocyanate at low concentrations is a strong and selective inhibitor of microbial iron oxidation. This curtails severe ARD that lessens the effectiveness of phosphate in precipitating Fe and Al phosphates. Combined phosphate and thiocyanate treatment has been tested on sulfidic waste materials at kg scale in laboratory humidity cell and column leach tests and at 600 ton scale in field trials. Sources of phosphate tested include phosphate rock, commercial agricultural phosphates such as dicalcium phosphate, and waste material from phosphate beneficiation. Thiocyanate treatment of waste rock reduced ARD 50% or more compared to untreated material. Low dosages of phosphate materials combined with thiocyanate treatment reduced ARD beyond that achieved with thiocyanate alone. This treatment, especially if combined with an effective waste and water management strategy, offers a promising approach to source control of ARD in both newly and previously mined waste materials.

Additional Key Words: biooxidation, sulfide oxidation, source control of ARD

Introduction

The environmental and economic impacts resulting from the onset of acid rock drainage (ARD) is the most serious long term closure issue facing the international mining industry. Control of ARD at the source, i.e., stopping the oxidation of pyrite and other metal sulfides, requires control of biological and chemical oxidation processes. Biological control is achieved primarily by stopping the activity of acidophilic iron-oxidizing bacteria catalyzing oxidation of Fe^{2+} to Fe^{3+} at low pH. Fe^{3+} oxidizes sulfide minerals much more rapidly than does oxygen.

Thiocyanate anion, SCN^-, is highly inhibitory to biooxidation of pyrite (Bryner and Jameson, 1958; Olson et al., 2003a). A few mg/L of SCN^- inhibits iron oxidation by *Acidithiobacillus ferrooxidans* (Cox et al., 1979) and sulfur oxidation by *A. thiooxidans* (Suzuki et al., 1999). Thiocyanate contamination of commercial stirred tank bioleaching operations has caused process failures (Miller, 1997); as little as 5 ppm causes drastic reduction in bioleaching rates (Hackl et al., 1989). Thiocyanate is selectively inhibitory toward acidophiles because of their unusual physiology--they uniquely possess an inside-positive membrane potential to counteract the influx of protons and the force against which protons must be extruded (Matin, 1999; Ingledew, 1990). Thiocyanate anion is highly lipophilic and its intracellular accumulation as a consequence of the membrane potential inhibits the cells, probably as a result of cytoplasmic acidification (Ingledew, 1990) and binding of SCN^- to other cellular constituents (Cox et al., 1979). Consequently, maintenance of >10 mg/L thiocyanate in leachates in laboratory weathering tests virtually eliminates biooxidation of iron at low pH, thereby reducing sulfide oxidation in proportion to the role microorganisms play in a particular system (Olson et al., 2003a; Olson et al., 2003b).

However, even if biooxidation of iron is eliminated, sulfide oxidation by oxygen continues. This may occur either by direct attack on sulfide minerals or by oxidation of dissolved ferrous iron to ferric iron.

Controlling oxidation of sulfides with phosphates has been proposed. There are many potential advantages in using phosphate for ARD control including 1) phosphate precipitates Fe^{3+} and Al^{3+} forming iron and aluminum phosphates that may coat and armor iron sulfide surfaces (Evangelou, 1995; Georgopoulou et al., 1996), 2) considerably less acid is produced if iron and aluminum are precipitated as phosphates rather than as hydroxides, 3) precipitation of iron phosphate removes Fe^{3+} oxidant (Renton and Stiller, 1989), 4) phosphate rock (apatite) neutralizes acid, and in some cases phosphate rock is also associated with carbonates (Kalin et al., 1998; Spotts and Dollhopf, 1992), and 5) phosphate is non-toxic and, as phosphate rock, is relatively inexpensive. Agricultural phosphate products (e.g., Dical) or even biogenic structures such as fish bones (Conca and Wright, 2001), may have advantages over phosphate rock in being lower in impurities and more soluble or reactive.

Although phosphate treatment may armor pyrite surfaces with a $FePO_4$ coating, this coating fails under severe low pH ARD conditions produced by bacterial sulfide oxidation (Huang, 2004). Consequently, inhibition of biocatalyzed ARD with thiocyanate may stabilize these coatings. Furthermore, inhibition of biooxidation could increase the effectiveness of phosphate treatment by the other mechanisms described above.

Combined phosphate and thiocyanate treatment offers a comprehensive approach to the control and prevention of ARD. This paper reports on laboratory tests comparing the

effectiveness of various sources of phosphate combined with thiocyanate treatment for stopping sulfide oxidation. Initial results are reported also from a new field test of the technology.

Thiocyanate and Phosphate: General Considerations

Thiocyanate. Sodium thiocyanate, NaSCN, is available world wide from several chemical suppliers and vendors in solid form or in a 50% to 55% solution. It costs about \$1.00/lb to \$1.45/lb depending on the form and quantity obtained. In addition, many mining operations, particularly precious metal mines, have thiocyanate-containing waste streams. In some instances it may be possible to selectively treat these waste streams to remove metals and cyanide then reapply them containing thiocyanate only to waste rock dumps for control of ARD.

Thiocyanate is highly and selectively toxic toward acidophilic microorganisms, especially iron oxidizers, and is less toxic to higher forms of life. It is readily biodegraded at neutral pH but is stable toward biodegradation anaerobically and under acidic (pH <5), aerobic conditions. Abiotically, SCN hydrolyzes very slowly at low pH although the rate increases at high solution redox potentials.

There are no published reports of thiocyanate resistance or biodegradation with acidophiles. An unpublished report (Sobolewski, 1993) showed 10 to 60 mg/L thiocyanate solutions applied to columns containing coal refuse reduced acidity and sulfate up to 80% compared to untreated columns. However, after a period of 1 to 2 months, effluent thiocyanate concentrations declined and ARD resumed. Apparently, thiocyanate was converted to ammonia--effluent after 79 days from a column receiving 60 mg/L thiocyanate showed only 16 mg/L thiocyanate and 10 mg/L ammonia-N. The N in ammonia accounted for the difference in SCN-N between the feed and effluent. The results suggested biodegradation of thiocyanate to ammonia, though no follow-up microbiology work was done. The report concluded that the observed thiocyanate degradation makes it unsuitable as a control agent for ARD from coal, but that thiocyanate possibly might be more effective in controlling ARD from non-coal sources.

It is likely thiocyanate biodegradation produced the ammonia in the coal column effluents. It is uncertain if thiocyanate was degraded by neutral pH thiobacilli growing in less acidic zones in the upper reaches of the columns, or by hitherto undescribed organisms or reactions occurring at acidic pH values of the column effluents. Thiocyanate resistance in acidophiles would be difficult, given the fundamental nature of its accumulation and binding to active sites of enzymes.

We also have observed ammonia concentrations of a few mg/L in leachates from column tests with thiocyanate-treated waste rock (Olson et al., 2003a, 2003b). However, acidophilic microorganisms could not be adapted to thiocyanate nor did they biodegrade thiocyanate under aerobic conditions at low pH (<4). Ammonia production was instead attributed to slow abiotic hydrolysis of thiocyanate, consistent with the mechanism proposed by Barbosa-Filho and Monhemius (1994).

Phosphates. There are a number of sources of phosphate materials that could be applied to ARD treatment and control. Phosphates occurring as hydroxylapatite, $Ca_5(OH)(PO_4)_3$, or fluoroapatite are widely available as inexpensive phosphate rock. This form of phosphate only becomes available at acidic pH. Consolidated clay, a waste product of phosphate beneficiation, contains fine particles of apatite and is also a potential source of phosphate (Renton and Stiller, 1989).

Other forms of phosphate are more expensive but are lower in impurities and might also be effective at lower dosages. One of these is "Dical", an agricultural product containing 70:30 dicalcium phosphate and monocalcium phosphate. Dical has a water soluble component, $Ca(H_2PO_4)_2$, and an acid soluble component, $CaHPO_4$. Another product is tribasic calcium phosphate or "Trical", which can be produced by calcining of phosphate rock, driving off F.

These phosphate materials exhibit only a modest acid neutralizing capacity (ANC) in a conventional ANC test with HCl adapted from the Sobek procedure (AMIRA, 2002). They exert their greatest acid neutralizing effect by precipitating Fe and Al phosphates, thereby avoiding the Lewis acidity occurring with precipitation of hydroxides. Tests employing artificial ARD solution containing Fe^{3+} and Al^{3+} sulfates are required to give a more accurate test of ANC of phosphate-containing materials (M. Logsdon, personal communication).

Despite their relatively benign nature, it may be undesirable to release thiocyanate or phosphate into receiving waters. In this event, drainage or seepage containing these chemicals could be treated in relatively inexpensive and straightforward manner to reduce their respective concentrations to acceptable levels using one or more proven active or passive water treatment processes.

Test Samples and Methodology

Sulfidic Rock Sample

Massive sulfide waste rock was obtained from the Red Dog Mine in Alaska. It was crushed to <12.7 mm and 5 kg splits were prepared as column test charges. X-ray diffraction analysis indicated the waste rock contained 9% pyrite and 9% sphalerite. By X-ray fluorescence the material contained 9.3% Fe, 6.9% Zn and 11% S.

Phosphates

Florida phosphate rock (PR) and "Dical" were obtained from Mosaic, formerly Cargill (Tampa, Fla.). The phosphate rock was >90% fluoroapatite, contained 14.2% P and was used as received (- 10 mesh). It had a slurry pH in water of 7.3. Dical was supplied as small pellets, <1 mm in size, and contained 19.5% P. The slurry pH in water was 3.3.

Laboratory Column Tests

Red Dog waste rock was agglomerated with sodium thiocyanate solution alone (50 mg SCN/kg rock) or NaSCN solution plus phosphate rock (20 g/kg) or Dical (5 g/kg). Duplicate untreated controls ("full ARD") were agglomerated with water only. The columns were not inoculated; the rock contained indigenous sulfide-oxidizing microorganisms.

Agglomerated waste rock charges were loaded into glass columns 10 cm diameter x 0.5 m in height. Columns were leached biweekly with a) 350 mL deionized water (controls), b) 350 mL of 100 mg/L SCN (as NaSCN) solution (SCN-only treated columns), or c) 350 mL SCN solution alternating with deionized water (i.e., NaSCN solution in week 2, deionized water in week 4, NaSCN solution in week 6, etc.) for the columns co-treated with phosphate rock or Dical. In this manner, thiocyanate was maintained in the columns initially agglomerated with phosphate rock or Dical. This was necessary because the amount of leach solution applied to the columns was much higher than precipitation at the mine site. This would have washed out the water soluble NaSCN much more quickly than would occur naturally. After week 16, all columns except one of the SCN treated columns were leached with deionized water only. The purpose of omitting NaSCN was to determine if ARD became reestablished after it was rinsed out of the columns.

Between leaching events columns were aerated in one week cycles of dry air and moist air at a rate of approximately 0.5 L/min.

Leachates were analyzed for pH, redox potential, conductivity, and sulfate. Dissolved metals and P were analyzed by ICP spectroscopy. Ammonium was determined colorimetrically.

Results and Discussion

Column Tests with Red Dog Waste Rock

Soluble salts from the rock rendered initial column effluents acidic. The pH in leachates from duplicate columns containing untreated waste rock continued to decline to a mean value of pH 2.2 after 26 weeks (Fig. 1). Solution redox potentials in these solutions increased to a mean value of about 630 mV (Fig. 2).

Leachates from duplicate columns treated with thiocyanate maintained a higher pH and much lower Eh over the 16 weeks that thiocyanate was maintained in the system. Thiocyanate inhibits iron-oxidizing bacteria that are important contributors to ARD. At the concentrations employed in this test, there should have been little or no biooxidation of iron. Consequently, the pH and Eh values in the NaSCN-treated columns should largely reflect the rate of abiotic (i.e., O_2) oxidation of the sulfides in the waste rock.

The highest pH occurred in leachates from waste rock treated with NaSCN plus phosphate rock and NaSCN plus Dical, owing to acid consumption by these phosphate-containing materials. Eh values were similar to NaSCN-only treatment although Dical appeared to reduce Eh values beyond those observed with other treatments, perhaps due to precipitation of $FePO_4$.
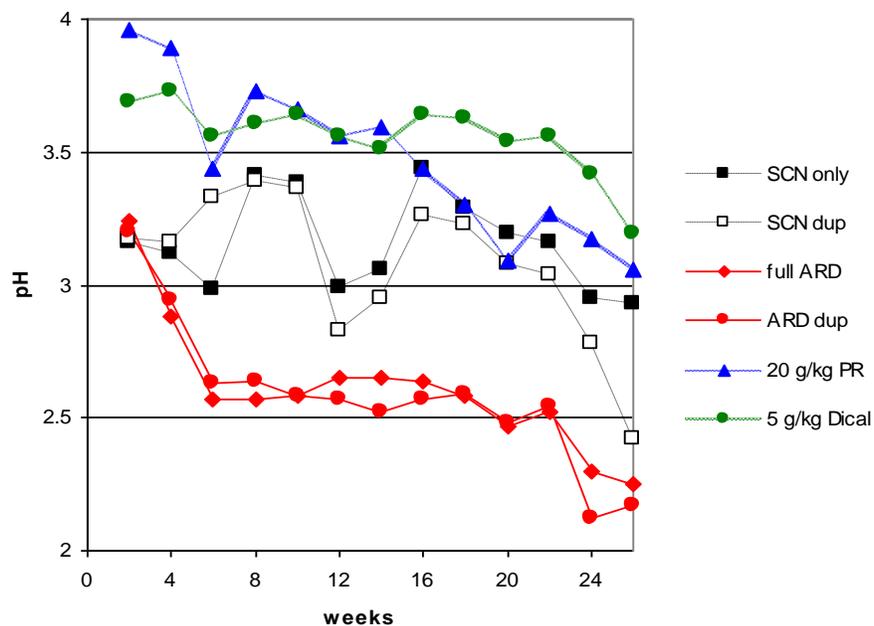
Figure 1. Time course of leachate pH from columns containing Red Dog waste rock.
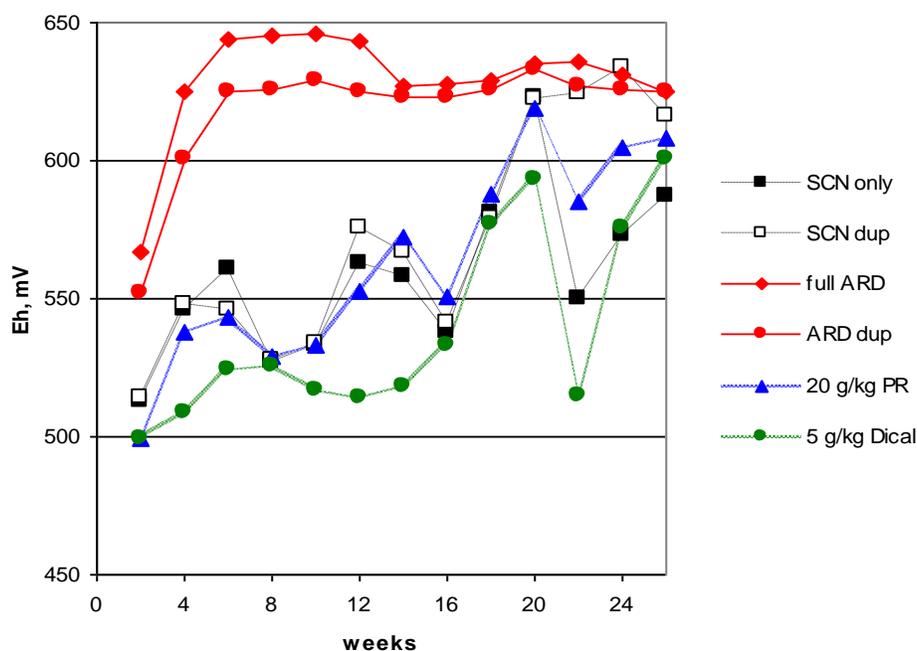
Figure 2. Time course of leachate Eh from columns containing Red Dog waste rock.

Sulfate production is another indicator of oxidation of metal sulfides to metal sulfates; in this case sphalerite and pyrite. Clearly, treatment with NaSCN biocide substantially reduced the rate of sulfate production (Fig. 3), and indicated microorganisms were responsible for most of the ARD production in the untreated columns. Dical plus NaSCN further reduced sulfate leaching. Linear regression analysis of the data from the first 16 weeks of the test showed 78% reduction in the sulfate leaching rate with NaSCN treatment, 80% reduction with NaSCN plus phosphate rock and 92% reduction with NaSCN plus Dical compared to untreated controls (Table 1). Thus, the abiotic rate of oxidation (NaSCN treatment only) was reduced an additional 64% with NaSCN plus Dical treatment.

The pattern of Zn extraction resembled sulfate extraction shown in Fig. 3 and the molar ratio of sulfate to Zn in leachates was fairly close to 1.0. Correspondingly, reductions in Zn leaching rates with the various treatments were similar to those observed for sulfate (Table 1). This was expected because sphalerite is one of the most reactive sulfides and tends to be oxidized first in systems containing other sulfide minerals with higher electrochemical potentials (i.e., pyrite). Thus, even though the waste rock contains more iron than zinc, after 16 weeks the molar ratio of Zn to Fe in leachates from control and NaSCN treated columns ranged from 12:1 to 15:1. The reduction in Fe leaching rate with NaSCN treatment was comparable to the reduction in sulfate and zinc leaching. However, Fe was leached more slowly from the NaSCN plus phosphate rock column compared to NaSCN only and virtually no Fe leached from the NaSCN plus Dical column. These reductions in Fe leaching are attributed to precipitation of iron phosphate. Dical was more efficient in supplying soluble phosphate than phosphate rock.

Soluble P was detected in leachates from the Dical column but not from the phosphate rock column. Reactivity of the phosphate rock could be improved by finer grinding.
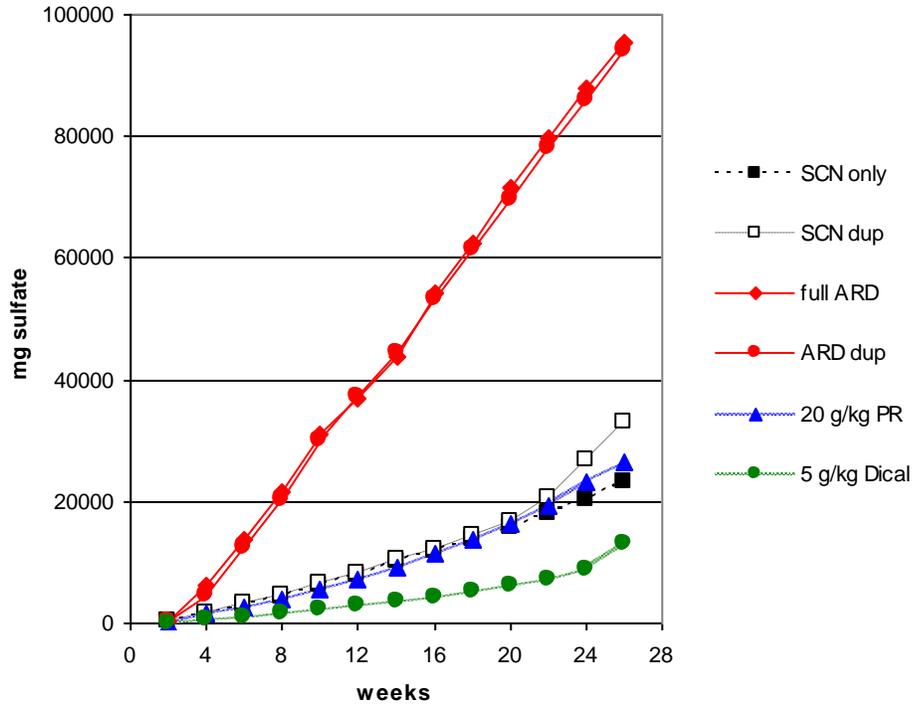
Figure 3. Cumulative leaching of sulfate from columns containing Red Dog waste rock.

Table 1. Reduction (%) in leaching rate of ARD indicators with various treatments compared to untreated control columns (weeks 2 to 16).

Treatment	Sulfate	Zinc	Iron
NaSCN	78	78	82
NaSCN + PR	80	82	95
NaSCN + Dical	92	96	99.9

Column leachates were analyzed for ammonium concentrations in the initial leach (week 2) and in weeks 6, 10 and 14. Ammonium was detected at a concentration of 5.0 to 7.1 mg/L (N-NH_3) in the initial leach of the untreated waste rock (full ARD columns), possibly from blasting residues. It was not detected in leachates from week 6. Matix interferences prevented analysis of ammonium in subsequent samples from these columns. Ammonium was detected in all leachates from the other columns. Leachates from the SCN-only treated columns contained 2.3

to 7.2 mg/L NH_3-N, similar concentrations were observed in the phosphate rock-treated column (4.2 to 9.1 mg/L). Leachates from the Dical treated column contained 22 to 32 mg/L $N-NH_3$. These higher concentrations were due to ammonium contained in the Dical itself—water extraction of Dical indicated it contained 0.09% $N-NH_3$. No ammonium was detected in a water extract of phosphate rock.

The presence of ammonium in leachates from SCN-treated waste rock in weeks 6, 10 and 14 may result from abiotic hydrolysis reactions, as suggested in previous test work (Olson et al., 2003a, 2003b). Biodegradation of thiocyanate does not occur at the observed leach solution pH values of 2.8 to 3.9. However, we cannot rule out the possibility that certain zones in the columns may have had locally higher pH values potentially allowing for growth of neutral pH thiocyanate oxidizing bacteria as may have been the case in the Sobolewski (1993) report.

Discontinuance of NaSCN application after week 16 resulted in decreasing concentrations of SCN in leachates to less than 10 mg/L within 2 or 3 leach cycles. Below this concentration microbial iron oxidation may resume. Indeed, decreasing pH and increasing Eh after 16 weeks occurred in leachates from the treated columns (Figs. 1 and 2), indicative of reestablishment of microbial iron oxidation. Similarly, increases in sulfate leaching rates occurred also after NaSCN application was discontinued (Fig. 3). Although NaSCN is lethal to acidophilic iron-oxidizing microorganisms, some cells may have been protected in biofilms or in certain parts of the rock not exposed to NaSCN.

In sum, 1) NaSCN treatment alone reduced sulfate, Zn and Fe leaching comparably, probably reflecting the abiotic (O_2) oxidation rate, 2) NaSCN plus phosphate rock or Dical reduced the iron leaching rate compared to NaSCN treatment alone, 3) NaSCN plus Dical reduced the rate of zinc and sulfate leaching, 4) ARD resumed when SCN was leached out of the system.

The reduction of zinc and sulfate leaching with Dical reflects removal of Fe from solution, probably as ferrous and ferric phosphates. These precipitates a) may have formed a coating to reduce access of O_2 to the sulfides and/or b) simply removed residual ferric iron oxidant from solution. This ferric iron could have formed from Fe^{2+} oxidation by O_2 or by a small fraction of activity of iron-oxidizing microorganisms not completely inhibited by NaSCN.

Field Trials at Red Dog Mine

Preliminary field tests at the Red Dog mine in summer 2002 indicated thiocyanate treatment of waste rock in 100 ton test pits reduced sulfate leaching by about 50% (Olson et al., 2003b). Based on those results and results obtained from column tests described above, a second field test was begun in July, 2004. The goal was to confirm the initial field test results and to determine if thiocyanate-phosphate co-treatment could further reduce sulfide oxidation. A 4000 ton stockpile of waste rock crushed to <3" size was used as the test material. A subsample from this stockpile had been used in the laboratory column tests described above. Test pits were loaded with 600 tons each of sulfidic waste rock and were treated with NaSCN or NaSCN plus Dical during loading (Fig. 4). Two test pits were untreated controls.

Leach solutions draining from test pits resulted solely from rainfall or snowmelt. These were collected in 500 gallon plastic drums and analyzed for ARD constituents. Drums were drained between sample collections and the total volumes were recorded so the mass of leached dissolved constituents could be determined. As summer progressed, distinct differences arose in the masses of ARD constituents leached from treated pits compared to untreated pits. Notably,

TDS, sulfate and zinc leaching was reduced over 50% in pits treated with Dical plus NaSCN compared to the untreated controls. Sampling is scheduled to resume in spring, 2005.

Figure 4. Loading of test pits at Red Dog mine.

Test Work with Other Materials

Additional laboratory test work is in progress to evaluate other sources of phosphate. A key question being addressed in these tests is whether there is evidence for reduction in the abiotic pyrite oxidation rate with phosphate treatment.

Humidity cell tests are in progress with rock supplied by Kennecott. Unlike the Red Dog material, sulfides in this material occur almost exclusively as pyrite. The rock was crushed and blended with NaSCN and several sources of phosphate including 1) Dical, 2) Florida phosphate rock, 3) consolidated clay, a refuse material from phosphate beneficiation containing mostly clay but also containing about 25% fluoroapatite, and 4) tribasic calcium phosphate ("Trical").

Column tests are also underway with waste rock supplied by Solid Energy, New Zealand's largest coal producer. This waste rock contains pyrite as the dominant sulfide. Florida phosphate rock, N. Carolina phosphate rock, and Dical are being tested with this material.

Additional test work has also begun with samples of waste rock supplied by Kinross Gold, BHP Billiton, and Rio Tinto.

These tests are aimed at determining initial performance in the laboratory of the thiocyanate-phosphate treatment approach. Depending on the outcome, they may be followed with one or more field trials.

Although the dual chemical approach to control ARD at source is not completely effective in all situations, substantial reductions in long term water treatment capital and operating costs can be realized through dramatic reduction in ARD characteristics (Mudder and Olson, 2004).

Finally, a long term research strategy is being examined in which source control of ARD could be achieved on a selective basis within waste disposal sites. The strategy would be based upon successful employment of aerial infrared thermal imagery to identify ARD "hot spots" which could in turn be selectively treated "in-situ" using the combined dual chemical approach described in this research.

Acknowledgments

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