

TOWARD SOURCE CONTROL OF ACID ROCK DRAINAGE¹

Gregory J. Olson², Thomas R. Clark, Terry I. Mudder, and Mark Logsdon

Abstract. Source control of acid rock drainage (ARD) requires consideration of both biological and abiotic mechanisms of metal sulfide oxidation. A promising approach is to couple a biocide with phosphate for application to sulfidic waste materials. This approach aims to 1) inhibit or kill with thiocyanate (SCN) the iron-oxidizing acidophilic microorganisms that accelerate sulfide oxidation and 2) precipitate FePO₄ and AlPO₄, thereby removing ferric ion oxidant and Lewis acidity, and, in the process, armoring the surface of pyrite to retard its abiotic oxidation. Thiocyanate effectively reduces sulfide biooxidation if it is applied efficiently and is not washed out of the system by rainfall or adsorbed to the rock. Several sources of phosphate including phosphate rock, waste material and agricultural products were characterized and tested in combination with SCN for their ability to retard oxidation of sulfidic waste rock. Waste rock sources include samples from base metal and precious metal mines and a coal mine. The acid neutralizing capacities (ANC) of different sources of phosphate were compared and evaluated using an artificial ARD solution which included iron and aluminum sulfates. Thiocyanate alone in laboratory tests sharply reduced ARD production, approaching the abiotic rate of sulfide oxidation. Whether thiocyanate plus phosphate further reduced ARD production depended on the mineral sulfide composition of the waste rock and the parameter measured. The abiotic sulfide oxidation rate of sphalerite-containing waste rock was reduced with phosphate treatment, most likely by removal of residual ferric iron from leach solutions. Phosphate did not further reduce abiotic sulfide oxidation rates with a pyritic waste rock, but did significantly reduce the soluble iron and other metal content of leachates. The combined thiocyanate plus phosphate treatment minimized biooxidation, removed ferric ion oxidant, and restricted formation of Lewis acidity but has not shown evidence of armoring pyrite. The laboratory test work guided the set up and operation of a 3000 t field test. ARD production was reduced over 50% in the first season with combined thiocyanate and phosphate treatment. However, washout of thiocyanate and its adsorption to rock reduced its concentrations in leachates to near zero in the second year of the test, greatly reducing the effectiveness of chemical treatment. Water soluble forms of thiocyanate (NaSCN) are best used to reduce ARD in situations where rainfall infiltration is low. The development of slow- or controlled-release thiocyanate products combined with phosphates would be beneficial.

Additional key words: ARD prevention, phosphate, thiocyanate

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² Gregory J. Olson, Vice President, Thomas R. Clark, Senior Scientist, Little Bear Laboratories, Inc., Golden, CO 80403; Terry I. Mudder, Managing Director, TIMES, Ltd., Sheridan, WY 82801; Mark Logsdon, Principal Geochemist, Geochimica Inc., Aptos, CA 95003.

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Introduction

The most rational way to reduce ARD is to control it at the source by minimizing biological and abiotic oxidation of sulfide minerals, especially pyrite. The relative importance of biological versus abiotic oxidation of sulfides varies depending on the environmental conditions and the sulfide minerals involved. Elimination of biooxidation with biocides such as thiocyanate (SCN) provides an estimate of the abiotic sulfide oxidation rate. Using this approach, biooxidation was estimated to account for 80% or more of SO_4^{2-} production in laboratory tests with pyritic materials (Olson et al., 2003a). In field testing situations, biooxidation accounted for at least 31% to 68% of sulfide oxidation (Mudder et al., 2005; Olson et al., 2003b; Mudder and Olson, 2004). These field estimates of the importance of biooxidation probably are underestimates as contact of biocides with sulfidic rock is expected to be less efficient on larger scale. However, it is clear that both biooxidation and abiotic reactions must be controlled for a comprehensive approach to solving the ARD problem.

Control of Biooxidation of Metal Sulfides

Ferric iron is the most important oxidant of metal sulfides in environmental situations. Acidophilic iron oxidizing microorganisms are the rate limiting factor in oxidation of Fe^{+2} to Fe^{+3} at pH values <5 . Consequently, controlling the activity of these microorganisms with biocides such as SCN (Olson et al., 2003a) or anionic surfactants (Kleinmann et al., 1981) has the potential to significantly reduce ARD. The action of thiocyanate on metal-sulfide oxidizing microorganisms has been known for a long time (Bryner and Jameson, 1958). A few parts-per-million of SCN in solution is lethal to these microorganisms whether they are planktonic or attached to surfaces. Another advantage of thiocyanate is its stability under acidic conditions. It does not biodegrade at pH values less than 4 to 5 (Olson et al., 2003b) and abiotic degradation is very slow except at high redox potentials. Thiocyanate is biodegradable under aerobic conditions at neutral pH. Efficient reduction in biooxidation of sulfides requires efficient distribution of thiocyanate-containing solutions in the sulfidic waste material. Minimization of thiocyanate washout, for example through compaction and/or with a cover system, is also important with water soluble forms of thiocyanate such as NaSCN.

Control of Abiotic Metal Sulfide Oxidation

A number of approaches toward control of abiotic oxidation of sulfides have been proposed. These have included use of silica (Fytas and Bousquet, 2002), permanganate (developed by DuPont), or phosphate (Evangelou, 1995; Georgopoulou et al., 1996; Nyavor and Egiebor, 1995) to create armoring layers on metal sulfide surfaces. Achieving efficient armoring with sufficient longevity appears to be the major challenge. Highly acidic conditions produced by biooxidation of sulfide minerals render FePO_4 armoring unstable (Huang, 2004).

Phosphate has a number of attributes that make it attractive for source control of ARD (Renton and Stiller, 1989; Spotts and Dollhopf, 1992; Kalin et al., 1998; Conca and Wright, 2001; Harris and Lottermoser, 2003). In addition to its potential for armoring sulfide minerals, phosphate precipitates Fe^{3+} at relatively low pH thereby removing this oxidant from solution. Precipitation of Fe and Al phosphates avoids Lewis acidity from hydrolysis and precipitation of metal hydroxides. Phosphate in many forms also neutralizes proton acidity.

Combined Approach to Source Control

Combined application of thiocyanate and phosphate has the potential to control ARD at the source by acting on both biotic and abiotic components of sulfide oxidation. Furthermore, co-applying these two chemicals enhances the performance of each. For example, thiocyanate controls biooxidation of Fe, preventing extreme ARD conditions that would overwhelm phosphates' beneficial actions and that would destabilize FePO_4 coatings and precipitates. Phosphate removes ferric iron from solution which reduces redox potential, thereby slowing abiotic hydrolysis of SCN. Sodium thiocyanate and various forms of phosphate are relatively inexpensive and available in bulk world-wide.

The objectives of this paper are to 1) discuss the factors affecting thiocyanate performance in reducing biooxidation of sulfides, 2) characterize the phosphate products that could be considered for large scale application against ARD, 3) evaluate in the laboratory the performance of combined NaSCN and phosphate in reducing sulfide oxidation from mine rock samples of various sulfide contents and acid neutralizing capacities, 4) describe results from the second season of a field test of combined thiocyanate and phosphate performance and 5) discuss the conditions required, limitations, and future R&D needs for achieving source control of ARD using combined thiocyanate and phosphate treatment of sulfidic rock.

Samples and Methodology

Chemicals

Chemicals obtained included reagent grade NaSCN (Sigma Aldrich) and powdered, extra pure tribasic calcium phosphate, $\text{Ca}_5(\text{OH})(\text{PO}_4)_3$ ("Trical", EMD Chemicals). Samples of commercial phosphates available in bulk were obtained from a number of sources (Table 1). Most of the phosphates were in the form of phosphate rock (apatite) except Dical which is a relatively soluble acidic phosphate.

Table 1. Phosphate sources

Phosphate	Source	Composition	%P	Slurry pH ¹
Florida phosphate rock	Cargill	>90% fluoroapatite	14.2	7.3
Florida consolidated clay	Cargill	25% fluoroapatite	5.3	7.7
N. Carolina phosphate rock	PCS Phosphate	68% apatite, 20% to 25% carbonate	11.4	7.5
Togo phosphate rock	Ravensdown Fertilizer Cooperative, Ltd.	Fluoroapatite	16.3	6.9
Dicalcium phosphate (Dical)	Cargill	70:30 blend of CaHPO_4 and $\text{Ca}(\text{H}_2\text{PO}_4)_2$	19.5	4.3
Multifos® (defluorinated phosphate rock)	Mosaic ²	92%-93% $\text{Ca}_3(\text{PO}_4)_2$, balance is other phosphates	18.2	6.8

¹1:2 slurry in water after 12 to 24 h

²During this study Cargill and IMC Global merged to form The Mosaic Company

Abiotic Degradation of Thiocyanate

Fifty mL of an aqueous 100 mg/L thiocyanate (as NaSCN) solution was mixed with an equal volume of artificial ARD solution containing 500 mg/L Fe^{+2} (as ferrous sulfate) and 500 mg/L Fe^{+3} (as ferric sulfate) in 0.022N H_2SO_4 . The initial pH was 1.99 and the Eh was 684 mV

(SHE). The solution was placed in an amber bottle and was held at room temperature. Periodically the thiocyanate concentration was determined colorimetrically (APHA, 1992).

Adsorption of Thiocyanate by Waste Rock

Pyrite-rich massive sulfide waste rock (100 g, provided by Teck Cominco) was added to 200 mL of NaSCN solution (50 mg SCN/L) in 1-liter Erlenmeyer flasks. The slurry was agitated gently (110 rpm, orbital shaker) at room temperature for 24 h. Solution samples were withdrawn periodically, centrifuged (1200 x g, 5 min) to remove particles, and analyzed for thiocyanate concentration.

Thiocyanate adsorption also was determined by placing 1000 g waste rock in a shallow plastic tray and adding 100 mL of 997 mg/L SCN solution. This resulted in a small excess of free solution. The tray was covered and incubated in the dark at room temperature for 19 days. Periodically solution samples were removed after bringing the tray to its original weight with deionized water and gentle mixing of the slurry. Samples were centrifuged and analyzed for dissolved thiocyanate.

Acid Neutralization Capacity (ANC) Test Procedures

Multifos[®] and Florida and North Carolina phosphate rock were pulverized to <150 μm . Consolidated clay, reagent tribasic calcium phosphate, Dical (97% <1.18 mm) and Togo phosphate rock (80% <212 μm) were used as received.

Conventional ANC tests were done according to the method of Smart et al. (2002). Modified ANC tests were done with 2.00 g of phosphate shaken in 100 mL artificial ARD solution for 24 hours at room temperature. Artificial ARD solution contained 60 mM Fe^{3+} (as ferric sulfate) plus 60 mM Al^{3+} (as aluminum sulfate) in 0.05 N sulfuric acid. Each 100 mL aliquot theoretically required 41 meq NaOH to neutralize (assuming 3 mmol H^+ produced/mmol of metal). Slurries were neutralized to pH 4.6 or to pH 6.9 with 1.0 N NaOH. Samples were removed 30 min after pH adjustment for determination of dissolved metal and P concentrations.

Microbial Culture Media

Iron-oxidizing microorganisms were enumerated by most probable number determinations using sterile plastic 24-well tissue culture plates (Costar 3524, Corning). Wells were filled with a sterile medium consisting of (g/L deionized water) ferrous sulfate heptahydrate, 33.4; ammonium sulfate, 0.4 g; magnesium sulfate heptahydrate, 0.4; potassium dihydrogen phosphate, 0.04. The pH was adjusted to 2.0 with H_2SO_4 . Plates were incubated 3 weeks at room temperature. In other cases, solids were inoculated into Erlenmeyer flasks containing this medium with a lower concentration of ferrous sulfate (20 g/L).

Attempts were made to culture thiocyanate degrading bacteria in S7 medium at pH 6.6 (Hutchinson et al., 1965) in shake flasks incubated at room temperature with agitation at 160 rpm for up to three weeks. A low pH modification of this medium was made by reducing sodium phosphate to 0.025 g/L.

Weathering Tests of Mine Rock Treated with Thiocyanate and Phosphate

Rock samples were obtained from mining companies (Table 2). Material provided by Teck Cominco was a massive sulfide containing pyrite and sphalerite. Kennecott material was a weathered metamorphosed basalt (phyllite) containing quartz, sericite, pyrite, chlorite and dolomite. The rock was mined from a massive sulfide deposit and was exposed for 7 years.

Solid Energy material was a mixed mudstone sandstone from the Brunner Coal Measures derived from the Stockton mine site, New Zealand.

Table 2. Rock samples used in laboratory weathering tests

Supplier	% S	Major sulfide mineral	ANC ¹ , kg/t	NP ² /AP ³	Test cell	Particle size
Solid Energy (New Zealand)	0.70	Pyrite	0	0	Column	<12.7 mm
Kennecott	5.35	Pyrite	15	0.10	Humidity cell	<6.35 mm
Teck Cominco (Red Dog Mine)	9.1	Pyrite, sphalerite	0	0	Column	<12.7 mm

¹ANC, acid neutralizing capacity

²NP, neutralization potential

³AP, acid potential

The rock samples were crushed if necessary, screened and blended. Pulverized sub-samples were characterized for total S, sulfide-S, acid neutralizing capacity, and maximum potential acidity ($30.6 \times S$ content, Smart et al., 2002). Sample charges were agglomerated with 1) deionized water only (untreated control), 2) NaSCN solution (50 mg SCN/kg rock), or 3) NaSCN solution plus one of several forms of phosphate. Dosages and forms of phosphate are described in the results and discussion section. Agglomerated charges were loaded into glass columns (5 kg, 10 cm x 0.5 m) or plastic humidity cells (1 kg) for leaching tests. Columns were leached biweekly with deionized water or with NaSCN solution. Leachates were analyzed for ARD indicators including dissolved metals (by ICP spectroscopy), SO_4^{2-} (turbidimetric barium chloride method), acidity (by titration of boiled, peroxide treated samples), and pH, Eh and conductivity (APHA, 1992). Between leaching events columns and humidity cells were held at room temperature (Kennecott and Teck Cominco rock) or at 12°C to 14°C (Solid Energy rock). In the latter case, the reduced temperature approximated the cool climate at the mine site.

In most cases, laboratory columns and humidity cells received repeated application of NaSCN solution despite the fact that field application of thiocyanate would be done infrequently or perhaps only once. This scheme was necessary because solution application rates in laboratory accelerated weathering tests far exceed the equivalent yearly rainfall. Consequently, thiocyanate would be washed out of laboratory columns far faster than it would in the field. In order to understand the potential for thiocyanate inhibition of biocatalyzed ARD, or to determine whether combined thiocyanate and phosphate treatment reduces the abiotic rate of sulfide oxidation, it is necessary to conduct weathering tests where thiocyanate is uniformly distributed in waste rock. Once these factors are understood, achieving the proper conditions in the field becomes the next goal. This is a separate challenge that is best addressed by field tests.

Field Tests of Thiocyanate and Phosphate

Thiocyanate (60 g/t) and Dical (0.067 to 0.24 wt%) were applied to waste rock in 600 ton (545 mt) test pits at Red Dog mine in July, 2004. The waste rock was crushed to <7.6 cm and contained 4.8% Zn and 9.1% Fe occurring mainly as sphalerite and pyrite. Leach solution from test pits was collected in tanks and analyzed for ARD parameters to assess performance of chemical treatment compared to untreated controls. Results from the 2004 season sampling have been described (Mudder et al., 2005). Results to date in 2005 are described below.

Results and Discussion

Fate of Applied Thiocyanate

The dosage of water soluble NaSCN that is applied to waste rock must take into account its degradation, adsorption and wash out. These matters are discussed below.

Thiocyanate degradation. Thiocyanate degrades at a significant rate only under certain environmental conditions. It biodegrades under aerobic conditions at neutral to alkaline pH but does not biodegrade at pH values less than about 4 to 5 (Olson et al., 2003b). Abiotically at high redox potentials (>700 mV) spontaneous “autoreduction” of Fe^{+3} -SCN complexes occurs (Barbosa-Filho and Monhemius, 1994). In this reaction Fe^{+3} is reduced to Fe^{+2} and thiocyanate is oxidized, ultimately forming cyanate which hydrolyzes to produce ammonia and carbon dioxide. Such high redox potentials would be rare in environmental ARD situations, especially if SCN were applied to control biooxidation of iron. Consequently, SCN should be stable when applied at low pH. However, it was necessary to test this assumption. The rate of disappearance of SCN in artificial ARD solution containing equimolar concentrations of Fe^{+2} and Fe^{+3} sulfates at pH 2.0 was approximately 5%/year (Fig.1). A concentrated solution of NaSCN in deionized water (500 mg/L SCN) showed no loss of thiocyanate over this time period.

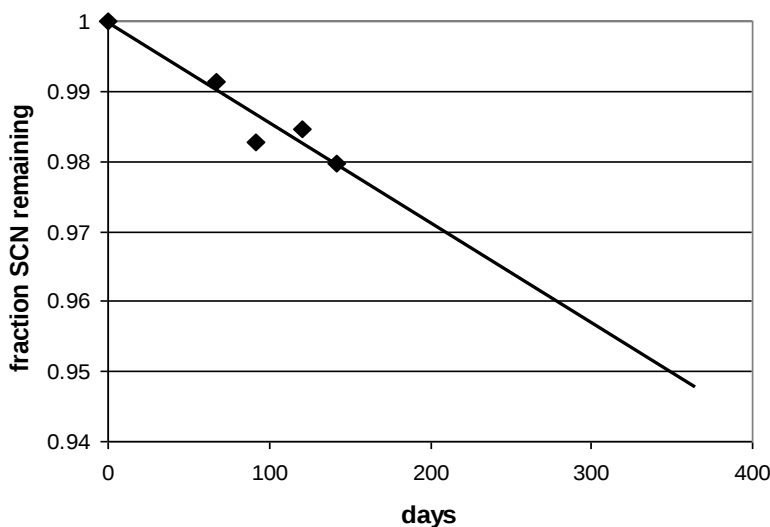


Figure 1. Persistence of thiocyanate in artificial ARD solution with least squares linear regression line forecasted one year.

Previously NH_4 was detected in leachates from SCN-treated columns and humidity cells at concentrations high enough to suggest significant SCN degradation (Olson et al., 2003a). This contradicts the observed stability of SCN at low pH (Fig. 1). Subsequently we determined that the colorimetric method to measure NH_4 (phenate method, Standard Methods, 1992) degrades SCN forming NH_4 . The extent of SCN degradation decreases with the age of the test reagents, while detection of NH_4 itself is not as affected by this factor. Therefore, this method of NH_4 analysis is not applicable to SCN-containing solutions. Sobolewski (1993) found apparent bioconversion (no microbiology was done) of SCN to NH_4 , measured potentiometrically in

acidic leachates from coal column tests. This analytical method would not be expected to convert SCN to NH_4 . Although SCN was initially effective in controlling ARD, its degradation led Sobolewski to conclude SCN would not be effective against ARD, at least in coal mining situations. Higher pH zones ($\text{pH} > 5$) may have occurred in the upper portions of the coal columns which could have supported growth of SCN-degrading bacteria.

Adsorption of thiocyanate to rock. As adsorbed thiocyanate is no longer toxic to Fe-oxidizing microorganisms it is important to quantify its adsorption in planning effective dosages. Short term (24 h) tests with Teck Cominco Red Dog Mine waste rock showed a linear correlation between particle size and amount of SCN adsorbed. After 24 h < 2.36 mm material adsorbed 35 mg SCN/kg, the 2.36 mm x 3.35 mm material 16 mg SCN/kg and the 6.35 x 12.7 mm material 7 mg SCN/kg.

Longer tests with < 12.7 mm rock showed Langmuir-type adsorption kinetics, adsorbing 51 mg SCN/kg after 19 days. These results compare closely with the 48 mg SCN adsorbed/kg of Red Dog waste rock observed in the previous small column tests with finely ground material (Little Bear Laboratories, Inc., 2003). Adsorption of SCN to < 7.6 cm waste rock in three test pits at Red Dog mine over a one year period of time amounted to 47, 50, and 51 mg SCN/kg, based on subtracting the mass of SCN collected in leachates from the mass of SCN originally applied. At least with this material, lab tests with finely ground material predict adsorption to coarser rock, which takes much longer to occur.

The Red Dog rock adsorbed much higher amounts of SCN than previously observed (Little Bear Laboratories, Inc., 2003) with a porphyry Cu tailing (8.4 mg/kg) and a Carlin-type refractory Au ore (7.6 mg/kg). The nature of SCN binding to Red Dog waste rock is not known, but it appears not to involve pyrite or sphalerite as a flotation concentrate enriched in these minerals did not adsorb higher concentrations of SCN than did waste rock.

Thiocyanate adsorption tests were not performed with New Zealand waste rock. Mass balance calculations from column tests with this material (described below) indicated SCN adsorption of 19 mg/kg to 46 mg/kg, depending on treatments.

Thiocyanate washout. Washout of water soluble NaSCN may be problematic if it is applied without proper water management to reduce rainfall infiltration. An environmentally acceptable slow release form of SCN would reduce washout and protect SCN from biodegradation if applied to neutral pH environments. Copper thiocyanate is a model controlled release form of SCN as it is insoluble in water but soluble in acidic, oxidizing (i.e., ARD) solutions (Olson et al., 2003a). However, in most situations the release of copper would be objectionable.

Comparison of Phosphate Sources for Application Against ARD: ANC Tests

In order to compare various phosphate sources for use against ARD, we measured the neutralization of proton acidity as well as precipitation of Fe^{+3} and Al^{+3} phosphates. Conventional ANC tests react a slurry of pulverized rock with acid followed by back titration to neutral pH to determine the acid consumption of the material (Smart et al., 2002). This methodology must be modified for phosphate-containing materials. An artificial ARD solution was devised, composed of dilute H_2SO_4 and Fe^{+3} and Al^{+3} sulfates. ANC of phosphates using this solution was much higher than in a conventional ANC test (Table 3). Multifos[®] had the highest ANC of the materials shown in Table 2. Even higher ANC values resulted when the pH was brought only to 4.6 which is near the minimal solubility of Al and Fe phosphates. At this

pH phosphate in solution occurs as H_2PO_4^- . Further neutralization to pH 7 consumes base as this species converts to $\text{HPO}_4^{2-} + \text{H}^+$.

Table 3. Acid consumption of phosphate materials by conventional and modified ANC tests.

Phosphate	Conventional ANC kg H_2SO_4 /t	Modified ANC kg H_2SO_4 /t	Modified ANC to pH 4.6 kg H_2SO_4 /t
Florida phosphate rock	94	353	407
N. Carolina phosphate rock	312	448	475
Togo phosphate rock	130	309	348
Dicalcium phosphate	negative	228	289
Multifos [®]	278	478	534

Duplicate tests done in the absence of phosphates required 37.6 and 38.1 meq NaOH to bring 100 mL of artificial ARD solution to neutrality. This is 92% to 93% of the theoretical 41 meq required assuming 3 mmol H^+ formed/mmol Fe or Al by hydrolysis.

Reaction of phosphates may have been incomplete after 24 h as high purity reagent tribasic calcium phosphate (Trical, 98% <63 μm) had an ANC of 784 kg H_2SO_4 /t (to pH 4.5) which is only 80% of theoretical.

After 24 h of contact time between artificial ARD solution and phosphates and prior to neutralization, Fe had precipitated to various extents depending on the source of phosphate (Table 4). Only N. Carolina phosphate pebble and Multifos[®], showed loss of dissolved Al after 24 hours in artificial ARD. AlPO_4 is more soluble than FePO_4 at low pH, accounting for the lower removal of Al from solution. Dissolved P was present in solution in all phosphate-containing tests at these pH values. Dissolved P was highest with Dical reflecting the solubility of its $\text{Ca}(\text{H}_2\text{PO}_4)_2$ component.

Table 4. Concentration of dissolved metals and P (mg/L) in modified ANC tests

phosphate	---After 24 h in artificial ARD---				NaOH added to pH 4.6			Neutralized to pH 6.9		
	pH	Fe	Al	P	Fe	Al	P	Fe	Al	P
None (control)	1.7	3430	1781	<1.0	3.6	104	<1.0	3.1	32	<1.0
Florida	2.0	939	1837	231	5.8	258	<1.0	1.2	27	<1.0
North Carolina	2.6	810	1670	83	13.0	176	<1.0	1.6	33	<1.0
Togo	1.9	1615	1804	400	2.1	208	<1.0	1.7	31	<1.0
Dical	1.8	1289	1820	1964	1.7	33	9.3	19.2	41	23.8
Multifos [®]	2.2	129	1485	508	17.1	84	9.4	5.0	61	<1.0

Loss of Al and Fe from solution when NaOH was added to the control flask to bring the pH to 4.6 and to 6.9 (Table 4) probably reflects their precipitation as hydroxides. Upon neutralization, flasks containing the phosphates also precipitated Fe and Al, probably as phosphates and as hydroxides. However, no dissolved P was detected except in the case of Multifos[®] at pH 4.6 and Dical at both pH values. The higher dissolved Al, Fe and P content with Dical at pH 6.9 may reflect the higher solubility of Fe and Al phosphates at pH 6.9 as compared to pH 4.6 and that a higher fraction of Fe and Al precipitated as phosphates with this material.

The combined content of Fe and Al in 100 mL of artificial ARD solution (12 mmol) if all precipitated as phosphate would require 372 mg P, or 18.6% of the mass of the 2.00 g charge of phosphate solids. Only Dical and Multifos[®] contain this amount of P (Table 1). The remaining samples could not supply enough P to precipitate all the metals.

Weathering Tests of Solid Energy Rock Treated with Thiocyanate and Phosphate

This waste rock contains relatively low S content (0.70%) but has almost no acid neutralizing capacity. Weathering tests compared untreated rock, NaSCN treated rock and rock treated with NaSCN plus Florida phosphate rock, North Carolina phosphate rock or dicalcium phosphate (Table 5). Biweekly leach solution was deionized water (untreated rock) or 100 mg SCN/L (as NaSCN) solution (all others).

Table 5. Treatments of Solid Energy waste rock in column weathering tests and corresponding reductions in SO_4^{2-} leaching rate (wks 4 to 12), metal leaching and acidity production (first 16 weeks).

Initial treatment	Sulfate leach rate, mg/kg/wk (% of control)	acidity, cum. g (% of control)	Fe, cum. g (% of control)	Al, cum. g (% of control)
Untreated	356 (100%)	28.5 (100%)	5.2 (100%)	1.9 (100%)
NaSCN (50 mg/kg)	52 (15%)	12.0 (42%)	1.6 (30%)	1.2 (65%)
NaSCN (50 mg SCN/kg) low irrigation ¹	54 (15%)	8.9 (32%)	0.98 (19%)	1.0 (54%)
NaSCN (50 mg/kg) + Florida PR (1wt%)	50 (14%)	4.4 (15%)	0.18 (4%)	0.59 (32%)
NaSCN (50 mg/kg) + NC PR (1 wt%)	44 (12%)	1.0 (4%)	0.02 (0.4%)	0.09 (5%)
NaSCN (50 mg/kg) + Dical (0.25 wt%)	65 (18%)	6.2 (22%)	0.17 (3%)	0.79 (43%)

¹ irrigation rate 20% that of other columns, leach rate is for first 24 weeks

The SO_4^{2-} production rate was taken as the sulfide oxidation rate and was 356 mg/kg/wk in the untreated column (Table 5), corresponding to 1.7% of S/wk. The leachate pH declined to 1.6 (Fig. 2) and the Eh increased to over 800 mV (SHE) after a few leach cycles. Large numbers of iron-oxidizing microorganisms ($>2.4 \times 10^4/\text{mL}$) were detected by most probable number determination on a leachate sample from the untreated column. These results indicated significant biooxidation was occurring, even at comparatively cool temperatures of 12°C to 14°C.

Thiocyanate treatment alone reduced the SO_4^{2-} production rate by 85%. As no viable Fe oxidizing microorganisms were detected in leach solution or solids from this column this rate represented the abiotic rate of sulfide oxidation of this waste rock under the testing conditions. The leachate pH was somewhat higher than in the untreated column but was still fairly acidic (Fig. 2).

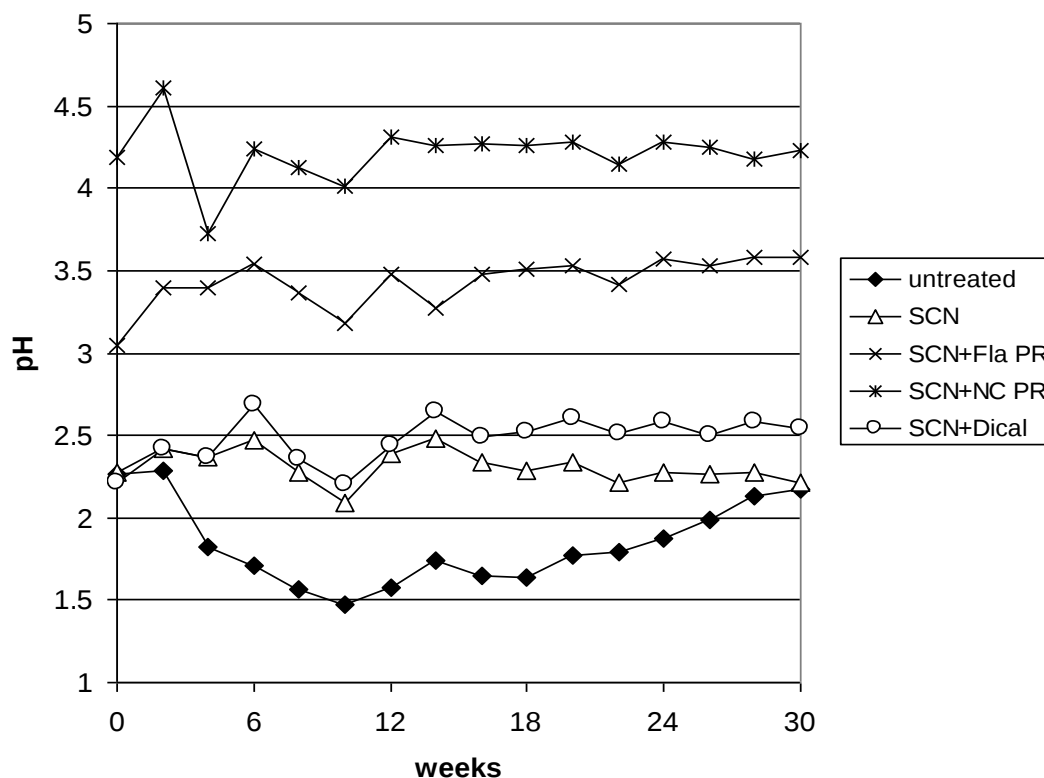


Figure 2. pH in biweekly leachates from columns containing New Zealand waste rock. The untreated column was leached with NaSCN solution beginning in wk 18.

Nearly identical reduction in ARD occurred in a column that received NaSCN (50 mg SCN/kg) only initially and that was leached with deionized water only at 20% of the irrigation rate of the other columns to more closely approximate local precipitation at the mine (Table 5). The low SO_4^{2-} leaching rates persisted for 24 weeks until thiocyanate in leachates declined to less than 5 mg/L after which time ARD indicators in column leachates began to increase. This indicates little or no biooxidation of sulfides occurred for nearly 6 months, despite the fact that thiocyanate had been applied only initially. During this time a total of 1.05 liters of water had been applied, amounting to 0.455 m^3 of water/tonne of waste rock/year. Although this corresponds to a modest 26 cm annual “rainfall” on the shallow 10.5 cm diameter x 0.5 m tall column, it is more realistic to calculate “rainfall” on a mass basis. At a rock density of 1.3 this would correspond to 5.9 meters of rainfall/year falling on a 10 m tall pile of waste rock. A single thiocyanate treatment of this waste rock is effective in preventing biooxidation for a much longer period of time than was observed with the Red Dog material, perhaps due in part to lower adsorption of thiocyanate.

Treatment of waste rock with NaSCN plus phosphate (Dical or phosphate rock) did not further reduce the abiotic sulfide oxidation rate (Table 5). This indicates armoring of the pyrite by formation of a FePO_4 coating had not occurred. Leachate pH values from the column treated with thiocyanate plus Dical were only slightly less acidic than with thiocyanate treatment only, reflecting the acidic character of Dical. Phosphate rock has higher acid neutralizing capacity and

leachates from columns treated with thiocyanate and Florida or North Carolina phosphate rock were much less acidic (Fig. 2).

Though the abiotic rate of sulfide oxidation was not reduced by phosphate, treatment of rock with NaSCN plus phosphate significantly reduced leaching of iron and aluminum compared to NaSCN treatment alone (Table 5). The combined effects of metal removal and acid neutralization by phosphate is shown by acidity reductions of up to 96% compared to the untreated control (Table 5).

The untreated column began receiving biweekly leaching with 100 mg/L SCN solution in week 18 to determine the effectiveness of SCN against ongoing ARD. This treatment resulted in the redox potential in leachates decreasing to 650 mV by the end of the test (week 30) and the SO_4^{-2} leaching rate declining to 26 mg/kg/wk over the last 8 weeks of the test. No viable Fe oxidizing microorganisms could be cultured from surficial solids at the end of the test, indicating SCN was lethal even to established, attached microbial populations.

No SCN degrading bacteria could be cultured from solids (2 to 3 g) from any of the columns inoculated into SCN liquid medium at pH 6.6 (week 18) or at pH 4.7 (week 20). These results are consistent with our past observations that SCN degrading microorganisms do not grow under acidic conditions (Olson et al., 2003b).

The results with combined NaSCN and phosphate treatment of New Zealand waste rock indicate that source control of abiotic sulfide oxidation was not achieved with phosphate under the conditions of the test. Rather, phosphate acted as an in-place chemical treatment for ARD. Although the underlying rate of sulfide oxidation was not altered by phosphate, significant reductions in leaching of metals occurred through acid neutralization and precipitation of Fe and Al phosphates. This reduction would substantially reduce ARD water treatment costs (Olson et al., 2005).

Weathering of Kennecott Rock

This material contained more sulfur (5.3%) than New Zealand rock but also contained acid neutralizing material in the form of dolomite. Weathering tests compared untreated rock to rock treated with NaSCN or with NaSCN plus various sources of phosphate (Table 6). Initial leachates from this rock were acidic (pH ca. 2.1), reflecting the weathered nature of the sample.

Table 6. Treatments of Kennecott rock in humidity cells and corresponding reductions in SO_4^{-2} leaching rates.

Initial treatment	Sulfate leach rate, mg/kg/wk (% of control)
Untreated (mean of duplicates)	977 (100%)
NaSCN (50 mg SCN/kg, mean of duplicates)	78 (8%)
NaSCN (50 mg/kg) + Florida PR (0.5wt%)	87 (9%)
(2.0 wt%)	71 (7%)
NaSCN (50 mg/kg) + consolidated clay (0.5 wt%)	90 (9%)
(2 wt%)	105 (11%)
NaSCN (50 mg/kg) + Dical (0.10 wt%)	100 (10%)
(0.50 wt%)	70 (7%)
NaSCN (50 mg/kg) + Trical (0.5 wt%)	121 (12%)
(1.0 wt%)	78 (8%)

Leachates from humidity cells loaded with untreated rock remained highly acidic while leachates from rock treated with only NaSCN gradually increased to pH 3.5 to 4.0 over several leach cycles (Fig. 3). Apparently, inhibition of biooxidation allowed the dolomite to buffer acid production from abiotic sulfide oxidation. Somewhat higher leachate pH values were observed with rock treated with NaSCN plus phosphates.

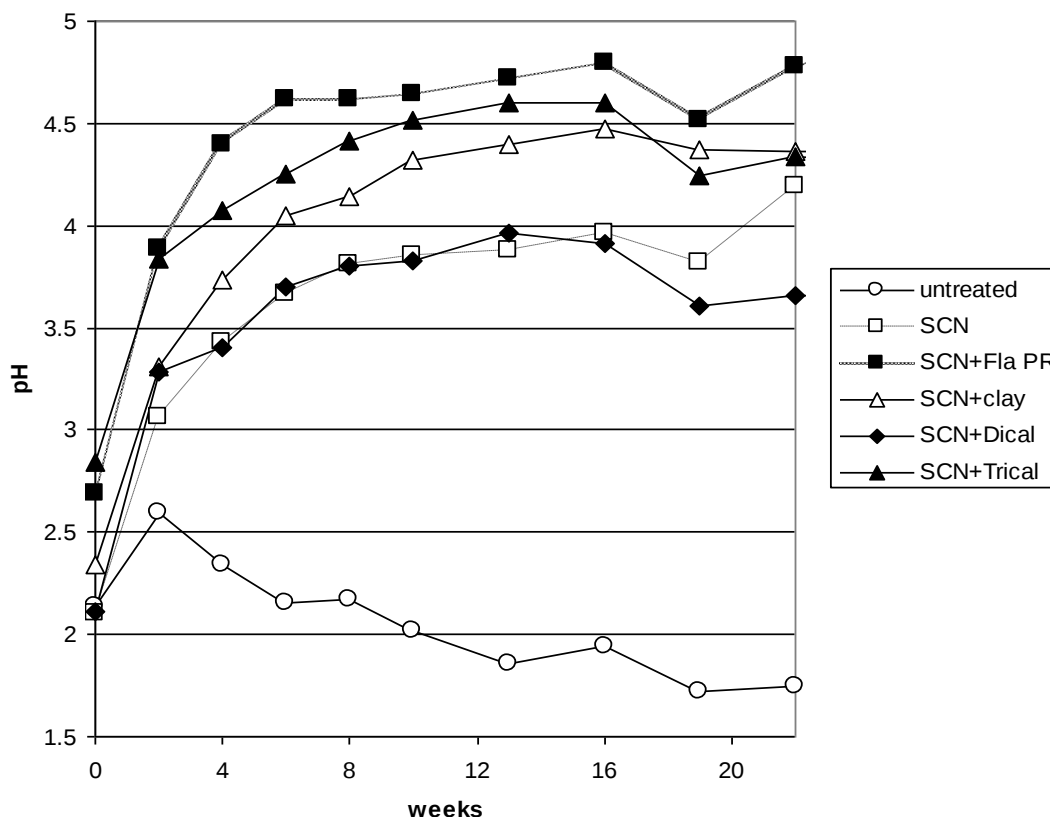


Figure 3. pH in leachates from humidity cells containing Kennecott rock. Results with higher dosages of phosphates (Table 6) only are shown.

None of the SO_4^{-2} leaching rates with combined NaSCN and phosphate treatments were reduced significantly beyond that with NaSCN alone (Table 6), as was observed with the New Zealand waste rock. This again indicates the abiotic rate of sulfide oxidation was not slowed by phosphate.

Very little Fe was leached from any of the treated rock samples; acidity in the week 22 leachates was reduced over 99% in all treatments compared to the controls.

Some of the humidity cells after 22 weeks were treated with NaSCN and soluble phosphate in an attempt to form FePO_4 coatings thereby reducing the abiotic rate of SO_4^{-2} production. The approach aimed to produce FePO_4 on the pyrite surfaces by providing 1) soluble phosphate, 2) a pH suitable for FePO_4 armoring (pH 3.0 or higher, Evangelou, 1995) and 3) Fe^{+3} either in the exopolymers of attached Fe-oxidizing bacteria (in previously untreated humidity cells) or from peroxide oxidation (in previously treated humidity cells).

These conditions were achieved by leaching a control (untreated) humidity cell with 100 mg/L SCN (as NaSCN) solution to stop biooxidation of Fe, followed by leaching with 0.01M sodium phosphate buffer (pH 5.2) until a leachate pH of 4.1 to 4.2 was achieved. A cream-colored precipitate formed in the void spaces. A sample of this precipitate was dissolved in acid and had a Fe and P composition consistent with FePO_4 dihydrate. The SO_4^{2-} leaching rate over weeks 25-34 following the NaSCN-phosphate buffer treatment was 38.5 mg/kg/week, or 3.9% of the rate of the untreated rock (Table 6).

A second humidity cell previously treated with NaSCN was treated with sodium phosphate buffer (pH 4.4) containing 6% H_2O_2 . The SO_4^{2-} leaching rate following this treatment was 39.6 mg/kg/wk.

These SO_4^{2-} leaching rates were lower than the abiotic rates in the other tests during weeks 8 to 22 (Table 6) or the 60 to 83 mg/kg/wk observed in these tests that continued concurrently with the armoring tests. This is indirect evidence for armoring. Scanning electron microscopy to confirm possible FePO_4 formation was not performed due to the complex nature of the mineral samples in the humidity cells.

It should also be mentioned that duplicate tests with each of these armoring treatments exhibited poor draining (“perched” buffer solution in the humidity cells) and less efficient contact of the solutions with the solids. The subsequent SO_4^{2-} leaching rates in these humidity cells were higher, 64 and 51 mg/kg/wk, and at the low end of the range of the abiotic rates above.

Weathering of Teck Cominco Waste Rock: Lab and Field Tests

Earlier lab test work with this high sulfide waste rock showed a combination of NaSCN and either phosphate rock (2.0 wt%) or Dical (0.5 wt%) reduced SO_4^{2-} leaching beyond that achieved with NaSCN alone (Olson et al., 2004). NaSCN plus Dical was especially effective, reducing the abiotic sulfide oxidation rate by 71%. Test pits containing 600 short tons (545 mt) of this waste rock at the mine were treated with NaSCN (60 g/mt) and NaSCN plus Dical (0.067 wt% or 0.24 wt%) in summer 2004. NaSCN treatment reduced the SO_4^{2-} leaching rate by 31% and combined NaSCN plus Dical treatment reduced it by 53% to 68%, after rinse out of soluble salts in the first few weeks (Mudder et al., 2005).

The pH values in the treated test pits were initially near or above 3.0 but declined to pH 2.3 to 2.4 by the end of summer 2004. Phosphorus began appearing in leachates from the test pit treated with SCN plus Dical (0.24 wt %) as the pH declined to 2.7 and lower. The increasing acidity apparently was dissolving precipitated FePO_4 . Leachate samples collected in 2005 from all test pits remained at pH values less than 2.5.

Sulfate and other ARD parameters increased in chemically treated test pits in 2005. By this time the initial thiocyanate treatment had been rinsed out by rainfall and also had been adsorbed by the rock. Consequently, biocatalyzed sulfide oxidation increased as large numbers of iron-oxidizing microorganisms ($>2.4 \times 10^6/\text{mL}$) were detected in leachates from these test pits. Of the 32.5 kg SCN applied, 4.5 to 6.4 kg (14% to 20%) was detected in leachates. Assuming no degradation, 26 to 28 kg remained adsorbed to rock in the test pits. This amounted to 48 to 51 g/kg, matching lab test results of amount of SCN adsorption by this rock as described above. Adsorbed SCN is no longer toxic to Fe-oxidizing microorganisms.

The performance of chemical treatment in ARD control already was declining in the final solution samples collected in 2004, despite the presence of over 100 mg/L SCN. Apparently,

SCN had washed out of upper portions the test pits and allowed reestablishment of biooxidation. The trend continued over the winter as *in situ* temperatures, initially cooler in treated pits compared to untreated test pits in summer 2004, became warmer in treated pits in autumn and winter 2004-2005.

Another factor to be considered with this waste rock is the need to use a form of phosphate with higher acid neutralizing capacity than Dical, such as Multifos[®] (Table 3). Test pit leachates with NaSCN plus Dical were consistently more acidic (pH 2.8 to 3.2) than those in column tests (pH 3.6), perhaps due to the higher solution application rate to lab columns, resulting more dilute leach solutions. Consequently, a second set of lab column tests was performed with waste rock treated with NaSCN plus Multifos[®] or with NaSCN plus Multifos[®] and Dical.

Leach solutions from untreated (control) waste rock became more acidic and oxidizing than solutions from rock treated with NaSCN plus phosphate (Fig. 4). The SO₄⁻² leach rate from untreated columns was 462 mg/kg/wk compared to 105 mg/kg/wk and 111 mg/kg/wk in columns initially treated with NaSCN plus Multifos[®] and NaSCN plus Multifos[®] and Dical, respectively.

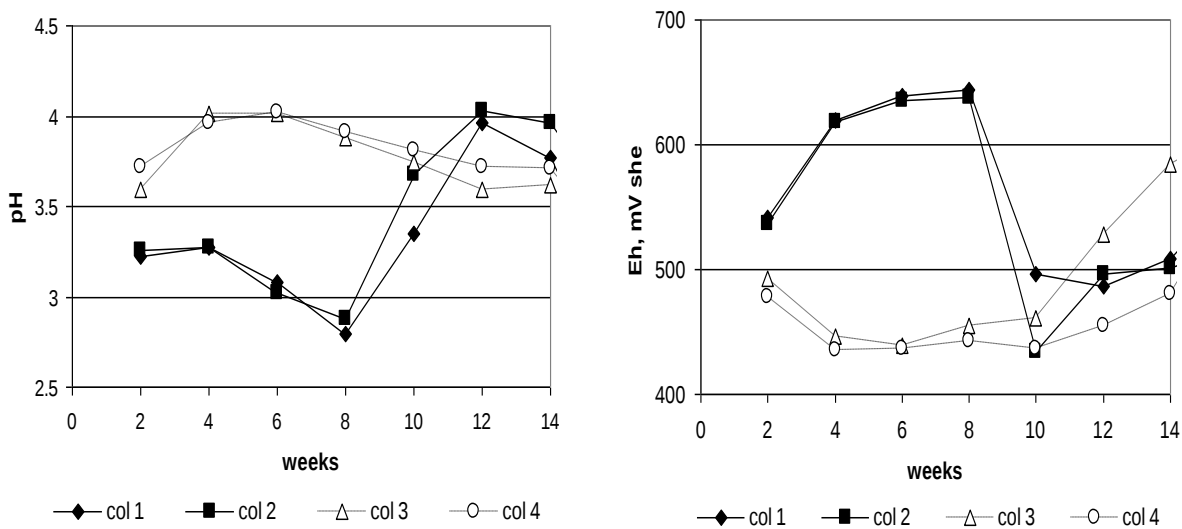


Figure 4. Leachate pH and redox potential changes in column tests with Teck Cominco waste rock. Columns 1 and 2 were untreated until just prior to week 10 sampling when they were emptied, blended with NaSCN (50 mg/kg) and Multifos[®] (0.5 wt. %, col. 1) or with NaSCN plus Multifos[®] (0.4 wt. %) and Dical (0.1 wt. %, col. 2), then refilled. These columns were leached with water only. Columns 3 and 4 were initially blended with NaSCN plus Multifos[®] (col. 3) or NaSCN plus Multifos[®] and Dical (col. 4). These columns were leached with 100 mg/L SCN (as NaSCN) in weeks 4, 6 and 8 and with deionized water in subsequent weeks.

Treatment of the control columns in week 10 with NaSCN and phosphate resulted in leachates with increased pH and decreased Eh. The combined Dical and Multifos[®] treatment resulted in leachates with detectable phosphorus and correspondingly lower concentrations of dissolved iron than treatment with Multifos[®] alone.

Leachates from columns initially treated with NaSCN plus phosphate showed increased Eh and ARD formation in the weeks following discontinuance of NaSCN application, as was observed in test pits. The results indicate a blend of Dical and Multifos[®], combining the soluble phosphate of the former and the acid neutralizing capacity of the latter, together with NaSCN treatment, may be more beneficial than Dical alone in control of ARD production from this waste rock.

Summary and Outlook

Thiocyanate controls the biotic component of ARD by arresting biooxidation of Fe. Even at cool temperatures (12°C to 14°C) biooxidation of Fe may be significant. Consequently, if efficiently applied, thiocyanate reduces the rate of sulfide oxidation to that of abiotic processes only.

Thiocyanate as NaSCN applied to waste rock at low pH (<4) degrades only very slowly with a half life on the order of years. Thiocyanate adsorption occurs and must be accounted for in determining chemical dosages. Red Dog waste rock adsorbed as much as 50 mg SCN/kg. The extent of adsorption can be predicted from laboratory tests. Efforts are being directed toward development of slow- or controlled-release form of thiocyanate. In the meantime, thiocyanate should be applied using technical approaches that minimize washout of the chemical in combination with other well proven disposal techniques such as surface water diversion and physical compaction to reduce infiltration. A slow- or controlled-release form of thiocyanate would also minimize biodegradation if it is applied to near neutral pH mine wastes.

Treatment of sulfidic waste rock with combined NaSCN and phosphate in one of several forms available in bulk can reduce the rate of sulfide oxidation beyond that of NaSCN treatment alone. This further reduction with phosphate is due to neutralization of acid and precipitation of FePO₄ which removes Fe⁺³ oxidant, avoids production of Lewis acidity upon neutralization and, ideally, coats and armors metal sulfide surfaces. Conditions for coating formation probably require Fe⁺³ iron at the surface of the mineral, adequate soluble phosphate and the correct pH (Evangelou, 1996). If the pH is too low (i.e., <3) soluble phosphate treatment is ineffective because precipitation of FePO₄ is reduced and existing FePO₄ precipitates are destabilized. Consequently, co-treatment with NaSCN is required to prevent the severe low pH produced by biooxidation of pyrite. Coating was not evident (abiotic sulfide oxidation rates were not lower) when sulfidic waste rock was simply mixed with phosphate sources and NaSCN and then weathered, even at pH values above 3.0. However, abiotic sulfide oxidation rates were lower following treatment of Kennecott rock with soluble phosphate at pH 4 and with Fe⁺³ ions presumably supplied by Fe oxidizing bacteria or by H₂O₂.

Proper combinations of acid neutralizing phosphate (e.g., tribasic calcium phosphate) and acidic, soluble phosphate (e.g., dicalcium phosphate) may provide adequate dissolved phosphate at the correct pH. Current research efforts are aimed at better defining conditions for armoring sulfide minerals through precipitation of iron phosphate coatings and characterizing their chemical nature.

Under the proper situations combined phosphate and thiocyanate treatment of sulfidic materials to reduce ARD can be accomplished using chemicals obtained in bulk quantities from existing suppliers. If the phosphate and thiocyanate can be maintained within the fresh sulfide containing materials the onset of ARD can be restricted. This requires a comprehensive plan for

waste management that includes physical compaction and water management to minimize infiltration, which should be part of any proper waste management plan regardless of chemical addition. The reduced inhibition of ARD in our field test at Red Dog compared to the lab studies is reflected in the fact essentially no attempt was made to restrict water infiltration and movement through the waste material. Furthermore, this waste rock was an extremely challenging situation for ARD control as it contained very high sulfide content, much of it in the form of easily oxidized sphalerite, and exhibited very high thiocyanate adsorption. ARD is expected to be easier to control with thiocyanate and phosphate in most other types of waste rock where pyrite is the dominant sulfide mineral and thiocyanate adsorption is not abnormally high.

Consideration also must be given to leaching of phosphate and thiocyanate into receiving waters (Olson et al., 2005). Environmental controls to limit the relatively non-toxic thiocyanate and phosphate from entering the environment in drainage or seepage can be applied if needed. Clearly, the impacts of these constituents on the environment are far less than low pH solutions containing elevated levels of potentially toxic metals.

Ultimately, the more widespread application of this technology may require products that combine thiocyanate and phosphates in slow release forms, to simplify application, reduce costs and to minimize runoff of these chemicals into surrounding environments.

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