

Acid Rock Drainage (ARD) Inhibition by Sulfite Used as Part of the Inco Process for Cyanide Removal

Leslie Hardy and Paul Morton
AMEC Foster Wheeler Environment & Infrastructure, Canada

ABSTRACT

Calcium sulfite (CaSO_3) has been used as an ARD inhibitor at coal ash sites for over a decade. Sulfite is considered a redox buffer and oxygen scavenger because it readily oxidizes to sulfate. Site history at a gold mine in Canada indicates sulfite can persist for decades in saturated mine tailings and inhibit the onset of ARD.

Sodium metabisulfite (SMBS, $\text{Na}_2\text{S}_2\text{O}_5$) was used as part of the Inco process to treat cyanide in 300,000 tonnes of tailings. A mass balance was developed for nitrogen, sodium, calcium and sulfur. The mass of reagents used is consistent with the mass discharging in water from the tailings, and the percentage of nitrogen discharged is lower than the other elements. Most of the nitrogen added as cyanide remains sorbed to the tailings as strong acid dissociable cyanides such as iron-cyanide complexes, and nitrogen gas is formed by biodegradation of cyanide and ammonia.

This paper discusses why the mine tailings have not become acidic as expected based on acid-base accounting or humidity cell results. The mill used approximately 270 tonnes of SMBS to treat 100,000 tonnes per year of tailings, giving a concentration of approximately 900 mg/kg as sulfur or 2,250 mg/kg as sulfite. Sulfite readily oxidizes to sulfate on exposure to air, and the ion chromatography laboratory method does not routinely distinguish sulfite from sulfate. The water concentrations reported as sulfate may actually be a combination of sulfite and sulfate. Sulfite contributes to titratable alkalinity, and the measured alkalinity versus total inorganic carbon indicates the continued presence of sulfite. Calcium sulfite has a much lower solubility than SMBS, and calcium from the lime used in the Inco process prevents depletion of sulfite from the tailings. Field observations and humidity cell results indicate that calcium sulfite in the tailings inhibits the onset of acid rock drainage.

Keywords: sulfite, sodium metabisulfite, INCO process, cyanide, acid rock drainage

INTRODUCTION

A gold mine in Canada used sodium cyanide and a carbon in pulp process to recover gold and the Inco process to remove cyanide from the effluent. The mine processed 100,000 tonnes of ore per year for three years, and the resulting 300,000 tonnes of tailings is impounded on permafrost ground behind a tailings dam constructed across a creek bed. Based on the 2% sulfide content of the tailings and some of the humidity cell test results, the tailings are predicted to create acid rock drainage. Mining and milling activities ceased in the 1990s, and most of the tailings porewater continues to have a high pH, with only preliminary indications of acid rock drainage.

Groundwater and surface water monitoring commenced in 1999, including the flow rate and chemistry of the toe seepage and decant water from the tailings impoundment. In recent years, the flow rate has increased and a conceptual remediation plan has identified that tailings relocation could be required. Based on recent monitoring data and information presented in previous reports, a revised interpretation of the mine tailings geochemistry was developed.

The hypothesis presented in this paper is that the onset of acid rock drainage is inhibited by sulfite which was added to the tailings at a concentration of 2,250 mg/kg as part of the Inco process to remove cyanide from the tailings. The inhibition of the onset of ARD by calcium sulfite was first reported by Hao and Dick (2000) who completed laboratory experiments to evaluate the geochemical mechanism. This paper presents field evidence for ARD inhibition, and is apparently the first reported observation of sulfite inhibiting the onset of ARD at a mine site.

INCO PROCESS DESCRIPTION

The mill used the Inco SO₂/ Air process to oxidize cyanide in the tailings and tailings water prior to storage in the tailings pond. The following discussion about the Inco process is primarily based on Mudder, Botz & Smith, 2001, and Breuer, Jeffery & Meakin, 2011. This process description leads to an accounting of the mass of reactants used at the mill versus measured values in the tailings decant and toe seepage water.

The Inco process is based upon conversion of free cyanide and weak acid dissociable (WAD) cyanide complexes to cyanate using a mixture of sulfur dioxide (SO₂) and air in the presence of a soluble copper catalyst at a controlled pH. The specific amounts of reagents used vary between mine sites, and this mine used sodium metabisulfite (Na₂S₂O₅) in a liquid solution.

When the Inco process is applied to tailings liquids (i.e. homogeneous systems in chemistry terminology) all of the free cyanide and WAD-cyanide is converted to cyanate (i.e. it is stoichiometrically converted; see Breuer, Jeffery & Meakin, 2011). However, cyanide reacts very strongly with iron on tailings solids to form strong acid dissociable (SAD) iron-cyanide complexes which are not affected by the Inco process. When the Inco process is applied to tailings slurries (i.e. heterogeneous systems), most of the cyanide remains sorbed to the tailings solids as SAD-complexes. Residual metals liberated from the WAD-cyanide complexes are precipitated as hydroxides. Therefore, the Inco process oxidizes free cyanide and WAD-cyanides to the less toxic form of cyanate, but most of the cyanide remains complexed onto iron in the tailings as SAD-cyanides.

Table 1 summarizes the annual reagent usage listed in a design document for the mine.

Table 1 Design reagent usage at mill

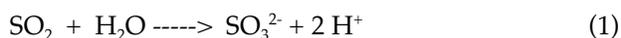
Reagent	Formula	Design Consumption Rate (kg/tonne)	Mine Lifetime Usage (tonnes)
Sodium Cyanide	NaCN	1	300
Lime	CaO	4.6	1,400
Sodium Hydroxide	NaOH	0.18	54

Hydrochloric acid	HCl	0.18	54
Copper Sulfate	CuSO ₄ *5H ₂ O	0.27	81
Sodium Metabisulfite	Na ₂ S ₂ O ₅	2.7	810

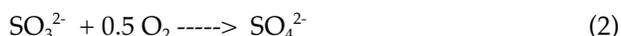
The design usage of sulfur dioxide (3.6 g/g CN), lime (8.7 g/g CN) and copper (0.13 g/g CN) is consistent with the average data presented for twelve mine sites in Mudder, Botz & Smith, 2001. The average usage is: sulfur dioxide (4.8 g/g CN), lime (3.7 g/g CN), and copper (0.1 g/g CN). The theoretical usage of SO₂ in the process is 2.46 grams of SO₂ per gram of WAD-cyanide oxidized, but in practice the actual usage ranges from about 3.0 to 5.0 grams of SO₂ per gram of WAD- cyanide oxidized. Based on the design document for the mill and the reviewed literature, the amount of reagents used at the mine is consistent with other mine sites.

Sulfite

The Inco process has been described as using sulfur dioxide, although Breuer, Jeffery & Meakin, 2011 state that the active reagent is actually sulfite which forms when SO₂ hydrates as shown in equation 1.



Sulfite (SO₃²⁻) is a redox buffer and oxygen scavenger because it readily oxidizes to sulfate according to equation 2.



As presented by Hao and Dick, 2000, sulfite consumes oxygen by the oxidation to sulfate according to equation 2, and this prevents the aerobic oxidation of pyrite which is the first step in the formation of acid rock drainage. Warren Dick (personal communication, 2013) stated that sulfite recovered from flue gas desulfurization at coal fired power plants has been co-disposed with pyrite bearing coal ash at several sites in the Ohio, USA, region, and more than a decade of monitoring data indicates that the sulfite is inhibiting the onset of acid rock drainage. The oxidation of sulfite to sulfate occurs slowly at low temperatures, high pH and water saturated conditions (which limits oxygen influx to the tailings), and the continued presence of sulfite in the tailings after two decades would be expected under the site conditions. However, sulfite in water samples cannot be preserved, and would be expected to readily oxidize to sulfate according to equation 2.

The source of sulfite used in the Inco process can be gaseous or liquid SO₂, sodium sulfite, or sodium metabisulfite (SMBS). This mine used SMBS based on cost and reagent handling considerations. Solid SMBS is made by evaporating a sodium sulfite solution, and when added to water, the bisulfite ion converts to sulfite. Table 2 summarizes the approximate aqueous solubility of various forms of sulfite.

Table 2 Aqueous solubility of various sulfites

Form of sulfite	Aqueous solubility (mg/L)
Sodium metabisulfite	450,000
Sodium sulfite	270,000
Magnesium sulfite	5,000
Calcium sulfite	54

SMBS and sodium sulfite are highly soluble in water, but calcium sulfite is orders of magnitude less soluble. Therefore, in the presence of high calcium concentrations in groundwater, sulfite will tend to precipitate as calcium sulfite and this is a constraint on the concentration of sulfite in water at the mine. In the tailings area, calcium is primarily derived from the 'lime' (CaO, also known as quicklime) used to control the pH for the Inco process. If calcium was not present in the tailings

water, the concentration of sulfite in the discharge would have been much higher, and the source would have been depleted more quickly.

High concentration aqueous sulfite solutions have a pH of about 9, and unlike sulfate (SO_4^{2-}), sulfite (SO_3^{2-}) can contribute to acid titrable alkalinity. The equilibrium pH point between SO_3^{2-} and HSO_3^- (i.e. the pKa) is 7.17, and when titrated to the standard alkalinity titration endpoint of pH = 4.5, sulfite buffers the addition of acid and contributes to the measured total alkalinity. Sulfate does not contribute to measurements of alkalinity because the pKa of SO_4^{2-} and HSO_4^- is 1.99 and alkalinity titrations only extend to an endpoint pH of 4.5. Therefore, in addition to carbonate alkalinity, as measured separately by total inorganic carbon (TIC), sulfite also contributes to total alkalinity. The potential contribution of sulfite is not explicitly recognized in textbook definitions of alkalinity, although weak acids such as sulfurous acid (H_2SO_3) can contribute to total alkalinity.

METHODOLOGY

Surface water and groundwater sampling commenced at this mine in the 1990s. Tailings decant and toe seepage water samples have been collected approximately every three weeks (271 samples in 14 years) and analyzed for a comprehensive suite of analytical parameters including pH, alkalinity, chloride, sulfate, sulfide, metals, ammonia, nitrate, nitrite, and cyanides (free cyanide, WAD-cyanide, SAD-cyanide, thiocyanate, and cyanate). Groundwater has been sampled less frequently, with most locations being sampled five times since 2009. In 2013, some additional parameters and modified sampling protocols were used in conjunction with the standard parameters and methods. These modifications included the collection of unpreserved dissolved metals samples, and field measurements of sulfide in water. Additional parameters added in 2013 included total inorganic carbon (TIC), total organic carbon (TOC), and monitoring of the well headspace for biogenic gases (oxygen, carbon dioxide, and methane) using a landfill gas meter. Field parameters measured during the water sampling included pH, conductivity and dissolved oxygen.

Groundwater under flowing the tailings impoundment dam is collected by the seepage pond and the seepage is then continuously released to surface water. This seepage flow rate was measured daily using calibrated flow meters, and is consistent with water balances completed for the mine site. There appears to be minimal groundwater underflow from the tailings dam beyond that accounted for by the seepage meter because of the presence of permafrost ground. The observed seepage flow rate was approximately 50 L/min from 1999 to 2008, and has since increased to approximately 200 L/min.

Solid phase tailings samples were previously analyzed for standard acid base accounting, humidity cell testing, and field kinetic testing. The average sulfide content of the tailings was 2%, and the neutralization potential ratio of 0.5 indicates that the acid generating potential is greater than the neutralization potential. Based on these results, the tailings would be expected to generate acid rock drainage.

Sampling and analysis for sulfite in both soil and water is difficult due to the oxidation to sulfate by atmospheric oxygen and environmental analytical laboratories often cannot distinguish sulfite and sulfate when analyzing water samples by ion chromatography. The measurement of sulfite in water is also apparently limited by the formation and potential loss of SO_2 gas from water samples. There are analytical methods to measure sulfite in solids samples, although these methods are limited by the presence of sulfide minerals which can prevent the accurate measurement of sulfite.

RESULTS AND DISCUSSION

Reagent Mass Balance

The mass of a water quality parameter discharged is calculated as the volume of water times the concentration. The total mass for an element can be determined based on the various water quality parameters, and these values can then be compared to the mass of reagents used at the mill. For the

reagents listed in Table 1, water quality parameters are available to quantify the amount of sodium, calcium, sulfur and nitrogen discharged from the tailings area into the creek.

The volume of tailings water released was determined using a 10 day moving average centered on a date with water chemistry data. Graphs of the water discharged and corresponding water chemistry are presented on Figure 1 and the results are summarized on Table 3.

Inorganic nitrogen data is often reported by laboratories as mg/L-N to allow direct comparison between nitrogen species, and the total cyanide concentration as mg/L-N is calculated as shown on equation 3.

$$\text{Total Cyanides as N} = (14.01 \text{ g/mol}) * [(\text{CN}^-)/26.02 + (\text{SAD-CN})/26.02 + (\text{OCN}^-)/42.02 + (\text{SCN}^-)/58.08] \quad (3)$$

By calculating total cyanides as N, a direct comparison with the breakdown products (ammonia, nitrate, and nitrite) can be completed as presented on Table 3. Total N is the sum of the various cyanide species (free cyanide, SAD-cyanide, cyanate, thiocyanate) and the measured inorganic nitrogen species (ammonia, nitrate, nitrite) formed by the degradation of the cyanides. WAD-cyanide is not included in this calculation as this cyanide fraction is included in the SAD-cyanide fraction reported by the laboratory as total cyanide. Note also that the measured WAD-cyanide values are higher than can be accounted for by the measured concentrations of metals that form WAD-cyanide complexes (e.g. copper) which indicate that in this case the WAD-cyanide test is actually measuring organic-cyanide complexes (Dzombak, Ghosh and Wong-Chong, 2006).

The total cyanide mass discharged reached an inflection point in about 2002 when the concentrations decreased to near non-detect levels; however, the concentration of the nitrogen breakdown products (ammonia, nitrate, and nitrite) has remained steady since monitoring began. This observation is consistent with the continued breakdown of the SAD-cyanide complexes on the tailings.

Mass balance calculations for the data presented on Figure 1 versus the mass of mill reagent chemicals used are presented on Table 3. Most (57%) of the sulfur added at the mill as sodium metabisulfite and copper sulfate is accounted for by the mass of sulfur measured in the discharge. For comparison, only 6.2% of the nitrogen added at the mill as cyanide is accounted for by the various nitrogen compounds analyzed (ammonia, nitrate, nitrite, free cyanide, SAD-cyanide, cyanate, thiocyanate). The lower value for nitrogen is consistent with the fact that most of the cyanide remains sorbed to the tailings as iron-cyanide complexes, and some nitrogen would also be lost as nitrogen gas (N₂) from the biodegradation of cyanide and ammonia. The higher percentage for sulfur may be due to the observation that this measurement is dominated by "sulfate" which is likely a combination of sulfate and sulfite, and also due to oxidation of sulfide minerals in the tailings.

Groundwater and Soil Gas Chemistry

Sample data and the calculations used to infer the presence of sulfite are presented on Table 4. The data presented is categorized as Well Series A to D, and sample data from a monitoring well representative of these categories is presented. There are approximately 30 groundwater monitoring locations.

Monitoring well headspace gas measurements show methane at percent level concentrations at four monitoring wells on the upgradient side of the tailings, and oxygen at (or above) atmospheric concentrations in the other monitoring wells within the tailings. The highest oxygen concentration measured was 23.9% using a calibrated GEM 2000 Plus. Well headspace gas monitoring was repeated three times using four different landfill gas meters. Reproducible results show the presence of methane at four wells, and that at most monitoring well locations oxygen is present at near atmospheric concentrations. These results are consistent with the presence of dissolved oxygen and lack of detectable sulfide in the water.

For monitoring wells classified as Well Series A (two wells on upgradient side of tailings), the pH is near 9, and sulfite was identified (but not quantified) in the ion chromatograms for the 2013

samples. These samples were not preserved to prevent oxidation of sulfite to sulfate, and the calculations on Table 4 show that slightly more than half of the total alkalinity expressed as CaCO₃ would be from sulfite, and this would represent approximately 10% of the total sulfur in the water sample.

Well Series B represent approximately 20 locations primarily within the mine tailings, and along a creek downgradient of the tailings dam. For Well Series B, the pH remains near 7.5, and the calculated sulfite concentration needed to provide the missing alkalinity ranges from 5 mg/L to 170 mg/L, with most locations having a calculated sulfite concentration of less than 80 mg/L. These calculated sulfite concentrations are consistent with the low solubility of calcium sulfite as shown on Table 2. Furthermore, the calculated concentrations of sulfite are consistent with the missing sulfur fractions when comparing the reported sulfate and total sulfur concentrations.

For monitoring wells classified as Well Series C (two wells on downgradient side of tailings dam), acid rock drainage is apparently starting in 2014. Since 2013 the sulfate concentration tripled, the pH decreased to slightly below 6, and the total alkalinity decreased to 35 mg/L. The reported 1990 mg/L of sulfate represents 651 mg/L of sulfur, and the measured total dissolved sulfur was 634 mg/L. This indicates that essentially all of the sulfur in the sample is present as sulfate. At both of these locations in 2013, acid rock drainage had not yet started, and the calculated sulfite concentration was consistent with Well Series B. At these two locations, it appears that the available sulfite has been depleted, and oxidation of the mineral sulfides has started.

For monitoring wells classified as Well Series D (four locations on or immediately downgradient of the tailings dam), the sulfate and total sulfur concentrations are low, and the amount of sulfite that would be required to provide the missing alkalinity is comparable to Well Series B. The water chemistry shown for Well D on Table 4 includes 583 mg/L of sulfate (measured on an unpreserved sample, and later confirmed by the laboratory), but only 1.6 mg/L of dissolved sulfur as measured in the acidified dissolved metals sample. In 2013, duplicate samples had reported sulfate concentrations of <5 mg/L and the dissolved sulfur concentration in duplicate samples was 1.6 mg/L. These samples are from water table monitoring wells, and the low sulfur concentration at these locations immediately downgradient of the tailings dam appears to indicate that sulfur is being lost from the water as sulfur dioxide gas.

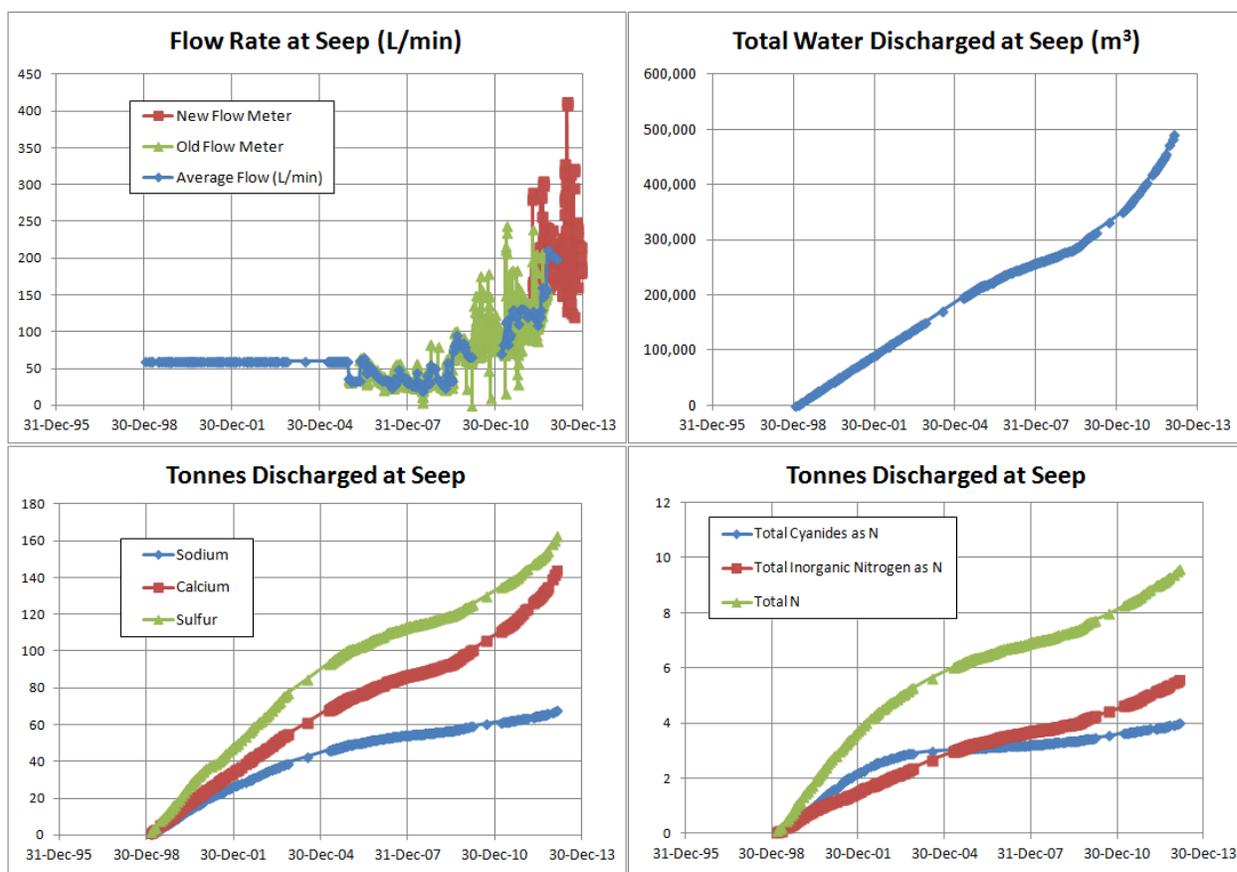


Figure 1 Graphs showing flow rate and total volume of water released from the tailings, and the total mass of sodium, calcium, sulfur and nitrogen compounds discharged

Table 3 Mass balance for mill reagents released from tailings 1999-2013

Parameter	Sodium	Calcium	Sulfur as S	Cyanides as N	Total Inorganic Nitrogen as N
Flow Weighted Average Concentration (mg/L)	139	294	331	8.7	11.3
Tonnes Discharged at Seep	68.0	144	162	4.3	5.6
Tonnes of Reagents Added at Mill	270	990	285		159
Tonnes Discharged as Percentage of Reagents added at Mill	25.2%	14.6%	57.0%		6.2%

Total water discharge from tailings from 1999 to 2013 was 490,800 m³

Like carbon dioxide (CO₂), when sulfur dioxide (SO₂) degases from water samples, acid is removed from the water and the pH rises. This effect is consistently seen in the monitoring data (with the exception of the two wells in Well Series A) where the field measured pH is lower than the laboratory measured pH. When CO₂ degases from a water sample, the pH rises but the total alkalinity in the sample bottle is unchanged due to the precipitation of calcite (CaCO₃). However, when SO₂ degases from a sample, the pH rises and sulfur is lost from the water sample as a gas. The loss of SO₂ usually occurs under acidic conditions, but several water samples collected

downgradient of the tailings dam have minimal amounts of both total sulfur and sulfate (i.e. Well Series D). This lack of sulfur in the water samples from this area could indicate that sulfur is either being precipitated as a solid, or lost as a gas.

The groundwater gradient steepens below the tailings dam, and this creates a larger surface area of water within the capillary fringe above the water table resulting in enhanced gas-water partitioning. Observations during groundwater sampling in 2013 indicate that the tailings porewater is charged with gas. This is likely to be nitrogen gas (N₂) created during the biodegradation of cyanide and ammonia. Nitrogen gas has a very high Henry's law constant (1540 L*atm/mol) and will partition from the water into the gas phase. Small amounts of nitrogen gas generated by the oxidation of cyanide and ammonia creates a high partial pressure of dissolved gas, and when the sum of the partial pressures exceeds the confining pressure, bubbles of gas can form (both in the tailings or in the sample bottle). Bubbles of gas were noted during the field sulfide testing and during the groundwater sampling. The presence of high partial pressures of dissolved gas provides a plausible mechanism to account for the lack of sulfur downgradient of the tailings dam despite the neutral pH and the high aqueous solubility and low Henry's law constant (0.8 L*atm/mol) for sulfur dioxide. Samples were flown from the mine on commercial jet aircraft, and the lower air pressure at altitude may have allowed bubbles to form which could effectively partition sulfur dioxide from the water into the gas phase.

Due to analytical limitations, there are only indirect measurements of sulfite in the soil and groundwater at this site. The presence of sulfite is indicated by the mass balance of the mill reagents, and measurements of pH, sulfate, total sulfur, total alkalinity, total inorganic carbon (TIC), and electrical charge balance. The lack of iron oxidation noted in unpreserved water samples for metals analysis collected in 2013 also indicates the potential presence of an oxygen scavenger such as sulfite. Additional calculations can also account for the alkalinity consumed by the oxidation of some of the Fe²⁺ in the unpreserved metals sample bottles. By accounting for this loss of alkalinity, the charge balances shown on Table 4 can be improved. The low dissolved sulfur and sulfate concentrations measured at locations downgradient of the tailings dam indicate the loss of sulfur from the water samples as SO₂ gas. Finally, the observation that sulfide oxidation did not occur in the humidity cell testing of untreated tailings samples even after two years, despite the 2% sulfide content, is indicative of the presence of sulfite on the tailings. Humidity cell samples that had been pre-treated with acid to accelerate the testing process produced acid rock drainage as expected, and this is consistent with the loss of sulfite from the acidified tailings samples as SO₂ gas.

CONCLUSIONS

A former gold mine in Canada used sodium metabisulfite (SMBS) as the source of sulfite (SO₃²⁻) in the Inco process to remove cyanide. Documents for the mine show that the rate of reagent usage at the mine was consistent with other mines. A mass balance shows that approximately 57% of the sulfur added at the mine mill can be accounted for in the water discharge from the tailings, but only 6% of the nitrogen can be accounted for as the various measured nitrogen compounds. These results indicate that most of the cyanide remains on the tailings solids as strong acid dissociable (SAD) complexes such as iron-cyanide; however, biodegradation of these cyanide complexes is continuing.

As shown on Table 2, the aqueous solubility of calcium sulfite is orders of magnitude lower than for SMBS or sodium sulfite. The use of lime (CaO) to stabilize the pH in the Inco process has resulted in high calcium concentrations in the tailings, and the low solubility of calcium sulfite has limited the leaching of sulfite from the tailings. The oxidation of sulfite to sulfate (SO₄²⁻) is slow under the site conditions (i.e. low temperature, high pH, water saturated) and the continued presence of sulfite in the tailings under these conditions would be expected. However, sulfite in water samples cannot be preserved, and would be expected to readily oxidize to sulfate according to equation 2. Furthermore, laboratory analysis typically does not distinguish sulfite from sulfate, and the reported concentrations of sulfate are likely a combination of these two sulfur species.

Calcium sulfite recovered from flue gas desulfurization inhibits the onset of ARD in pyrite bearing coal ash waste and this process has been documented in the scientific literature. The observations at this mine site are consistent with the inhibition of the onset of ARD due to the presence of calcium sulfite on the mine tailings. This paper presents field evidence for ARD inhibition, and is

apparently the first reported observation of sulfite inhibiting the onset of ARD at a mine site. If monitoring shows that sulfite is being depleted, SMBS could be injected into the mine tailings to maintain the soil and water concentrations of calcium sulphite needed to inhibit the onset of ARD.

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Table 4 Example data and calculations

Parameter	Units	Well A	Well B	Well C	Well D
Date Sampled		27-Jun-14	27-Jun-14	28-Jun-14	29-Jun-14
Measured Values					
pH - Field	pH	9.66	7.54	5.82	7.10
pH - Lab	pH	8.74	8.14	6.52	8.20
Dissolved oxygen - field	mg/L	0.25	0.37	2.58	0.66
Oxygen (well headspace)	%	20.9	19.7	20.5	21.0
Carbon dioxide (well headspace)	ppm	520	830	950	520
Methane (well headspace)	%	nd	31	4	nd
Calcium	mg/L	77.6	112	587	143
Magnesium	mg/L	0.81	49.8	57.5	55.5
Sodium	mg/L	22.7	21	82.0	19.7
Potassium	mg/L	8.18	8.22	5.92	3.5
Iron	mg/L	0.40	11.7	87.4	20.1
Manganese	mg/L	0.06	4.15	17.9	4.87
Ammonia-N	mg/L	4.12	5.03	2.27	2.9
Alkalinity, Total (as CaCO ₃)	mg/L	80.2	581	35.7	204
Chloride	mg/L	2.5	<5.0	<0.4	<5.0
"Sulfate" as SO ₄	mg/L	136	31	1990	583
Sulfide	mg/L	<0.10	0.03	0.023	<0.02
Sulfur (S)-Dissolved	mg/L	132	11.9	634	1.6
Total Organic Carbon (TOC)	mg/L	28.3	48.4	10.8	74.3
Total Inorganic Carbon (TIC)	mg/L	9.2	89.1	4.9	19.7
Calculated Values					
"Sulfate" as S (32.06/98.06)	mg/L	44.5	10.2	651	191
Difference (Dissolved S - "Sulfate" as S)	mg/L	87.5	1.7	-16.6	-189.0
Cation Sum	meq/L	5.5	11.7	41.7	13.8
Anion Sum Using "Sulfate" and Total Alkalinity	meq/L	4.4	12.3	43.0	16.2
Balance (Cations/ Anions)	%	123%	96%	97%	85%

Alkalinity from Carbon (TIC*4.17) where 4.17 = 50.04/12.01	mg/L	38.4	372	20.4	82.1
Excess Alkalinity (Total - TIC*4.17)	mg/L	41.8	209	15.3	122
Sulfite Concentration Needed to Provide Excess Alkalinity (40.03/50.04)	mg/L	33.5	168	12.2	97.5
Sulfite as S (32.06/80.06)	mg/L	13.4	67.0	4.9	39.0
% of Dissolved S as Sulfite	%	10.1%	563%	0.8%	2422%
Anion Sum - Using TIC*4.17 and Sulphite Alkalinity	meq/L	5.34	16.4	42.5	18.7
Balance (Cations/ Anions)	%	102%	71%	98%	74%