Comparison of laboratory testing protocols to field observations of the weathering of sulfide-bearing mine tailings

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A B S T R A C T

A laboratory weathering study using a humidity cell procedure was conducted on two sulfide-bearing tailing samples from a metallurgical site in Ontario (Canada). The test was accompanied by microbiological studies to enumerate the major groups of sulfur-oxidizing bacteria and determine their potential role at different stages during the oxidation process. To evaluate the utility of this method, results were compared with those of previous laboratory and field studies on the same materials. The mineralogy of the laboratory samples differs only by the addition of a small amount of hydronium-bearing natrojarosite \([(Na,H₃O)Fe₃(SO₄)₂(OH)₆]\) to one sample. The progress of sulfide oxidation and the rates of solute release were determined to evaluate the extent of mineral dissolution. These processes were influenced strongly by the capacity of the material to generate acidity, which was enhanced by the presence of hydronium-bearing natrojarosite. Acid-neutralization processes occurring during the laboratory tests were affected by reaction kinetics, consistent with field observations. In particular, the extent of carbonate-mineral dissolution appears to be different in the laboratory than in the field, where more prolonged rock–water interaction allowed more complete chemical equilibration. As a consequence, the capacity of this test procedure to predict weathering reactions in mine tailings is limited by its inability to reproduce the weathering sequence observed in the field. The results of the microbiological study showed that distinct groups of sulfur-oxidizing bacteria operate at different stages of the oxidative process, as was observed in field studies where tailings oxidation occurred under natural conditions, suggesting that microbiological tests performed for laboratory studies are reflective of field conditions.

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1. Introduction

Sulfide-bearing wastes from mining and mineral processing, including waste rock or mill tailings, are typically deposited in piles or impoundments near the mine workings. In these piles sulfide minerals are exposed to air and water, resulting in sulfide mineral oxidation. Although not all sulfide-bearing wastes are acid generating, oxidation may lead to the generation of acid effluents and to the release of Fe, SO₄ and potentially toxic elements to surface water and groundwater, causing environmental damage. Some materials may need to be exposed to atmospheric conditions for a considerable time before acidic conditions develop (Bennett et al., 2000).

The variations in drainage quality observed from piles and impoundments is mainly a function of grain-size distribution, compositional variations (e.g. iron-sulfide and carbonate-mineral content) within individual mine-rock lithologies, and local climatic conditions. Moreover, oxidation of sulfide minerals can be enhanced by the presence of bacteria, which are able to survive in extreme environments such as acidic mine effluents. Bacteria catalyze the oxidative dissolution of sulfide minerals increasing the production of acidity in mine wastes (e.g. Blowes et al., 1995, 1998; Bennett et al., 2000) and maintain rapid oxidation under low-pH conditions. In the absence of bacteria, the rate of sulfide oxidation stabilizes as the pH decreases below 3.5 (Singer and Stumm, 1970).

One goal of the scientific community is to determine, with sufficient certainty, how sulfide-bearing wastes from a particular site will behave, in particular the rate at which the material oxidizes under a range of climatic conditions and the ability of site materials to neutralize acid. Different approaches to this question include detailed field investigations, laboratory studies and modeling studies. An advantage of conducting laboratory experiments is the lower cost and the more timely acquisition of data. Laboratory experiments also provide the opportunity to conduct experiments prior to the disposal of mine wastes. The supposition is that rates of acid-producing and acid-neutralizing mineral dissolution in the laboratory are sufficiently similar to those in the field to allow incorporation of the laboratory results into predictive models of full-scale waste piles (Bennett et al., 2000).

A laboratory test was conducted on a fresh sulfide-bearing tailings sample from a mine-waste disposal facility at the Kidd Creek metallurgical site near Timmins (Ontario), and a mixture of this

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The mineralogy of the tailings was determined by Jambor et al. (1993). The tailings were a silt to sand size, with 100% of the material less than 2 mm. The tailings sample contained 3 wt.% of hydronium-bearing natrojarosite. In addition, to determine drainage quality, microbial populations present in the tailings samples were enumerated after the experiment was terminated. The objectives of the experiment were to determine the influences of solid-phase composition, reaction conditions, and chemical equilibrium consideration on drainage quality and compare microbial populations present with those observed in the field. Results were compared to those obtained from previous saturated column experiments examined acid-neutralization relations in isolation from experiments conducted on the same material. The saturated column experiments examined acid-neutralization reactions in isolation from acid-producing reactions (Jurjovec et al., 2003; Jurjovec et al., 2003). In contrast, the humidity test cell experiments evaluate weathering when both acid generation and acid-neutralization reactions are allowed to occur simultaneously. Results also were compared with observations from detailed field studies conducted to evaluate variations in pore water chemistry and mineralogical composition in different weathering zones of the Kidd Creek tailings impoundment (Blowes et al., 1995; Al et al., 2000, and references therein).

Bacterial enumerations were undertaken to assess the changes in bacterial populations as the sulfide oxidation process proceeds under laboratory conditions. Results were compared with bacterial populations present in the Kidd Creek impoundment within zones presenting different stages of geochemical maturation (Blowes et al., 1995).

### 2. Materials

Solid materials used in this study are: a) one sample (labelled KC) of fresh unoxidized tailings collected at the concentrator at the Kidd Creek metallurgical site in Ontario, Canada; b) one sample (named KCJ) of the same tailings mixed with 3 wt.% of hydronium-bearing natrojarosite [Na₀.75(H₃O)₀.₂₄K₀.₀₁Fe₃(SO₄)₂(OH)₆] residue, a waste derived from the adjacent Zn refinery. Since 1985 the natrojarosite residue has been co-disposed with the tailings and deposited in a single impoundment (Al et al., 1994). The 3 wt.% of natrojarosite added to the KCJ sample represents the proportion co-disposed in the field. Jurjovec et al. (2003), who previously conducted experiments on these samples, observed that the presence of natrojarosite diminishes the ability of tailings to buffer acidic solutions.

The tailings are silt to sand sized, with 100% finer than 1 mm and a mean grain diameter of approximately 0.05 mm (Al and Blowes, 1999). The mineralogy of the tailings was determined by Jambor et al. (1993) to be as follows: 15 wt.% sulfides (mainly pyrite [FeS₂], followed by pyrrhotite [Fe₁₋ₓS], chalcopyrite [CuFeS₂], and sphalerite [Zn,FeS]), 8 wt.% carbonates ( siderite [FeCO₃], ankerite–dolomite [Ca,Fe,Mg] (CO₃)₂), and calcite [CaCO₃]) and Fe-oxides [Fe₂O₃], 49 wt.% quartz [SiO₂], and 24 wt.% chlorite [(Mg,Fe)₃(Si,Al)₄O₁₀(OH)₂] (Mg,Fe)₃(OH)₆). Minor amounts of amphibole, stilpnomelane [K₆₋₇Fe²⁺Mg,Fe³⁺₃₋₄Si₆Al₂O₁₀(OH)₂] and muscovite [K[Al₂Si₃O₁₀(OH)₂]] are also present. The mineralogy of the tailings is summarized in Table 1.

The hydronium-bearing natrojarosite residue also contains traces of other phases. A detailed mineralogical description is given in Blowes et al. (1995). The chemical composition of this residue is variable; in addition to Na, Fe, and SO₄ it contains variable amounts of As, Pb, Zn, K, Cd, Co, Cr and other metals. Components with an average content greater than 1 wt.% include S (40 wt.%) as S²⁺ and SO₄ (28.5 wt.%), H₂O (32 wt.%), Zn (6.7 wt.%), Na (2.4 wt.%), and Pb (1.6 wt.%). The compositions of the KC and KCJ samples are presented in Table 2. There are some minor discrepancies between the measurements presented here, and those presented by Jurjovec et al. (2003).

### 3. Methods

#### 3.1. Humidity cell procedure

The two test samples were subjected to alternating wet and dry weathering in humidity cells. A 1000-g sample of solid material was used. The samples were exposed to a continuous stream of air to promote oxidation, followed by leaching using a fixed volume of deionized water. The experiment was performed on each sample in a cylindrical cell (humidity cell), 20 cm in height and 8.9 cm in diameter. The protocol included weekly cycles consisting of 3 days of dry air and 3 days of water-saturated air pumped up through the sample, followed by a leach with water on Day 7. The fine-grained nature of the tailings can result in water retention during flushing, resulting in inefficient gas transport through the tailings. To enhance gas transport, side ports were installed above the packed tailings, which were used to flow air across the surface of the tailings. The weekly effluent was collected and concentrations of dissolved weathering products were determined. Before initiation of the weathering cycle, the samples were rinsed with three 500 ml volumes of distilled water to remove products that accumulated from sample oxidation during storage (week-0). Subsequent leaches are designated as week-1, week-2... week-n, and mark the end of the weekly cycle for that numbered week.

Determinations of Eh, pH, alkalinity and conductivity were made immediately after each weekly effluent collection. The Eh was measured using an Orion Pt redox electrode (model 96-78BN), checked against Zobell’s solution (Nordstrom, 1977). The pH was measured using an Orion Ross combination electrode (model 815600) calibrated with standard buffer solutions at pH 1, 4, and 7. Measurements of alkalinity were made on filtered samples using a Hach digital titrator and brom cresol green/methyl red indicator and with 0.16 N H₂SO₄. Samples for analysis of dissolved constituents were collected on a weekly basis, filtered using a 0.45 µm cellulose acetate membrane, and acidified to pH < 2 using trace-metal grade HNO₃ for the cation samples or left unacidiﬁed for SO₄ analysis. Analysis of SO₄ was by ion chromatography, and analysis of dissolved major cations and trace metals was by inductively coupled plasma optical emission spectrometry. Weekly loadings of the constituents of interest were calculated as: $Li(t) = Ci(t) × M(t)$, where $Li(t)$ = loading of solute i at

#### Table 1

<table>
<thead>
<tr>
<th>Mineral class</th>
<th>Mineral name</th>
<th>Formula</th>
<th>wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfides</td>
<td>Pyrite</td>
<td>FeS₂</td>
<td>13.2</td>
</tr>
<tr>
<td></td>
<td>Pyrrhotite</td>
<td>Fe₁₋ₓS</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>Chalcopyrite</td>
<td>CuFeS₂</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>Sphalerite</td>
<td>ZnS</td>
<td>0.2</td>
</tr>
<tr>
<td>Silicates</td>
<td>Chlorite</td>
<td>[Mg,Fe]₃(Si,Al)₂O₅(OH)₂ (Mg,Fe)₃(OH)₆</td>
<td>23.4</td>
</tr>
<tr>
<td></td>
<td>Amphibole</td>
<td>W₀₋ₓYₓZₓ₂(OH)₆</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>Stilpnomelane</td>
<td>KₓMg₉Fe₇⁺Fe³⁺Si₆Al₂O₆(OH)₂</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td></td>
<td>Albite</td>
<td>Na Al SiO₃</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>Muscovite</td>
<td>K[Al₂Si₃O₁₀(OH)₂]</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>Quartz</td>
<td>SiO₂</td>
<td>40.1</td>
</tr>
<tr>
<td>Carbonates</td>
<td>Ankerite–dolomite</td>
<td>CaFeMg(CO₃)₂</td>
<td>3.1</td>
</tr>
<tr>
<td></td>
<td>Siderite</td>
<td>FeCO₃ FeO₃</td>
<td>4.9</td>
</tr>
<tr>
<td>Fe-oxides</td>
<td>Gypsum</td>
<td>CaSO₄·2H₂O</td>
<td>0.5</td>
</tr>
</tbody>
</table>

* Where W=Na⁺/K⁺, X=Ca²⁺, Na⁺, Mn²⁺, Fe²⁺, Mg²⁺, Li⁺; Y=Mn²⁺, Fe³⁺, Mg²⁺, Fe²⁺, Al³⁺, Ti⁴⁺; and Z=Si⁴⁺, Al³⁺.

#### Table 2

<table>
<thead>
<tr>
<th>Concentration of S, Al, Ca, Mg, Fe (%) and Cd, Co, Cr, Cu, Na, Mn, Ni, Zn (ppm) in bulk samples before leaching</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
</tr>
<tr>
<td>------</td>
</tr>
<tr>
<td>KCJ</td>
</tr>
<tr>
<td><em>Narojarosite</em></td>
</tr>
</tbody>
</table>

**nd** = not determined.
week t (µg), Ci(t) = the concentration of solute at week t (µg/g) and M (t) = the effluent mass at week t (g). The value of Ci for elements that were below the analytical detection limit was assumed to be 50% the detection limit for these calculations.

Pore water geochemistry interpretation was carried out with the assistance of the geochemical code MINTEQA2 (Allison et al., 1990). The thermodynamic database was adapted from the speciation model WATEQ4F to include additional complexation constants and solubility data. The results of geochemical modeling provided saturation indices (SI) for minerals. During the laboratory tests, the solid-solution interaction time is short (hours) while in the field the contact time is longer; consequently equilibration of the leach water with many minerals was less likely than in the field. Therefore, saturation indices were an important aspect of the data interpretation approach used to propose reaction models, emphasizing the general tendency of a phase toward undersaturation or saturation conditions, rather than specific numeric values. Moreover, effluent samples were allowed to sit open to the atmosphere for 8 to 24 h, a period during which oxidation and precipitation reactions could occur. Upon completion of the experiments, a portion of the leached material from each column was used for mineralogical analyses by XRD, and the patterns compared with those obtained from a portion of the starting material.

3.2. Microbiological analyses

At the end of the experiments, solid samples were collected for microbiological analysis at approximately 3 cm increments along the length of the cell (top, middle, and bottom). The samples were stored under refrigeration (4 °C), and analyzed within 10 days. Techniques for the microbiological study included culturing a sample in an enrichment or selective liquid medium, with the ultimate objective of obtaining a culture of the desired microorganism (Gould & Kapoor, 2003). The media used in this study were the same used by Blowes et al. (1995) for microbiological characterization of the Kidd Creek mine tailings to enumerate the major group of sulfur-oxidizing bacteria and their potential role in the generation of acidic pore water.

Medium A, used to grow acidophilic iron-oxidizing bacteria (AIoB) consisted of 0.5 g/l of KHP04, 0.5 g/l of (NH4)2SO4, 0.5 g/l of MgSO4 7H2O and 33.4 g/l of FeSO4 7H2O (Tuovinen and Kelly, 1973). A second solution of ferrous sulfate with a pH of 3 was prepared separately. The two solutions were slowly mixed together, and the pH was adjusted to 2.2 using H2SO4 or NaOH. A 9-ml volume of the medium was dispensed into sterile test tubes, and 1 g of sample was added. A five-tube most probable number (MPN) method was used. Samples were diluted up to 10 times (1:10). During each dilution the samples were vortexed vigorously for 10 s. The test tubes were incubated for 4 weeks before recording the results. Observation of visible ferric iron precipitates indicated a positive result.

Medium B, used to grow acidophilic sulfur-oxidizing bacteria (ASOB) and neutrophilic sulfur-oxidizing bacteria (NSOB) consisted of 0.1 g NH4Cl, 3.0 g KH2PO4, 0.2 g MgCl2 6H2O, 5 g Na2S2O3 5H2O, and 0.1 g CaCl2 (Gherma et al., 1989). The final pH was adjusted to 4.2 for ASOB with H2SO4 and to 7.0 for NSOB. The inoculation procedure was the same as for AIoB. Observation of pH values <4.0 indicated a positive result for ASOB. A pH >6.8 indicated a positive result for NSOB. Enumeration of bacteria was performed using the most probable number (MPN) statistical technique (Cochran, 1950).

4. Results and discussion

4.1. KC sample results

The changes in pH, Eh and loading of major elements as a function of time for sample KC are presented in Fig. 1. The tests were carried out for 58 weeks, which is beyond the range of the standard monitoring time for humidity cell tests. Effluent pH values decreased from 7.96 to 7.20 during the experiment, indicating that the tailings from the concentrator at the Kidd Creek are not short-term acid producers. Values of Eh were fairly stable for the entire experiment and correspond to quite oxidizing conditions (Eh average=406 mV; SD=37). Values of electrical conductivity decreased sharply from week-1 to approximately week-20 (from 2.31 to 0.55 mS/cm), indicating depletion of the most soluble solid phases, after which the electrical conductivity values were relatively stable until the end of the experiment (week-58 conductivity =0.56 mS/cm). Constancy of pH, Eh and conductivity as a function of time are consistent with a balance between acid-producing and acid-neutralizing mineral dissolution rates, when conditions to promote sample oxidation are provided.

Calcium and SO4 loading distributions show a very good correlation (R²=0.98) over the entire experiment (Fig. 2). During the first 8–10 weeks, the saturation index (SI) values for gypsum (CaSO4 2H2O) are close to equilibrium values (Fig. 3), and the average SO4/Ca molar ratio in solution is close to 0.9. The dissolution of pre-existing soluble oxidation salts such as gypsum, present in the sample prior to sample collection or oxidation products formed during sample storage and drying, is expected to influence effluent chemistry during the first few weeks of the experiment. Gypsum was not unequivocally detected in the XRD pattern obtained for the starting material. Nevertheless Jambor et al. (1993) noted the presence of gypsum throughout tailings samples collected from the Kidd Creek impoundment.

Over the experimental period, SO4 and Ca weekly loading was substantial (from week-1 to week-10 cumulative loading is 5.33×10⁶ µg for SO4 and 2.43×10⁶ µg for Ca corresponding respectively to 5.55×10⁴ µmol and 6.07×10⁴ µmol), and then decreased sharply. After week-10 SO4/Ca molar ratios increased to approximately 1.5 and the weekly effluent samples became increasingly under-saturated with respect to gypsum suggesting that gypsum was no longer controlling SO4 and Ca concentrations in solution. The SO4 and Ca loadings continued to decrease sharply until ~week-20, following the conductivity trend. After week-20 changes in loading values were more gradual, but decreased further (cumulative loading from week-21 to week-58 is 4.26×10⁶ µg and 1.31×10⁶ µg respectively for SO4 and Ca corresponding to 4.43×10⁴ µmol and 3.28×10⁴ µmol).

Sulfate also is released by sulfide oxidation. Comparison of XRD patterns of the starting material and the leached material indicates that substantial pyrite remained at the end of the experiment. Pyrrhotite oxidation is likely because pyrrhotite oxidation proceeds 20–100 times faster than pyrite oxidation (Nicholson and Scharer, 1994; Blowes et al., 2003). Because the most intense pyrrhotite peaks overlap peaks of other phases present (e.g., chlorite), the extent of pyrrhotite depletion could not be discerned from only comparison of XRD patterns.

Calcium was likely derived from carbonate dissolution. Given that pH values were not observed to decrease, it can be assumed that the acidity produced by sulfide oxidation was completely neutralized by carbonate dissolution. The increases in SO4/Ca molar ratio late in the experiment are consistent with the observation that Ca is not the principal component in carbonates from the Kidd Creek tailings. Siderite, which usually contains negligible Ca, is the primary carbonate (60 wt.% of the total carbonate content), and it is also less soluble than calcium and magnesium carbonates (Blowes et al., 2003; Blowes and Ptacek, 2004, and references therein).

Calcium is most abundant in ankerite–dolomite (35 wt.% of the total carbonate content) and calcite (5 wt.% of the total carbonate content). Due to the limited mass of calcite, it can be assumed that the Ca contribution from calcite dissolution was not substantial. The Ca/Mg molar ratio in the Kidd Creek ankerite–dolomite averages ~2.38 (Jurjovec et al., 2002). The Ca/Mg molar ratio in solution is ~3 during the first 10 weeks, which is consistent with the dissolution of gypsum as the main source of Ca (combined with a modest contribution from calcite dissolution). Subsequently, from week-11 until week-28, the
average Ca/Mg molar ratio was 2.54, closer to the Ca/Mg ratio in ankerite–dolomite. This ratio suggests that dissolution of ankerite–dolomite is likely the principal source of both Ca and Mg. From week-29 until the end of the experiment, the rate of Ca release decreased and the Ca/Mg ratio declined to ~2. This decline may be due to Mg contributions from the dissolution of phases other than ankerite–dolomite. Alternatively, Ca may be controlled by precipitation of another phase, however, the SI values for Ca-bearing phases do not indicate that precipitation of any Ca-bearing phase was favoured.

In their experiment, Jurjovec et al. (2002) observed that dissolution of chlorite provided another source of Mg, which followed the depletion of the carbonate minerals. Nevertheless, direct comparison of the two experiments requires careful consideration due to the different nature of the leaching environment. Because weekly loadings of Mg and other elements present in chlorite (Si, Al, Fe) were not observed to increase, substantial dissolution of chlorite is not likely, consistent with the calculated SI values (Fig. 3). More likely, the mass of ankerite–dolomite had declined to the extent that siderite (which contains much more Mg than Ca) dissolution became more pronounced, resulting in the observed change in the Ca/Mg molar ratio. The comparison between XRD patterns of the starting material and the leached material supports the hypothesis of a shift from ankerite–dolomite to siderite dissolution (Fig. 4). Ankerite–dolomite was consumed during the experiment (no longer detectable in the leached material), whereas the mass of siderite likely decreased without resulting in complete depletion (maintaining the capacity to neutralize acidity produced by sulfide oxidation until the termination of the experiment).
The SI values for carbonates did not provide significant support in the data interpretation, because the effluent samples were consistently strongly under-saturated with respect to ankerite as well as siderite during the entire experiment, indicating a tendency for all of these minerals to dissolve. The Fe concentrations in the effluent samples were almost at all times, below the detection limit, likely due to precipitation of Fe(II) as carbonates in the tailings solid, or, more likely, due to precipitation of Fe(III) as an (oxy)hydroxide solid in the effluent collection vessel. Calcite SI values range from over-saturated to slightly under-saturated conditions during the first ~15–20 weeks (Fig. 3).

Manganese and Mg release rates did not show a strong correlation (Fig. 5), indicating different controls on either their origin or the occurrence of secondary reactions. Manganese (as well as Mg) is released mainly from carbonate dissolution. Manganese and Mg partitioning in carbonates from Kidd Creek is variable, which could explain the poor correlation between these elements in spite of a common origin. Al et al. (2000) studied the reactions at the carbonate-mineral surfaces on Kidd Creek samples and suggested that Mg and Mn released by ankerite dissolution may either precipitate as magnesite and rhodochrosite if the pore water pH is high, or remain in the aqueous phase. Magnesite and rhodochrosite SI values versus time (Fig. 3), suggest that secondary precipitation of rhodochrosite is favoured at some times. Precipitation of secondary phases, such as rhodochrosite or gypsum, can occur during dry cycles of the leaching test. The purpose of the three-day dry-air portion of the weekly cycle
is to evaporate some of the water that remains in the pores of the sample after the weekly leach, and thereby increase the opportunity for sulfide oxidation. Evaporation increases pore water cation/anion concentrations and precipitation may occur because the remaining water may become over-saturated with respect to some phases. The expected removal of soluble reaction products during the leaching step may be influenced by a number of factors. For example, there is potential for incomplete leaching of some reaction products during a specific week, followed by more complete removal in subsequent weeks leading to oscillations in total solid concentrations (TDS) in the weekly effluents. This same process could also account for apparently inconsistent trends for some parameters such as dissolved Mn, which may be controlled by mineral phases close to equilibrium. Nevertheless rhodochrosite precipitation is kinetically slow and equilibrium is unlikely to be attained (Sternbeck, 1997; Jensen et al., 2002).

As noted previously, due to the high pH values during the entire experiment, the concentrations of Fe remained very low, mostly below the detection limit of <0.01 µg/g. The Fe(II) that was mobilized by carbonate dissolution and sulfide oxidation was unstable under the pH–Eh conditions of the effluent samples leading to rapid precipitation of Fe(III) (oxy)hydroxides. Saturation indices for ferrihydrite and goethite are reported in Fig. 3. Nevertheless, because these values are calculated using an Fe concentration value, which was often assumed to be 50% of the detection limit, they cannot be considered significant in data interpretation.

Jurjovec et al. (2002) and Al et al. (2000) described the accumulation of siderite as secondary coatings around ankerite–dolomite grains, due to an incongruent dissolution of the latter phase. Nevertheless, there is no evidence that siderite precipitation is occurring in this experiment, probably due to the slow kinetics of precipitation in comparison with dissolution (Greenberg and Tomson, 1992; Jensen et al., 2002).

Concentrations of Al were less than the detection limit of 0.037 µg/g during all 58 weeks. Because Al is mostly present in aluminosilicate phases, it is not leached in significant amounts at these pH values. Moreover if the Al concentrations are assumed to be 50% of the detection limit, the effluent is over-saturated with respect to gibbsite during the entire experiment (Fig. 3). These calculations are in agreement with Jurjovec et al. (2002) who showed that gibbsite precipitation is the major process controlling Al concentration in solution.

The cumulative loading of Na, K and Si were respectively 1.3 × 10⁴ µg, 6.0 × 10⁴ µg, 8.8 × 10⁴ µg. These elements are not easily released through weathering and their loading tends to diminish versus time.

4.2. KCJ results

The KCJ effluent (KC tailings + 3 wt.% of natrojarosite residue) showed a wide range of pH values, ranging from 7.87 (Starting-pH) to 2.75 (week-57). In contrast to the KC sample, alkalinity was totally consumed by week-7 showing that the natrojarosite addition rapidly consumed the neutralization capacity provided by minerals in the tailings. These results are in agreement with those of Jurjovec et al. (2003), who showed that natrojarosite dissolution is an acid-producing reaction, which depletes the buffering capacity of the tailings. The acidity produced by natrojarosite dissolution promotes sulfide oxidation accelerating the oxidation rate. In the test cells, the pH continued to decrease until the end of the experiment, although not as sharply as in the early stages. The capacity of natrojarosite to dissolve at neutral pH, producing acidity, was also reported in field observations (Al et al., 1994, 2000). In this experiment geochemical
Calculations show that the effluent water is consistently undersaturated with respect to jarosite, natrojarosite and hydronium jarosite, indicating a tendency for these minerals to dissolve.

Values of Eh increased from ~450 mV in the first weeks up to ~650 mV in the final weeks. Values of conductivity were on average higher than values recorded for KC sample (with an average of 2.26 mS/cm).

For the KCJ sample the variability of pH, Eh and conductivity versus time indicates that the addition of a small amount of natrojarosite residue enhances the alteration of the solid assemblage present in the KC sample under identical leaching conditions.

In contrast to the KC sample, Ca and SO₄ release did not always show a strong correlation (Fig. 2). Both elements tended to decrease over time, but not necessarily along the same trend. The initial tendency of SO₄ loading to increase during the first few weeks (compared to the tendency for Ca concentrations to decrease) suggests that gypsum dissolution is not the only process releasing Ca and SO₄. Another important source of SO₄ during these first few weeks could be the dissolution of natrojarosite.

The Ca loading curves for KC and KCJ samples are in good agreement (Fig. 1); cumulative loadings at week-58 are 4.41×10⁶ µg for KC and 4.37×10⁶ µg for KCJ indicating that nearly the same mass of Ca was mobilized in both samples. It can be assumed that, after gypsum depletion, carbonates are the main Ca source because no other Ca-bearing minerals are present in the material. Moreover the Ca release rates are similar for KC and KCJ samples. The trend for the KCJ column starts to diverge significantly from KC after week-42. At this time a significant mass of Ca was still released from KC sample, whereas the Ca loading from the KCJ sample approached zero. Comparison of the cumulative Ca loading value from the KCJ column, including the Ca released during week-0 (for a total of ~5000 mg/kg), and the Ca content in the bulk sample (6700 mg/kg) confirms that ~75% of the Ca was removed from the KCJ column by week-42.

In contrast to the KC column, comparison of XRD patterns of the KCJ starting material and the leached material upon completion of the experiment showed complete depletion of both ankerite–dolomite and siderite (Fig. 6). Because Ca loading diminishes, but continues at a low value, a small carbonate fraction, which is no longer detectable by XRD, or other minor sources of Ca such as amphibole (Jambor et al., 1993) could still be present.

The SO₄ cumulative loading curves for KC and KCJ samples differ. Cumulative loadings at week-58 are 1.16×10⁷ µg for KC and 3.12×10⁷ µg for KCJ indicating that the mass of sulfur removed from KCJ is much higher than in the KC sample, consistent with a more rapid sulfide oxidation rate. The XRD pattern for the leached material shows that pyrite is not totally depleted at the end of the experiment (Fig. 6); therefore we could expect that the lowest pH value of 2.75 recorded within 58 weeks of experiment would decrease further if the acquisition of data was extended.

Assuming that Ca is a good indicator of the carbonate dissolution rate (because Fe and Mg are associated with other abundant phases), it seems that the rate of carbonate dissolution is not sufficiently rapid to neutralize all of the acidity produced by sulfide oxidation and natrojarosite dissolution under the experimental conditions. The high flushing rates, relative to the slow kinetics of carbonate dissolution, did not allow equilibrium with respect to carbonate minerals to be attained, thereby limiting the capacity of carbonates to neutralize acidity. Consequently, even before complete carbonate-mineral depletion, the pH decreases rapidly. Blowes et al. (1995) found that dissolution kinetics of carbonates influence neutralization processes in field settings, where a more prolonged pore water–tailings interaction is expected to occur. In fact, carbonates are not depleted in the low-pH zone (pH<4.0) as would be expected under these low-pH conditions. In this case carbonate-mineral dissolution kinetics play a key role in acidification/neutralization processes. The limitation of applying laboratory tests to predict field behaviour is the inability to reproduce the chronology of full-scale reactions.

In the KCJ column results, the release of magnesium is characterized by an irregular weekly loading for most of the experiment, which is similar to the KC curve only during the final part of the experiment. The first abrupt increase, at the beginning of the experiment, may be due to a rapid initiation of siderite dissolution (compared to KC sample) because of the lower pH of the effluent. There is a second abrupt increase which occurs around week-23. Carbonates are, however, clearly not the only Mg source, not only because Ca and Mg trends would be more similar, but also because KCJ Mg cumulative loading (1.90×10⁵ µg) is much higher than for KC (7.90×10⁴). Because the pH values are lower than for the KC sample, chlorite dissolution is probable. The chlorite SI goes from under-saturated to strongly under-saturated conditions (Fig. 3).

As observed for Mg, the Mn cumulative loading (3.70×10⁵ µg) for the KCJ column is much greater than for the KC column (4.96×10⁴ µg). In this case Mg and Mn loading distributions show an improved correlation (Fig. 5); in fact, in contrast to the KC cell, secondary precipitation processes involving Mn are not likely occurring. The trends in Fig. 7 indicate that at least two different sources for Mg and

![Fig. 6. KCJ sample: comparison between XRD patterns (CuKα radiation) of the starting material and the leached material upon completion of the experiment. The number (100) associated with the mineral names is the PDF intensity value.](image-url)
Mn are possible. In the first ~15 weeks (first significant peak in weekly loading curve) the predominant sources are carbonates whereas aluminosilicates (mainly chlorite) predominate in the second part of the experiment.

Weekly Fe loading values change from a few µg (early weeks) up to $4.49 \times 10^4$ µg (week-57). The iron sources are mainly carbonates, sulfides, oxides and chlorite. Because of high pH values during the first few weeks, Fe released from the solid-phase is easily removed from solution by Fe-oxide–hydroxide precipitation, likely as goethite, as indicated by the geochemical model calculations (Fig. 3). The concentration of Fe in solution increased after week-10, when the pH values declined, and continued to increase until the end of the experiment. Jurjovec et al. (2003) noted that, in their column experiments, Fe loading (together with that of Mg) tended to decrease when the pH reaches very low values, consistent with the reduced amounts of carbonates and chlorite. In this experiment Fe loading continued to increase with decreasing pH, because conditions favour both the oxidation of Fe-bearing sulfide and the dissolution of secondary Fe-bearing phases.

Dissolved Al concentrations are low up to ~week-5, followed by a rapid increase in loading. The first abrupt increase is likely due to gibbsite dissolution (Fig. 3). After gibbsite is depleted, the main Al sources become chlorite dissolution and subsequently other aluminosilicate dissolution, as is evident by an increase in Si loading.

The Na curve shows a limited cumulative loading ($3.22 \times 10^4$ µg). The mass of Na in KC and KCJ bulk samples are similar (around 5000 mg/kg), mostly hosted in albite. Despite this similarity, Na loading in weekly effluents from KCJ sample is consistently higher than from the KC sample, in particular in the first part of the experiment. This observation is consistent with natrojarosite dissolution as the principal source of Na in solution. The cumulative loading curve for K ($5.92 \times 10^4$ µg) is quite similar to KC and is attributed mainly to stilpnomelane and muscovite dissolution.

**Fig. 7.** Manganese loading plotted versus Mg loading for KCJ sample.

**Fig. 8.** Loading of metals versus pH over the 58 weeks of record for the KC and KCJ humidity cells.
4.3. Metal mobility (As, Cd, Co, Cr, Cu, Ni, and Zn)

Metal release from tailings to solution involves not only alteration and/or dissolution processes (e.g., metal sulfides and sulfates), but also de-adsorption processes (e.g., from the surfaces of Fe/Al oxides–hydroxides). Metal release to solution, therefore, is strongly influenced by pH changes and is not necessarily associated with release of other elements from the “host mineral”. Fig. 8 shows the loadings of trace metals versus pH recorded over the 58 weeks. Arsenic and Cr concentrations for both KC and KCJ samples were often below detection limits, and therefore not plotted, whereas Pb was never detected. The comparison between metal loadings for the KC and KCJ samples must account for the addition of the meteoric/residue, which contains significant metal concentrations.

Weekly metal loadings for the KC sample are quite low. This is due to the high pH values observed over the entire experiment, which limits metal mobility. In addition, some metals were likely removed by coprecipitation with or adsorption onto Fe-oxy-hydroxides formed in the sample collection cell. The highest loading values were observed for Zn, which is also the most abundant in the bulk sample (0.7 wt.%). The weekly loading goes from a minimum of $4.05 \times 10^2 \mu g$ to a maximum of $1.9 \times 10^3 \mu g$. Arsenic and Cr concentrations for both KC and KCJ samples were often below detection limits, and therefore not plotted, whereas Pb was never detected. The comparison between metal loadings for the KC and KCJ samples must account for the addition of the meteoric/residue, which contains significant metal concentrations.

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Results obtained for the three KCJ samples (where oxidation reactions had progressed the most and acid conditions were established) were negative for populations of **neutrophilic sulfur-oxidizing bacteria** and **acidiphilic sulfur-oxidizing bacteria**, whereas they were positive for **acidiphilic iron-oxidizing bacteria**. This latter population exhibited $2.4\times10^4$ cells/g as the most probable number (MPN) along the whole length of the cell. In the field a zone dominated by a single population of bacteria was not found. Nevertheless the predominance of **acidiphilic iron-oxidizing bacteria** occurred in the tailings zone representative of established oxidation and acidification (MPN = $1.3\times10^7$/g).

Therefore, the data obtained in the laboratory study, are qualitatively in good agreement with microbiological studies conducted at the Kidd Creek tailings impoundment, whereas MPN values determined in the laboratory are consistently lower. **Neutrophilic bacteria** were most abundant during the early stages of sulphide oxidation, when $O_2$ represents the main oxidant and pH values are still high, whereas **acidiphilic species** become predominant after acidic conditions are attained when Fe$^{3+}$ becomes the main oxidant.

**5. Conclusions**

The humidity cell procedure applied on tailings samples has some limitations, due to the unique characteristics of this type of material. With this design, sulfide mineral oxidation may be limited by oxygen diffusion through the partly saturated tailings due to water retention during weekly-cycles. In particular water retention and the inability to quantify oxygen diffusion during the experiment cause variable element loading rates, affecting the water geochemistry interpretation. Nevertheless results obtained over 58 weeks of observation have important environmental implications.

The comparison of $SO_4$ loading and pH–Eh values between the two approaches shows that oxidation reactions had progressed the presence of only 3 wt.% natrojarosite. These results are in agreement with previous laboratory studies as well as field observations. Metal mobility at high pH values is negligible, whereas metal loading at low-pH values is high and is environmentally significant. Mineralogical control of the pH is limited by the short leaching time, which did not permit the leach water to attain equilibrium with respect to the solid phases. In general the pH did not rigorously follow the acid-neutralization conceptual model proposed by Morin et al. (1988) for mill tailings and confirmed by Jurjovec et al. (2002) for the same Kidd Creek materials.

Even considering these limitations, the test yielded a predictive model for the Kidd Creek tailing impoundment which is not dissimilar from previous studies, differing primarily for early stages of the acid drainage generation. Microbiological studies under laboratory conditions showed a good agreement with field studies indicating that they can be used to accompany the testing protocol and used with confidence to evaluate the test results.

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**References**


