

TESTING A STANDARD TEST METHOD FOR LABORATORY WEATHERING ON SULPHIDE CONTAINING MINE TAILINGS

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Abstract

A Standard Test Method (ASTM D 5744), for laboratory weathering using a humidity cell procedure, was conducted on two sulfide containing tailings samples from a metallurgical site in Ontario (Canada). To test the reliability of this method, results were compared with those of previous studies on the same samples. The mineralogy of the samples differs only by the addition of a small amount of natrojarosite in one of the samples. The sulfide oxidation rate and release rates of elements during weathering were monitored. Both processes are influenced strongly by the capacity of the material to generate acidity, which was enhanced by the presence of natrojarosite. Acid-neutralization processes occurring during the laboratory test were affected by reaction kinetics. In the laboratory tests, the carbonate minerals more readily neutralized acid compared to field observations, where a more prolonged solid-solution interaction allowed chemical equilibration to be reached. As a consequence, the capacity of this standard test to predict weathering reactions is limited by its inability to reproduce the chronology of full scale reactions.

Introduction

Sulfidic wastes from ore processing, including waste rock or mill tailings, are typically deposited in piles or impoundments nearby the mine workings. In these piles sulfide minerals are exposed to air and undergo oxidation reactions. This oxidation may lead to generation of acid effluents and the release of Fe, SO₄ and potentially toxic elements into surface and ground waters, causing environmental damage.

The goal of the scientific community is to determine with sufficient certainty how sulfidic 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 topic include detailed field investigations and/or laboratory studies.

The advantage in conducting laboratory experiments is the lower cost and the more timely acquisition of data, but also the possibility to conduct experiments prior to disposal of mine wastes. The presupposition is that laboratory-scale measurements of oxidation rates of sulfidic mine wastes are sufficiently similar to field measurements so that the laboratory rates can be used with confidence in predictive models of full scale waste piles (Bennett et al., 2000).

In this study, a series of humidity test cell experiments was conducted under controlled laboratory conditions using fresh unoxidized tailings from a mine-waste disposal facility at the Kidd Creek metallurgical site near Timmins, Ontario. Results were correlated with those obtained from previous experiments conducted on the same material, which examined acid neutralization relations in isolation from acid-producing reactions (Jurjovec et al., 2002, 2003). In contrast, the humidity test cell experiments evaluate weathering when both acid generation and acid neutralization reactions are allowed to occur simultaneously.

The experimental results were used to estimate parameters controlling the oxidation rates of sulfide materials, and to predict mechanisms controlling the mobility of metals in the pore water.

Material

Solid materials used in this study are: a) one sample (labeled KC) of fresh unoxidized tailings collected at the concentrator at the Kidd Creek metallurgical site in Ontario, Canada; b) one sample (labeled KCJ) of the same tailings mixed with 3% wt. of natrojarosite, a waste derived from the adjacent Zn refinery. Since 1985 the natrojarosite has been co-disposed with mine tailings and deposited in a single impoundment. The 3% of natrojarosite added to the KCJ sample reproduces the proportion co-disposed in the field. Jurjovec et al. (2003), who previously conducted experiments on these samples, verified that the presence of natrojarosite diminishes the ability of tailings to buffer acidic solutions.

The mineralogy of the tailings was determined by Jambor et al. (1993) to be as follows: 15 wt. % sulfides (mainly pyrite [FeS₂], secondarily pyrrhotite [Fe_{1-x}S], chalcopyrite [CuFeS₂], and sphalerite [(Zn,Fe)S]), 8 wt. % carbonates (siderite [FeCO₃], ankerite-dolomite [Ca(Fe,Mg)(CO₃)₂], calcite [CaCO₃]) and Fe-oxides [Fe₂O₃], 49 wt.% quartz [SiO₂], 24 wt.% chlorite [(Mg,Fe²⁺)₅Al(Si₃Al)O₁₀(OH)₈], and the balance of other silicates and aluminum-silicates.

Methods

The Standard Test Method ASTM D 5744 is designed to enhance the mass release of acidity/alkalinity, metals, and other pertinent analytes from a 1000-g sample of solid material. This is done by providing conditions to promote sample oxidation and leaching using a fixed volume of water of specified purity. The test method is performed on each sample in a cylindrical cell (humidity cell). The protocol calls for weekly cycles consisting of three days of dry air and three days of water-saturated air pumped up through the sample, followed by a leach with water on Day 7. The weekly effluent produced is collected and concentrations of dissolved weathering products determined. The test duration is determined by the objectives of the test. Before initiation of the weathering cycle, samples are 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 they mark the end of the weekly cycle for that numbered week.

pH, Eh, alkalinity and conductivity were determined immediately after each weekly effluent collection. Weekly effluents were subsequently analyzed for SO_4 by ion chromatography, and other selected analytes by inductively coupled plasma optical emission spectrometry. Weekly loading of the constituents of interest was calculated as: $L_e = C_e \times M_e$, where L_e = loading of the constituent of interest in the effluent (μg), C_e = concentration of the constituent of interest in the effluent ($\mu\text{g/g}$) and M_e = weekly mass of the collected effluent (g). We assumed C_e for elements to be 50% the detection limit when its value was below that limit. Pore water geochemistry interpretation was carried out with the assistance of the geochemical code MINTQA2 (Allison et al., 1990). The thermodynamic database was adopted from the speciation model WATEQ4F which was appropriately implemented with solubility data of some minerals. The results of geochemical modeling include saturation index (SI) for minerals. During the leach, 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 used carefully in data interpretation to propose reaction models, disregarding their numeric value in specific weeks, instead considering the general tendency of a mineral phase toward undersaturation or saturation conditions.

Results and Discussion

Figures 1 and 2 show changes of pH, Eh and loading of elements vs. time over the 58-weeks of record for KC and KCJ humidity cells.

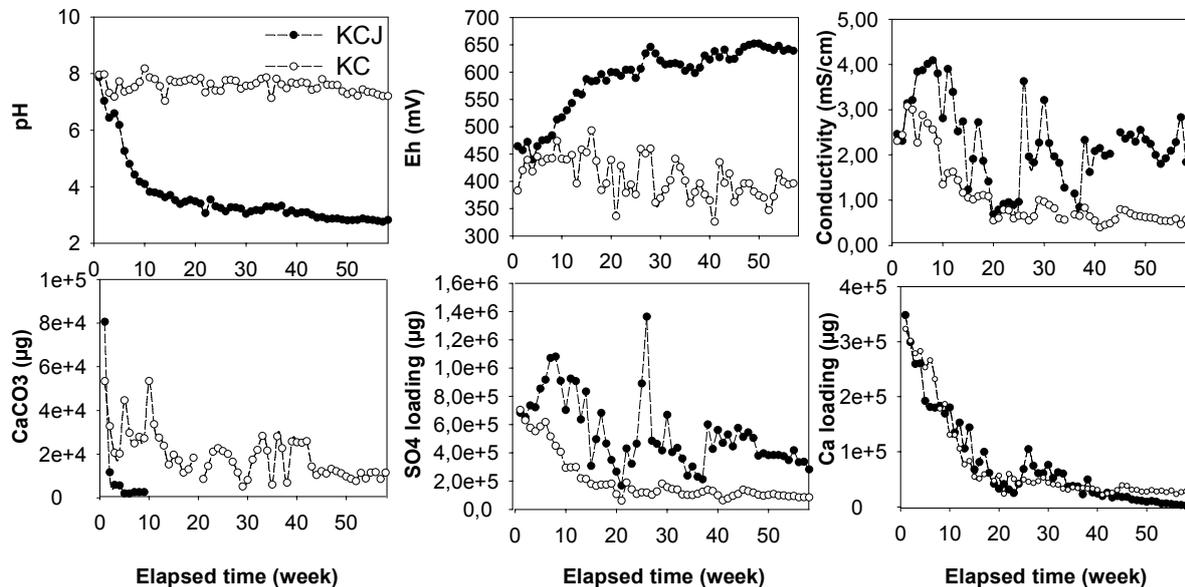


Figure 1. Changes of pH, Eh and Conductivity, and loading of CaCO_3 , SO_4 and Ca vs. time over the 58-weeks of record for KC and KCJ humidity cells.

1. KC sample results

Values of pH recorded in weekly effluents, with a starting pH of 7.96 and an ending pH of 7.20 (pH average = 7.57; Std. Dev. = 0.24) indicate that mill 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 oxidative conditions

(Eh average = 406 mV; Std. Dev = 37). Values of conductivity sharply decreased from week-1 to approximately week-20 (from 2.31 to 0.55 mS/cm), maintaining rather stable values from ~ week-20 until the end of the experiment (week-58 conductivity = 0.56 mS/cm).

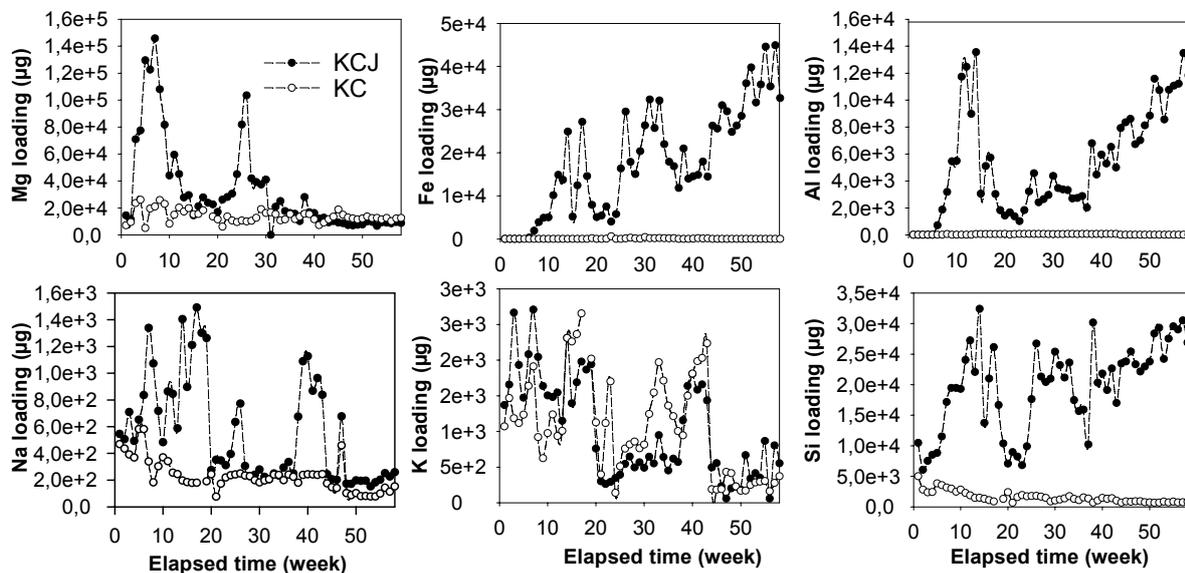


Figure 2. Loading of elements vs. time over the 58-weeks of record for KC and KCJ humidity cells.

Calcium and SO₄ loading distributions show a very good correlation ($R^2 = 0.98$) over the entire experiment (Fig. 3). During the first ~ 8-10 weeks, the saturation index (SI) values for gypsum [CaSO₄·2H₂O] are close to equilibrium values (Fig. 4), and the average SO₄/Ca molar ratio in solution is close to 0.9. Gypsum was observed in the tailings from the Kidd Creek impoundment; moreover it is a very common oxidation product in sulfide tailings that can also accumulate during sample storage. Over the elapsed time of the experiment, SO₄ and Ca weekly loading was substantial (from week-1 to week-10 cumulative loading is 5.33E+06 µg for SO₄, and 2.43E+06 µg for Ca), and decreased sharply. After week-10, weekly effluents become increasingly undersaturated with respect to gypsum while SO₄ and Ca loadings continued to decrease sharply until ~ week-20.

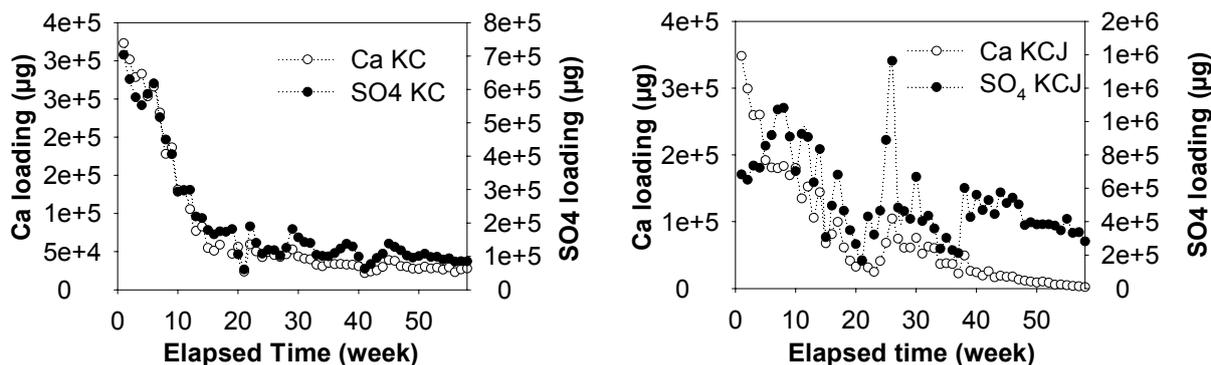


Figure 3. Comparison of loading of Ca and SO₄ vs. time over the 58-weeks of record for KC and KCJ humidity cells.

After week-20 changes in loading values are smoother, though maintaining the tendency to decrease (cumulative loading from week-21 to week-58 is 4.26E+06 µg and 1.31E+06 µg respectively for SO₄ and Ca). SO₄/Ca molar ratios increased to approximately 1.5 indicating that gypsum was no longer controlling their concentrations. An alternative source of SO₄ in solution was likely sulfide oxidation reactions, while Ca was likely derived mainly from carbonate dissolution. Since pH values were not observed to decrease, it can be assumed that the acidity

produced by sulfide oxidation was totally neutralized by carbonate dissolution. Siderite, which usually contains negligible Ca, is the primary carbonate in the Kidd Creek tailings (60% wt. of the total carbonate content), but it is also the least soluble of the carbonates; calcium is mainly present in ankerite-dolomite (35% wt.), and in calcite (only 5% wt.). 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 in the first 10 weeks consistent with the dissolution of gypsum as the main source of Ca. Subsequently and until week-28, the average ratio was closer to the ratio in ankerite-dolomite in the tailings indicating that dissolution of ankerite-dolomite is likely the main source for both Ca and Mg. After week-29 and until the end of the experiment, due to a decrease in Ca weekly loading, the Ca/Mg ratio declined to < 2. This decline may be due to the fact that either ankerite-dolomite is no longer the only phase contributing to Mg release to solution or Ca is controlled by precipitation. From the calculated SI values, precipitation of a Ca bearing phase was not evident. Jurjovec et al. (2002) showed in their experiment that chlorite represented another important source of Mg and, after carbonate depletion, was the main mineral controlling its concentration in solution. Nevertheless, the two experiments have to be carefully compared due to the different nature of the leaching solution. Since weekly loadings of Mg or other elements present in chlorite (Si, Al, Fe) were not observed to increase, substantial dissolution of chlorite is not likely, consistent with calculated SI values (Fig. 4). More likely, the mass of ankerite-dolomite had likely declined to the extent that siderite (bearing much more Mg than Ca) dissolution became more pronounced, inducing the observed variation in Ca/Mg molar ratio.

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 effluents and precipitated immediately as Fe-oxyhydroxides. Saturation indexes for goethite (Fig. 4) were > 0 for the entire experiment.

Concentrations of Al were below the detection limit of 0.037 µg/g during all 58 weeks. Since Al is mostly present in aluminum-silicate phases, it is not leached in relevant amounts at these pH values. Moreover the effluents are over-saturated with respect to gibbsite during the entire experiment (Fig. 4) 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 1.30E+04 µg, 6.04E+04 and 8.81E+04 µg. These elements are not easily released through weathering and their loading tends to diminish versus time.

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 neutralization capacity provided by minerals in the tailings with added natrojarosite was limited to the first few weeks. These results are in agreement with Jurjovec et al. (2003), who showed that natrojarosite dissolution is an acid-producing reaction which consequently reduces the buffering capacity of the tailings. The acidity produced by its dissolution quickly primes sulfide oxidation and enhances its rate. In the test cells, the pH continued to drop until the end of the experiment, although not so sharply as in the first part of it.

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).

In contrast to the KC sample, Ca and SO₄ loading distribution did not always show a strong correlation (Fig. 3). Both elements tended to decrease in solution over time, but not necessarily along the same trend. On the contrary, if the Ca loading curves for KC and KCJ samples are compared, there is good agreement (Fig. 1); cumulative loadings at week-58 are respectively 4.41E+06 µg for KC and 4.37E+06 µg for KCJ meaning 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 since 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 KCJ starts to diverge significantly from KC after week-42. At this time Ca was still released from KC sample, while Ca loading from the KCJ sample quickly approached 0. In contrast, the SO₄ cumulative loading curves are very different. Cumulative loadings at week-58 are respectively 1.16E+07 µg for KC and 3.12E+07 µg for KCJ indicating that the mass of sulfur removed from KCJ is much higher than in KC, and is consistent with a faster sulfide oxidation rate. Dissolution of carbonates was not sufficient to neutralize all of the acidity produced by the combination of sulfide oxidation and natrojarosite dissolution, because the acid generation was more rapid than acid neutralization, probably because the high leach rates did not allow equilibrium with the carbonate minerals to be attained. Jurjovec et al. (2002) noticed a similar behavior. The consequence is that, even before carbonate mineral depletion, the pH decreases rapidly because the capacity of carbonates to neutralize acidity is limited by the kinetics of their dissolution.

Magnesium is characterized by an irregular weekly loading for most of the experiment, and is similar to the KC curve only during the last part of the experiment. The first abrupt increase (at the beginning of the experiment) may be due to a quick initiation of siderite dissolution (compared to KC sample) because of the lower pH values. However, carbonates are clearly not the only Mg source, not only because Ca and Mg trends would be more similar, but also because KCJ Mg cumulative loading ($1.90E+06 \mu\text{g}$) is much higher than for KC ($7.90E+05$). Since pH values are lower than for KC sample, chlorite dissolution is probable. The chlorite SI goes from undersaturated to strongly undersaturated conditions (Fig. 4), with a second abrupt increase occurring around week-23 (see also SO_4). Weekly Fe loading values change from a few μg (early weeks) up to $4.49E+04 \mu\text{g}$ (week-57). The iron sources are mainly carbonates, sulfides, oxides and chlorite. Because of high pH values during the very first weeks, Fe released from the solid-phase is easily removed from solution by Fe-oxide-hydroxide precipitation, likely as goethite, consistent with equilibrium calculations (Fig. 4). The concentration of Fe in solution increased after week-10, after pH values declined, and continued to increase until the end of the experiment. In their column experiments Jurjovec et al. (2002) noted that 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 which promote sample oxidation are applied, and sulfide oxidation is enhanced.

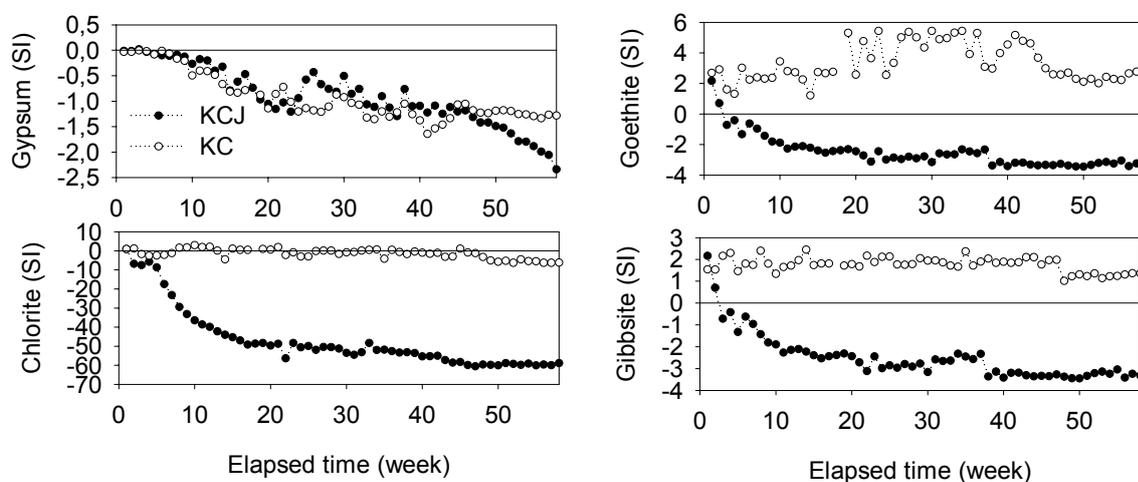


Figure 4. Saturation indices of some selected minerals vs. time over the 58-weeks of record for KC and KCJ humidity cells.

As shown for Fe, Al is removed from solution up to \sim weeks-5, followed by a rapid increase in loading. The first abrupt increase is likely due to gibbsite dissolution (Fig. 4). After gibbsite is depleted, the main sources of Al become chlorite dissolution and subsequently aluminum-silicates, as is evident by an increase in Si loading.

The Na curve shows a limited cumulative loading ($3.22E+04 \mu\text{g}$). The mass of Na in KC and KCJ bulk-samples are similar (around 5000 mg/kg), mostly contained in albite. Nevertheless, 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, consistent with natrojarosite dissolution as the main source of Na in solution.

The cumulative loading curve for K ($5.92E+04 \mu\text{g}$) is quite similar to KC and is attributed mainly to muscovite dissolution.

3. Trace metal mobility

Loadings of trace metals vs. time over the 58-weeks of record are shown in Figure 5 for the KC and KCJ humidity cells. Cadmium and Co curve trends (not shown) are similar to Zn.

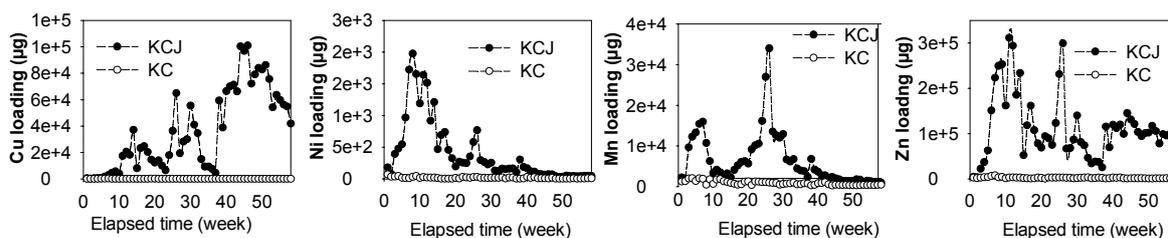


Figure 5. Loading of metals vs. time over the 58-weeks of record for the KC and KCJ humidity cells.

Weekly metal loadings for the KC sample are quite low. This is due to the high pH values observed over the entire experiment, which immobilizes metals. The highest loading values were observed for Zn (from a minimum of 4.05E+02 µg to a maximum of 7.76E+03 µg). Moreover Fe-oxy-hydroxide precipitation likely removed some of these metals from solution by adsorption or co-precipitation reactions.

Weekly trace metal loadings for KCJ sample are substantial compared to KC. Copper loading increased with a decrease in pH, while Zn, Ni, Cd and Co were significantly leached at higher pH values. Manganese had a similar trend to Mg, suggesting a common origin. The mean weekly loading for trace metals for KCJ in order of abundance (Zn > Cu > Mn > Fe > Al > Ni > Cd > Co) is different from that for the KC sample (Zn > Mn > Co > Fe > Cu > Ni > Cd; Al below DL) showing the strong pH influence in metal mobilization.

Conclusions

The humidity cell procedure applied on tailings samples presents some inconsistencies, due to the peculiar characteristic of this kind of material, leading to irregular loadings of some elements. Nevertheless results obtained over 58 weeks of observation allow some important environmental considerations.

The comparison of SO₄ loading and pH-Eh values between the two samples shows that, in spite of a very similar mineralogical composition, sulfide oxidation rate is strongly enhanced in KCJ sample, due to acidity produced by the presence of natrojarosite. These results are in agreement with previous studies. Metal mobility at high pH values is notably limited, while metal loading at low pH values is high and is environmentally significant. Mineral control of pH is limited by the short leaching time, which did not permit the leach water to reach equilibrium with respect to the solid phases. In general pH control 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 similar material. As a consequence, the capacity of the humidity test cells to develop predictive models without careful data interpretation could result in the inability of the test to reproduce the behavior of full scale waste piles.

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