ACID NEUTRALIZATION IN MILL TAILINGS AND THE EFFECT OF NATROJAROSITE ADDITION[1]

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Abstract: At many zinc refineries natrojarosite is precipitated to remove iron from leach circuits. The natrojarosite can be either disposed of in a separate settling pond or in the tailings impoundment mixed with concentrator tailings. To evaluate the potential effects of natrojarosite co-disposal with mill tailings, a series of laboratory column experiments was performed. The objective of the experiments was to assess the effects of natrojarosite addition to flotation tailings. The results of the experiments show that the pH of the effluent water is controlled by dissolution of the solid phases, including $(Ca,Mn,Mg,Fe)CO_3$ and $Al(OH)_3$, $Fe(OH)_3$, and aluminosilicate minerals. After complete dissolution of a buffering mineral, the pH decreases until equilibrium is attained with respect to the next buffering mineral. Similar pH buffering reactions are observed in the column where natrojarosite is present, and in the column where natrojarosite is absent. In the column effluent data these pH-buffering reactions are indicated by a series of near-constant pH-plateaus. The observed pH-plateaus were at: 5.7, 4.0, 1.7, and 1.3. The results show that the buffering capacity of tailings is consumed more rapidly when natrojarosite is added to the tailings. Concentrations of dissolved elements including Na and K are higher in the effluent water from the column containing natrojarosite.

Key Words: acid neutralization, natrojarosite, mill tailings, column experiments

Introduction

The precipitation of jarosite-type compounds $MFe_3(SO_4)_2(OH)_6$, where M=Na, K, H_3O, etc., is widely used in the metallurgical industry as a means of controlling iron, sulfate, or alkalis in processing solutions (1). The principal application of natrojarosite precipitation is for iron control in sulfate-based hydrometallurgical zinc circuits (1). In most cases, natrojarosite residue is disposed of in separate settling ponds. An alternative practice is to combine the natrojarosite residue with the concentrator tailings and dispose of the mixed waste in the tailings impoundment. The benefits and problems associated with co-disposal of natrojarosite residue and sulfide-rich mill tailings are poorly understood. Thermodynamic calculations suggest that natrojarosite is potentially unstable under medium to low Eh and below neutral pH (2). Field studies at the Kidd Creek metallurgical site, near Timmins, Ontario, indicate, that natrojarosite may be dissolving (3).

A conceptual hydrogeochemical model of acid neutralization of pore-water in mill tailings was proposed for uranium tailings in the Nordic Main impoundment near Elliot Lake, Ontario (4). The conceptual model suggests that the acidic water originating from sulfide oxidation in the unsaturated zone is buffered by a sequence of minerals. The pH is buffered by sequential dissolution of calcite, siderite, $Al(OH)_3$, and $Fe(OH)_3$. This model has been generalized for tailings containing sulfide minerals on the basis of observations made at a number of tailings impoundments (5,6,7). The acid neutralization reactions are divided into equilibrium dissolution reactions, including dissolution of carbonate and hydroxide minerals and kinetically controlled dissolution of aluminosilicate minerals (5,6,7). The dissolution of carbonate and hydroxide minerals is relatively fast, while the dissolution of aluminosilicate minerals at low temperatures is slow relative to groundwater flow rates. Therefore, whereas the pore-water in tailings attains equilibrium with respect to carbonate and hydroxide minerals, equilibrium with respect to aluminosilicates in mill tailings has not yet been observed.

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The importance of studying acid-neutralization reactions lies in their ability to control the pH of mill-tailings pore-water. The neutralization reactions thus indirectly control the mobilities and attenuation of metals in the tailings pore-water.

The objectives of this study were: (i) to examine the validity of the proposed conceptual model under controlled conditions, (ii) to determine the possible effects of natrojarosite co-disposal on the mill-tailings buffering capacity and (iii) to develop a procedure which would enable prediction of the future pore-water quality within the tailings.

Methods

Methods of investigation

A series of laboratory column experiments was performed. Here we present results obtained from two of these experiments. The solids used in the experiments were collected at the Kidd Creek metallurgical site, near Timmins, Ontario. The first column was packed with fresh, unoxidized mill-tailings, collected at the tailings concentrator (called the tailings column). The second column was packed with concentrator tailings combined with 3 wt. % of natrojarosite residue (the natrojarosite column). This proportion is similar to that found in the Kidd Creek impoundment.

The mineralogy of the mill tailings is as follows (8): 15.1 wt% of sulfides (pyrite, pyrrhotite, chalcopyrite and sphalerite), 8 wt% of carbonates and hydroxides, 49.1 wt% of quartz, and the balance of silicates and aluminosilicates (chlorite, amphibole, stiplnomelane, albite, muscovite). Electron microprobe analyses and X-ray studies indicate that calcite, dolomite, ankerite and siderite are present in the tailings, but are rarely of the end member composition. The average cation composition for siderite and ankerite was found to be: $Fe_{0.904}Mg_{0.066}Mn_{0.022}Ca_{0.0008}$ and $Fe_{0.259}Mg_{0.210}Mn_{0.003}Ca_{0.499}$ respectively. The relative proportion of carbonates in the main impoundment were concluded to be 5% calcite, 35% dolomite-ankerite and 60% siderite. Mineralogical investigation of Kidd Creek jarosite residue shows that the main component is zinc-bearing natrojarosite in which sodium is partially replaced by hydronium and potassium (9).

To simulate acidic pore-water generated in the unsaturated zone of some tailings impoundments, we used 0.1M H_2SO_4 as the column input solution. The experimental set-up consisted of a reservoir, a controlled-flow pump, a column and a sampling cell (Figure 1). Samples of column effluent water were collected *versus* time. The samples were filtered through 0.45μm nylon filters. The alkalinity, pH, and Eh were measured immediately after sampling. The pH and Eh were measured under sealed conditions. The pH was measured using an Orion Sure-Flow Ross 8165BN electrode calibrated with standard buffers 4 and 7. The Eh was determined using an Orion Eh 9678BN electrode, checked with ZoBell's (10) and Light solution (11). Concentrations of Fe were determined colorimetrically (12), concentrations of SO_4 were determined by ion chromatography, and concentrations of Na and K by flame atomic absorption. The concentrations of Al, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Li, Mg, Mn, Mo, Pb, Sr, V, and Zn were determined

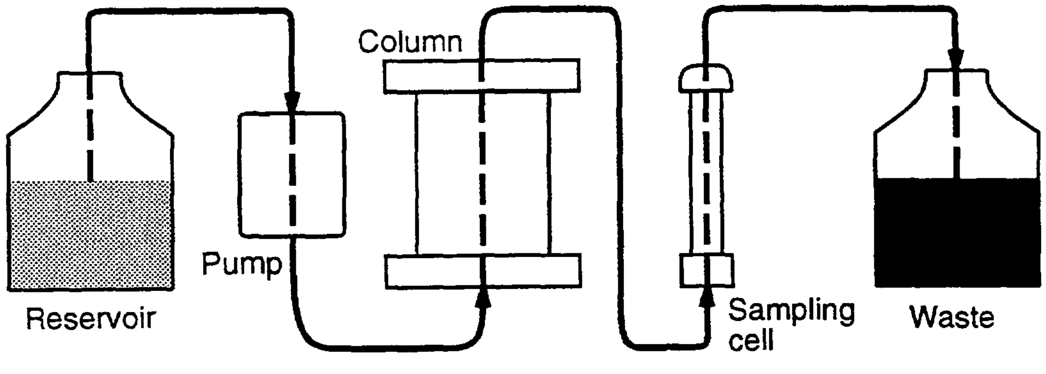

Figure 1. Experimental set-up.

by inductively coupled plasma emission spectroscopy. A conservative tracer test was performed prior to experiment, using chloride as a tracer. Concentrations of chloride were determined colorimetrically (13).

Methods of interpretation

The flow parameters were determined by modeling Cl concentrations measured during the tracer test, and by measuring flow rates. The modeled parameters obtained from the leading edges of the breakthrough curves using the nonlinear least squares optimization model CXTFIT (14) are given in Table 1. The porosity of the solid sample is close to the porosity observed in the field. The velocity, however, is an order of magnitude higher than the velocity observed in the field. This velocity was chosen to shorten the duration of the experiment.

Table 1. Flow parameters for the two column experiments.

Parameter	Plain Tailings	Tailings with Natrojarosite
Porosity	44%	44%
Dispersivity (cm)	0.28	0.26
Velocity (cm/h)	0.33	0.36

The pore-water geochemistry was interpreted by modeling measured parameters with the equilibrium geochemical speciation/mass transfer model MINTEQA2 (15). The thermodynamic database was adopted from the speciation model WATEQ4F (16). The degree of saturation in this paper is expressed as saturation index (SI), where SI is equal to the difference of logarithms of ion activity product and solubility constant ($SI = \log IAP - \log K_{sp}$). A saturation index value of zero indicates equilibrium, a negative value undersaturation, and a positive value supersaturation.

Results and Discussion

During an experiment a series of nearly horizontal pH-plateaus was observed. We define a "*pH-plateau*" as a portion of the pH-time curve, where (i), pH is nearly constant with respect to the abrupt changes in pH between the plateaus and (ii), dissolution of a mineral is believed to buffer the pH of the pore-water. The pH-plateaus are labelled according to the phase which is inferred to buffer the tailings pore-water. The pH-plateaus are expected to be slightly inclined due to changing ionic strength of the pore-water. The carbonate plateau is also inclined due to changing CO_2 partial pressure.

A series of Eh-plateaus has also been observed. We define an "*Eh-plateau*" as a portion of Eh-time curve where (i) Eh is nearly constant and (ii), Eh is believed to be maintained in a certain range due to dissolution of one or more minerals (ferrihydrite, goethite, and natrojarosite).

Plain Tailings Pore-water Geochemistry

Three pH-plateaus were observed for the plain tailings column: the carbonate pH-plateau (pH 5.78-5.13), the gibbsite pH-plateau (pH 4.05-3.75) and the aluminosilicate pH-plateau (pH~1.3). Geochemical calculations indicate that at the first pH-plateau the pore-water is not in equilibrium with either calcite or siderite (Figure 2). The column effluent is undersaturated with respect to calcite and supersaturated with respect to siderite. This observation is consistent with the carbonate mineralogy of the tailings. The solubility constant of solid solution depends on the proportion of the end members in the solid solution. The value is usually closer to the solubility constant of the end member which dominates the solid solution. The solubility constant for the Kidd Creek carbonate has not been determined. However, we believe that the pore-water is in equilibrium with respect to the carbonate solid solution $(Ca,Mg,Mn,Fe)CO_3$.

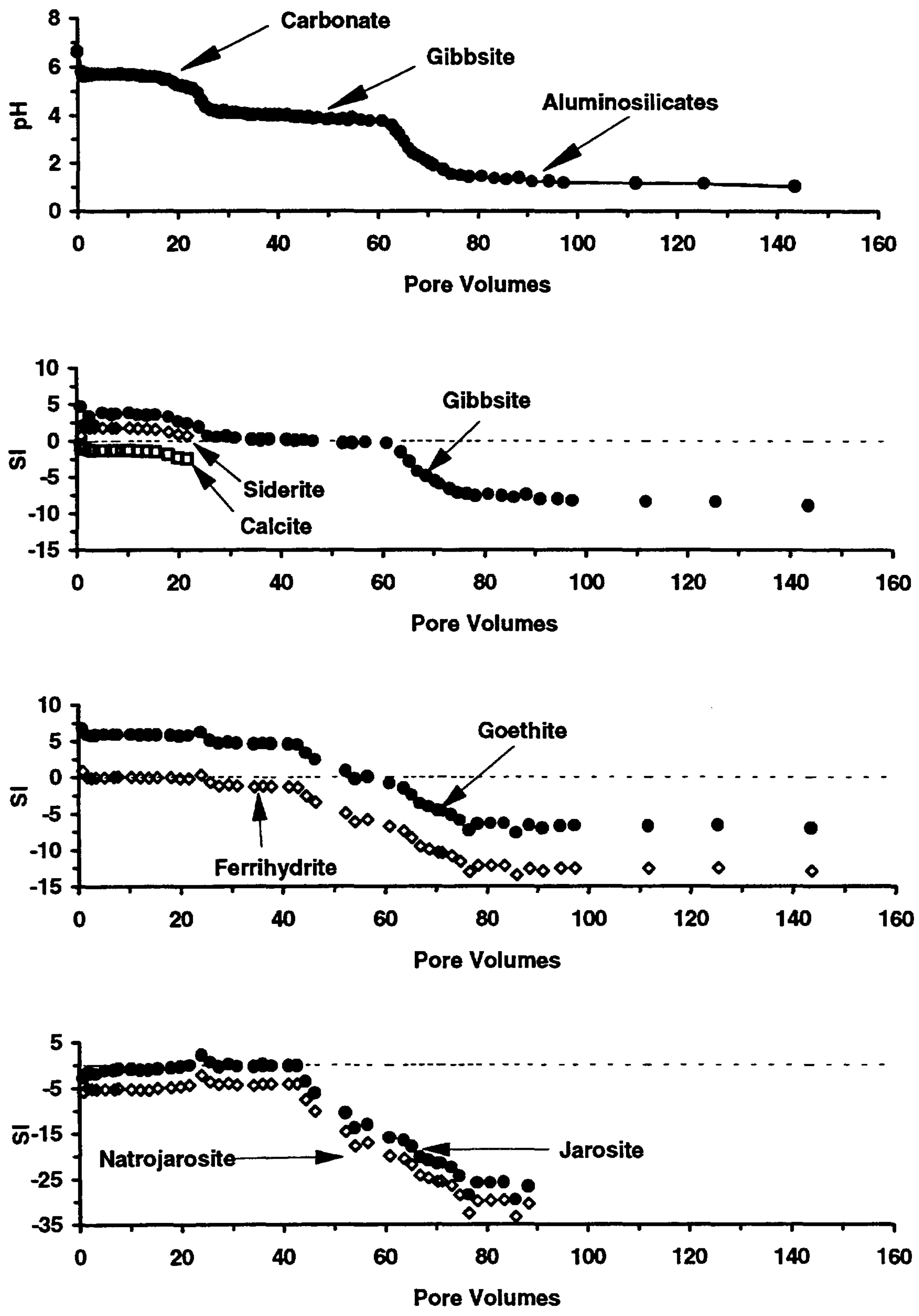

Figure 2. The measured pH and calculated saturation indices (SI) for the tailings column (SI = logIAP - logK_{sp}).

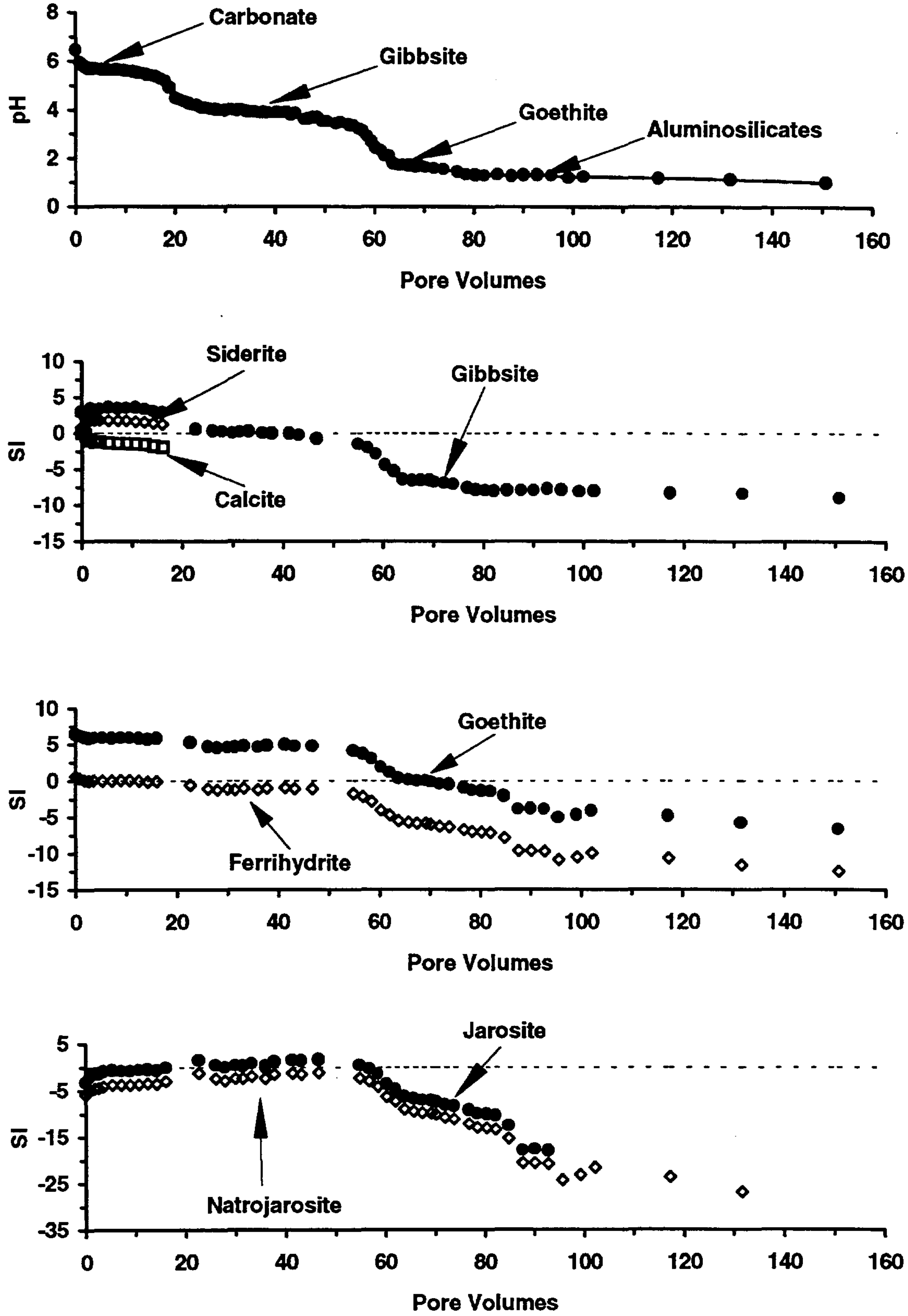

Figure 3. The measured pH and calculated saturation indices (SI) for the natrojarosite column (SI = logIAP - $\log K_{sp}$).

During the time when the pH is believed to be buffered by dissolution of carbonate minerals, the pore-water remains supersaturated with respect to gibbsite and goethite, indicating that the precipitation of these minerals is favored. The effluent water also remains at equilibrium with respect to ferrihydrite. The depletion of alkalinity (Figure 4), suggesting the depletion of carbonates, corresponds to the abrupt decrease in pH. Supersaturation of the pore-water with respect to gibbsite and goethite, and a fairly rapid decrease in pH indicate, that in spite of the high pore-water velocity, the local equilibrium can be assumed under the given conditions.

Geochemical calculations suggest that the pore-water at the second pH-plateau is in equilibrium with respect to gibbsite. Therefore, the pH is believed to be buffered by the dissolution of gibbsite. Gibbsite has not been isolated from the tailings column or from the *in situ* tailings. Goethite remains supersaturated through most of the second pH-plateau. It is interpreted that goethite is depleted at approximately the same time as gibbsite and it becomes undersaturated prior to the expected depletion of gibbsite.

The pH of the column effluent decreases abruptly to a pH of about 1.3, the last pH-plateau (Figure 2). This decrease in pH is believed to be less rapid than the first one and it is interpreted to be due to enhanced kinetically controlled dissolution of aluminosilicates at lower pH.

The Eh-time curve can be divided in four sections: the carbonate Eh-plateau (160-180 mV), the ferrihydrite Eh-plateau (360-400 mV), goethite Eh-zone (400-76 mV), and a zone when dissolved Fe(III) and Fe(II) species control the pore-water Eh. The first Eh-plateau is believed to be maintained at very low values due to dissolution of (Ca,Fe,Mg,Mn)CO_3 (Figure 4). Geochemical calculations suggest that as a phase is depleted, the Eh increases to the next plateau. A higher Eh value is attributed to ferrihydrite dissolution. As ferrihydrite becomes undersaturated, the Eh decreases abruptly from 400 to 76 mV. We believe that this decrease is due to the lower Fe^{3+} activity controlled by the solubility of goethite at a pH buffered by the dissolution of gibbsite. The Eh stabilizes around 220 mV after the goethite saturation index decreases to -10.

Geochemistry of Column Effluent Water from Tailings Mixed with Natrojarosite

The pH of the effluent water collected from the column containing mill tailings and natrojarosite is believed to be governed by dissolution of the following sequence of minerals: (Ca,Mg,Fe,Mn)CO_3 (pH 5.78-5.13), gibbsite (pH 4.05-3.75), goethite (pH 1.78-1.31), and aluminosilicates (pH~1.3).

The similarity of the two pH-time curves (Figure 4) and values of the saturation indices suggest that the same reactions determine the pH of the pore-water. We believe that a goethite pH-plateau in the natrojarosite column develops due to dissolution of natrojarosite and precipitation of goethite. Geochemical modeling suggests that the dissolution of goethite buffers the pH at a plateau of 1.78-1.31. Because the pore-water remains in equilibrium with respect to ferrihydrite until the pH drops to the last pH-plateau, it is expected that the amount of ferrihydrite precipitated in the column is also greater.

The Eh-time curve can also be divided into four sections: the carbonate Eh-plateau (160-180 mV), the ferrihydrite Eh-plateau (400-500mV), the goethite Eh-zone (550mV) and a zone when dissolved Fe(III) and Fe(II) species control the pore-water Eh. At the first Eh-plateau, where Eh is believed to be controlled by dissolution of (Ca,Fe,Mg,Mn)CO_3, the Eh is similar to that observed in the plain tailings column. At the ferrihydrite plateau, the Eh is slightly higher than in the plain tailings, possibly due to natrojarosite dissolution. When the pH drops due to depletion of gibbsite, the Eh increases to maintain equilibrium with respect to goethite and Fe(II) species under low-pH conditions. At about 85 pore volumes the Eh decreases.

Comparison of the Two Experiments

The comparison of the measured pH, Eh and alkalinity, as well as saturation indices calculated by the geochemical model MINTEQA2 show that the experimental method employed is repeatable. Similar pH, Eh, alkalinity and concentrations of species are measured in effluent regions where the same mechanisms are assumed to govern the behavior of the system. The small differences in tailings composition lead to slightly more rapid decrease in alkalinity and pH in the jarosite column. The difference in the Eh between experiments is consistent with the conceptual model of the acid-neutralization process, suggesting that Eh is a meaningful parameter in these experiments.

Substantially higher sodium and slightly higher potassium concentrations in the column containing natrojarosite demonstrate that natrojarosite is dissolving (Figure 5). Comparison of the measured pH (Figure 4) for both columns and calculated saturation indices show that the sequence of acid-neutralization mechanisms are similar in both columns. However, the pH and alkalinity of effluent water in the natrojarosite column decrease slightly more rapidly than in the tailings column, suggesting that the buffering minerals: (Ca,Mg,Fe,Mn)CO_3, gibbsite, ferrihydrite and goethite are depleted more quickly.

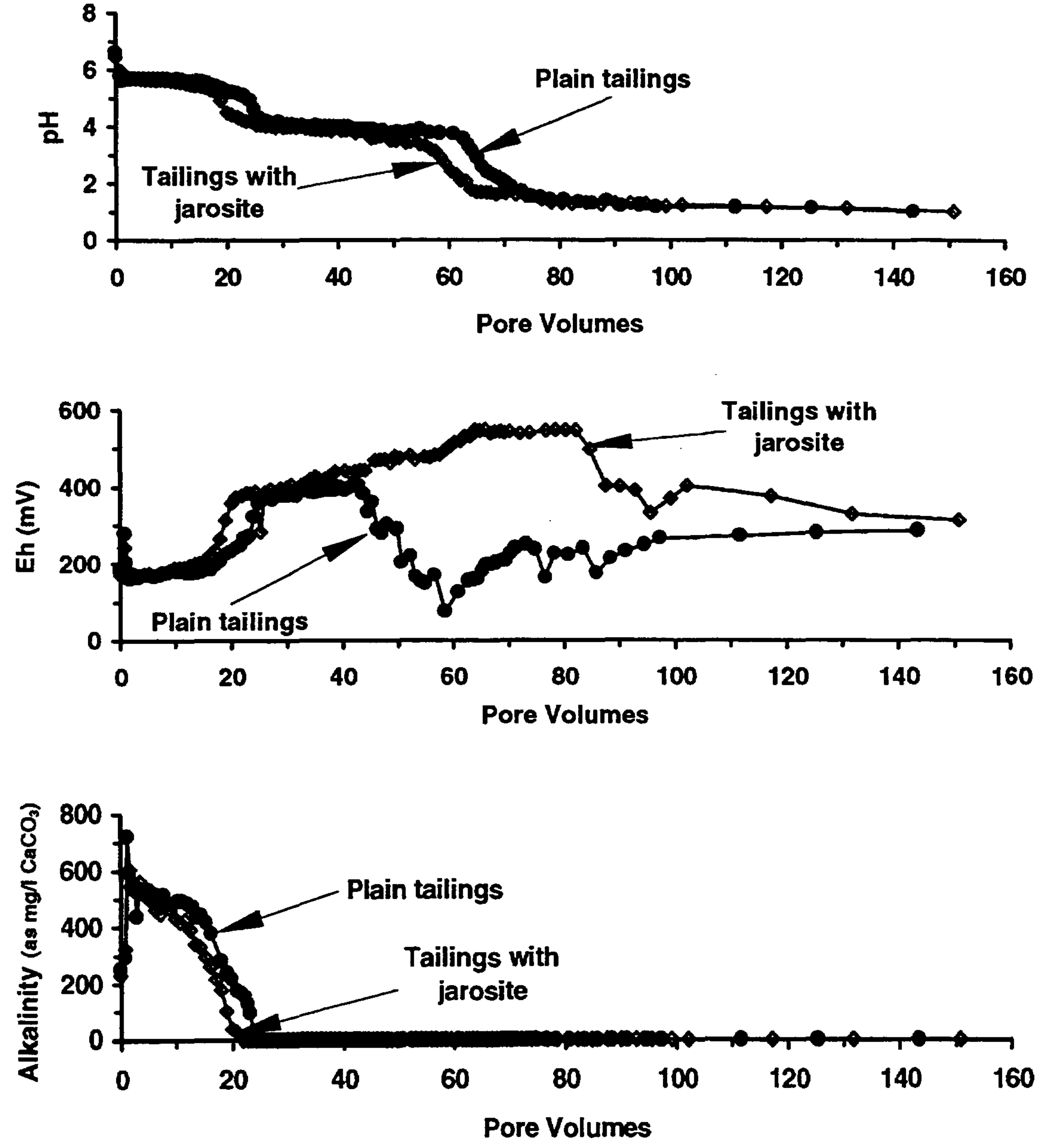

Figure 4. Comparison of the measured pH, Eh and alkalininty of the two experiments.

This observation demonstrates that natrojarosite dissolution is an acid-producing reaction under these conditions. Thus, the neutralization potential of the mill tailings is reduced when natrojarosite is added to tailings. The magnitude of this effect, however, is relatively minor. The persistence of high concentrations of Na throughout the duration of the natrojarosite-bearing column experiment suggests that the dissolution of natrojarosite is slow relative to the accelerated flow rates used in the column experiments.

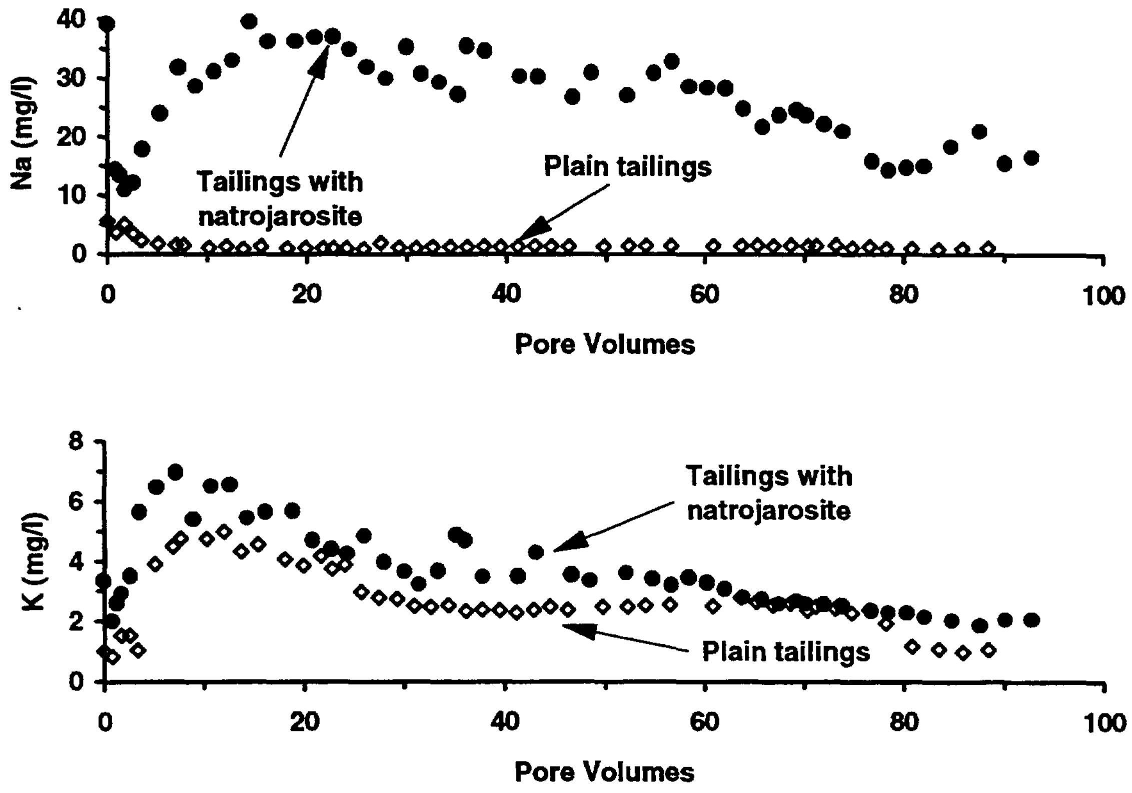

Figure 5. Comparison of Na and K concentrations for the two experiments. Higher concentrations of Na and K indicate that natrojarosite is dissolving.

Conclusions

A method for prediction of future effluent-water quality and estimation of mill-tailings neutralization potential has been developed. Comparison of measured pH, Eh and calculated saturation indices shows that this procedure is reproducible (Figures 2, 3, and 4). Moreover, the column-leach procedure is sensitive to small differences in the tailings composition. The procedure enables study of the pH-buffering mechanisms which control the geochemistry of the tailings and assists in the prediction of future effluent-water quality.

The results of the controlled laboratory column experiments indicate that dissolution of carbonates, $Al(OH)_3$, and $Fe(OH)_3$ controls the pH of the column effluent, and thus will control the mobility and attenuation of metals in a mill-tailings impoundment. This observation is consistent with the conceptual model proposed for the Nordic mine-tailings impoundment (4) that was extended for sulfide-bearing mine tailings (5,6,7).

The comparison of the experiments show the effects of natrojarosite dissolution acidic conditions, similar to those which prevail in many tailings impoundments. The dissolution of natrojarosite does not change the shape of the upper part of the pH-time curve, where the pH is believed to be buffered by carbonate and gibbsite dissolution. However, both plateaus are slightly shorter. In the natrojarosite column an additional pH-plateau develops due to the precipitation of goethite. Because the equilibrium pH of goethite is lower than that of gibbsite, the pH decreases more rapidly in the natrojarosite column. The amount of precipitated goethite, however, is small.

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