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Mechanisms Controlling Metal in Mill Tailings
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MANAGEMENT PERSPECTIVE

This work supports the ESD Issue Conserving Canada's Ecosystems (metals) and the business plan deliverables Thrust #3 (groundwater remediation). It also supports the EC Action Plan Conserving Canada's Ecosystems with the focus Develop and implement strategies to conserve ecosystems.

Migration of acid and metals from mine environments is a severe problem in Canada and the world. Laboratory column studies were conducted to quantify the acid neutralization potential and metal release of the Kidd Creek mine tailings. These tailings are co-blended with zinc refinery product. Very high concentrations of Zn (close to 400 mg/L) and Pb (> 3 mg/L) were released from the column containing plain tailings. In the column containing zinc refinery product, Zn concentrations were slightly higher and Pb release occurred longer than in the plain tailings column. Copper release was not observed in the plain tailings column, but was pronounced in the co-blended column. These results suggest that the addition of refinery waste with mill tailings leads to greater release of metals and should be avoided in the future management of mine wastes.

Develop and apply a reactive solute transport model to predict the acid neutralization process and extent of metal release. The results will assist in improving predictions of acid neutralization and metal migration at other mine sites in Canada, and will assist in the long-term management of mine wastes.

SOMMAIRE À L'INTENTION DE LA DIRECTION

Ces travaux appuient la question Conservation des écosystèmes du Canada (métaux) de la DGSE et le résultat de l'axe 3 du plan d'affaires (assainissement des eaux souterraines). Ils appuient aussi le volet Conservation des écosystèmes du Canada du plan d'action d'EC, avec l'objectif Élaborer et mettre en oeuvre des stratégies en vue de la conservation des écosystèmes.

La migration des acides et métaux des environnements miniers est un grave problème tant au Canada qu'à l'étranger. On a effectué des études sur colonne pour quantifier le potentiel de neutralisation de l'acide et la libération de métaux des stériles de la mine de Kidd Creek. Ces stériles ont été mélangés à des produits de raffinage du zinc. Des concentrations très élevées de Zn (proches de 400 mg/L) et de Pb (> 3 mg/L) ont été libérées de la colonne contenant des stériles seuls. Dans la colonne contenant aussi le produit de raffinage du zinc, les concentrations de Zn étaient légèrement plus élevées, et la libération de Pb a duré plus longtemps que dans le premier cas. On n'a pas observé de libération de cuivre dans la colonne de stériles seuls, mais la libération était prononcée dans la colonne de mélange. Ces résultats laissent penser que l'ajout de résidus de raffinage dans les stériles induisait une libération plus importante de métaux et devrait donc être évité à l'avenir dans la gestion des résidus miniers.

Développer et appliquer un modèle de transport de soluté réactif pour prédire le processus de neutralisation de l'acide et l'importance de libération de métaux. Les résultats permettront d'améliorer les prédictions de neutralisation de l'acide et de migration de métaux à d'autres sites miniers du Canada, et aideront à la gestion à long terme des résidus miniers.

Abstract

At the Kidd Creek site, natrojarosite residue, derived from the zinc refinery circuit, is mixed with mill tailings before final disposal in the tailings impoundment. Column experiments were conducted with fresh unoxidized mill tailings and a mixture of tailings containing the natrojarosite residue. Acidic water, simulating mine drainage water, was pumped through the columns. The effluent water geochemistry was interpreted with the assistance of MINTEQA2. The experimental results suggest that the effluent water pH was buffered by a series of acid neutralization reactions. The release of metals, including Cu, Pb and Zn, was affected by pore water pH, Eh and mineralogy of the tailings material.

Résumé

Au site de Kidd Creek, des résidus de natrojarosite, provenant de la filière de raffinage du zinc, est mélangé aux stériles avant l'élimination finale en bassin à stériles. Des expériences sur colonne ont été effectuées avec des stériles frais non oxydés et un mélange de stériles contenant le résidu de natrojarosite. De l'eau acide, simulant les eaux d'exhaure de la mine, a été injectée dans les colonnes. On a évalué la géochimie de l'eau d'effluent à l'aide de MINTEQA2. Les résultats de l'expérience suggèrent que le pH de l'eau d'effluent était tamponné par une série de réactions de neutralisation de l'acide. La libération de métaux, dont Cu, Pb et Zn, était influencée par le pH de l'eau interstitielle, Eh et la minéralogie des stériles.

Mechanisms Controlling Metal Release in Mill Tailings

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ABSTRACT

At the Kidd Creek site, natrojarosite residue, derived from the zinc refinery circuit, is mixed with mill tailings before final disposal in the tailings impoundment. Column experiments were conducted with fresh unoxidized mill tailings and a mixture of tailings containing the natrojarosite residue. Acidic water, simulating mine drainage water, was pumped through the columns. The effluent water geochemistry was interpreted with the assistance of MINTEQA2. The experimental results suggest that the effluent water pH was buffered by a series of acid neutralization reactions. The release of metals, including Cu, Pb and Zn, was affected by pore water pH, Eh and mineralogy of the tailings material.

INTRODUCTION

Weathering of mill tailings produces low pH waters containing high concentrations of metals. The US EPA (1994) reports that metal loadings from mine wastes cause environmental damage that is far greater than the effect of the acidity released from mine wastes. It is important, therefore, to understand the mechanisms controlling the mobility of metals in mill tailings pore water.

The weathering of tailings can produce low pH water. Many studies of mill tailings have focused on acid generation mechanisms (i.e., sulfide-mineral oxidation). Some researchers have noticed that a small amount of minerals, naturally present in the tailings, can buffer the acid produced in the unsaturated zone (Morin et al., 1986). This process slows the rate of expansion of the low pH zone within the tailings impoundment.

Based on field data from the Elliot Lake uranium mill tailings Morin et al. (1988) proposed a conceptual model of acid neutralization. According to this model, the pH of the uranium tailings pore water is buffered by dissolution of a series of minerals consisting of calcite, siderite, $Al(OH)_3$, $Fe(OH)_3$ and aluminosilicates. The dissolution of calcite maintains the pH of pore water to near neutral values. When calcite is depleted, the pore water pH drops to the next plateau. After the depletion of siderite, the pH of the pore water is buffered by dissolution of $Al(OH)_3$, followed by $Fe(OH)_3$ and aluminosilicates. Blowes (1990) showed that a similar conceptual model of acid neutralization can be applied to explain the movement of low pH conditions at three other sulfide mill tailings sites.

This conceptual acid neutralization model was proposed on the basis of field data. The data collection points were widely distributed in space and the groundwater flow pathways were assumed. The first objective of the current study was to assess this conceptual acid neutralization model under controlled laboratory conditions. Controlled conditions eliminate unknown influences, which might have affected the geochemical evolution of the tailings pore water at these field sites. The second objective was to collect geochemical samples of the mill tailings pore water through time: A laboratory experiment permits collection of data temporally, providing a more precise description of changes in the pH and Eh, and in the concentrations of dissolved metals. In the laboratory experiments the acid neutralization process was followed from the beginning to completion. Because reactions in mine tailings sites occur slowly, collecting field data at this level of temporal discretization would be costly and impractical.

The third objective was to determine the mechanisms controlling the release of dissolved metals to the tailings pore water. In addition to physical parameters, such as permeability and hydraulic head, the metal mobility depends on pH and Eh of the mill tailings pore water. For example, some heavy metals such as Pb become mobile as the pH decreases. Because of the toxicity of these metals at elevated concentrations, it is important to understand the mechanisms that control the pore water pH and Eh in mill tailings

impoundments. Understanding these mechanisms is an important aspect in developing groundwater remediation techniques at mine sites.

MATERIALS AND METHODS
Materials
The solids used in the experiments were collected at the Kidd Creek metallurgical site, near Timmins, Ontario. Fresh unoxidized mill tailings were collected within the flotation-concentrator. The mill tailings consist of: 15 wt% sulfides, 8 wt% carbonates and hydroxides, 49 wt% quartz, and the balance composed of silicates, aluminosilicates and sulfates (Jambor et al., 1993). 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 proportions of carbonates in the main impoundment were concluded to be 5% calcite, 35% dolomite-ankerite and 60% siderite.

The second sample, the natrojarosite residue was collected in the zinc refinery plant. Mineralogical investigation of the Kidd Creek jarosite residue shows that the main components are zinc-bearing natrojarosite and zinc ferrite. The trace components in the natrojarosite residue are various silicates, oxides, sulfates and sulfur (Jambor, 1993).

The solutions used in the experiment were a background solution, a tracer solution and an experimental solution. Background solution was prepared by dissolving reagent grade $CaCO_3$ and $CaSO_4$ in double deionized water in excess to saturation. The solution was bubbled with CO_2 to promote the dissolution of $CaCO_3$. The solution was then equilibrated with atmospheric CO_2. The tracer solution was prepared by adding reagent grade NaCl to the background solution. The experimental solution was prepared from ultra pure H_2SO_4 and double deionized water.

Analysis
Samples of column effluent were filtered through 0.45μm nylon filters. The alkalinity, pH, and Eh were measured immediately after sample collection using unfiltered samples. 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 (Garrels and Christ, 1990) and Light solution (Light, 1972). Concentrations of Fe (Gibbs, 1979) and Cl (Greenberg et al, 1992) were determined colorimetrically; concentrations of SO_4 were determined by ion chromatography. The concentrations of Al, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Li, Mg, Mn, Mo, Pb, Sr, V, and Zn were determined by inductively coupled plasma emission spectroscopy.

Experimental
The laboratory apparatus consisted of an input solution reservoir, pump, column and a sampling cell. Two experiments were conducted simultaneously. The first column was packed with fresh, unoxidized mill-tailings, collected at the flotation-concentrator (named 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 (Al et al., 1994). Both columns were saturated with the background solution. After saturation a conservative tracer test was conducted to determine the column flow parameters. To simulate acidic pore-water generated in the unsaturated zone of tailings impoundments, $0.1M$ H_2SO_4 was used as the input solution. Samples of column effluent water were collected versus time.

Methods of Interpretation
The pore-water geochemistry was interpreted with the assistance of the equilibrium geochemical speciation/mass transfer model MINTEQA2 (Allison et al., 1990). The thermodynamic database was adopted from the speciation model WATEQ4F (Ball and Nordstrom, 1991). 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
Acid Neutralization
Two experiments were conducted, one with unamended tailings from the Kidd Creek site, and one with tailings containing natrojarosite. The pH curves obtained for the effluent water from the two experiments are

similar in shape, but are shifted temporally (Figure 1). There are three long plateaus at pH 5.7, 4.0 and 1.3. The pH decreases from one pH-plateau to another are sharp, occurring over a few pore volumes. An additional pH-plateau, which occurs at pH 1.7, develops in the natrojarosite column only. The staircase shape of the pH curve is consistent with the acid neutralization model that was proposed by Morin et al. (1988). To assess which minerals control the geochemistry of the pore water, calculations were conducted using the geochemical mass-transfer model MINTEQA2 (Allison et al., 1990). The geochemical calculations show that saturation indices for siderite form a plateau that corresponds to the first pH-plateau (Figure 1). At this pH-plateau the values of the saturation index suggests supersaturation with respect to siderite. This is consistent with the mineralogy of the tailings and the theory of solid solutions. According to the solid solution theory (Glynn and Reardon, 1990), the solubility of a solid solution should be between the solubility of the end members and depends on the proportion of the end members contained in the solid.

The solubility of siderite is the lowest of the solubilities of the end members of ankerite-dolomite solid solution; the end members are siderite, calcite, magnesite, and rhodocrosite. Hence, the solubility of ankerite-dolomite solid solution is higher than the solubility of siderite. Consequently, the theory suggests supersaturation with respect to siderite, and is consistent with the observations. The solubility constant for the Kidd Creek ankerite-dolomite solid solution has not been measured. However, on the basis of the siderite saturation indices, the ankerite-dolomite solid solution should be near equilibrium with the pore water at the first pH-plateau (pH=5.7).

During the first pH plateau region, the pore water is supersaturated with respect to gibbsite and goethite, suggesting precipitation of both minerals at the beginning of the experiment. As soon as the alkalinity is depleted the pH drops abruptly to the second pH-plateau.

For both experiments, the pore water during the second pH-plateau, which occurs at pH 4.0, is in equilibrium with respect to gibbsite. The effluent water from the natrojarosite column in this region is supersaturated with respect to goethite, suggesting goethite precipitation is favored; the pore water of the plain tailings column is in equilibrium with respect to goethite. Geochemical modeling suggests that gibbsite is depleted earlier in the natrojarosite column, which is consistent with the earlier drop in pH of the column effluent water.

A pH plateau at pH 1.7 develops only in the natrojarosite column. The column effluent water of this plateau is in equilibrium with respect to goethite, which is derived from the natrojarosite residue. Natrojarosite dissolution in the natrojarosite column maintains higher concentrations of ferric iron, thus preventing goethite dissolution earlier in the experiment. The last pH-plateau develops in both columns at pH 1.3, when the pore water pH is probably affected by the dissolution of aluminosilicate minerals.

Metal mobility

Figure 2 shows the comparison of pH and concentrations of Zn and Pb. Concentrations of Zn in the pore water of both experiments increase abruptly at the beginning of the experiment. During this stage, pH is still high (5.7). These results indicate that Zn is mobile under high pH conditions and that the buffering reactions do not affect the mobility of Zn. The concentrations of Zn are higher in the pore water of the natrojarosite column. The difference in Zn concentrations between the two columns is significant between 30 and 70 pore volumes, which corresponds to the second pH-plateau (pH 4.0). The additional sources of Zn in the natrojarosite column are most likely Zn-ferrite and Zn substitutions in the natrojarosite. Microprobe analyses (Jambor et al., 1993) indicate that Zn is present in the Kidd Creek natrojarosite. Geochemical calculations indicate that dissolution of natrojarosite is favored, suggesting that a portion of this excess Zn may be derived from the dissolution of the natrojarosite. Zn-ferrite occurs in the residue as a spongy material with a large surface area, which promotes dissolution (Jambor, 1999, personal communication). Other possible sources of Zn, identified by Jambor and coworkers (Jambor et al., 1993) are sphalerite and Zn silicates. However, both constituents are present only in trace amounts and are sparingly soluble.

The concentration of lead remains below detection during the first 20 pore volumes when pH is high (pH=5.7). As the pH drops abruptly from 5.7 to 4.0, the concentration of Pb increases sharply. The concentration of Pb in the natrojarosite column increases earlier than in the plain tailings column. This observation is consistent with the earlier decrease in pH and depletion of alkalinity observed in the jarosite column. In the natrojarosite column, the concentration of Pb increases to 4 mg/l and remains high for approximately 40 pore volumes longer than in the plain tailings column. The concentration of Pb then slowly decreases. Higher concentrations of Pb in the natrojarosite column are consistent with the differences in mineralogy of the two columns. Additional Pb in the natrojarosite column is likely derived from anglesite contained in the natrojarosite residue. Natrojarosite residue also contains Pb silicates in trace amounts. Due to much their much lower solubility, Pb silicates are not likely to be the significant source of Pb.
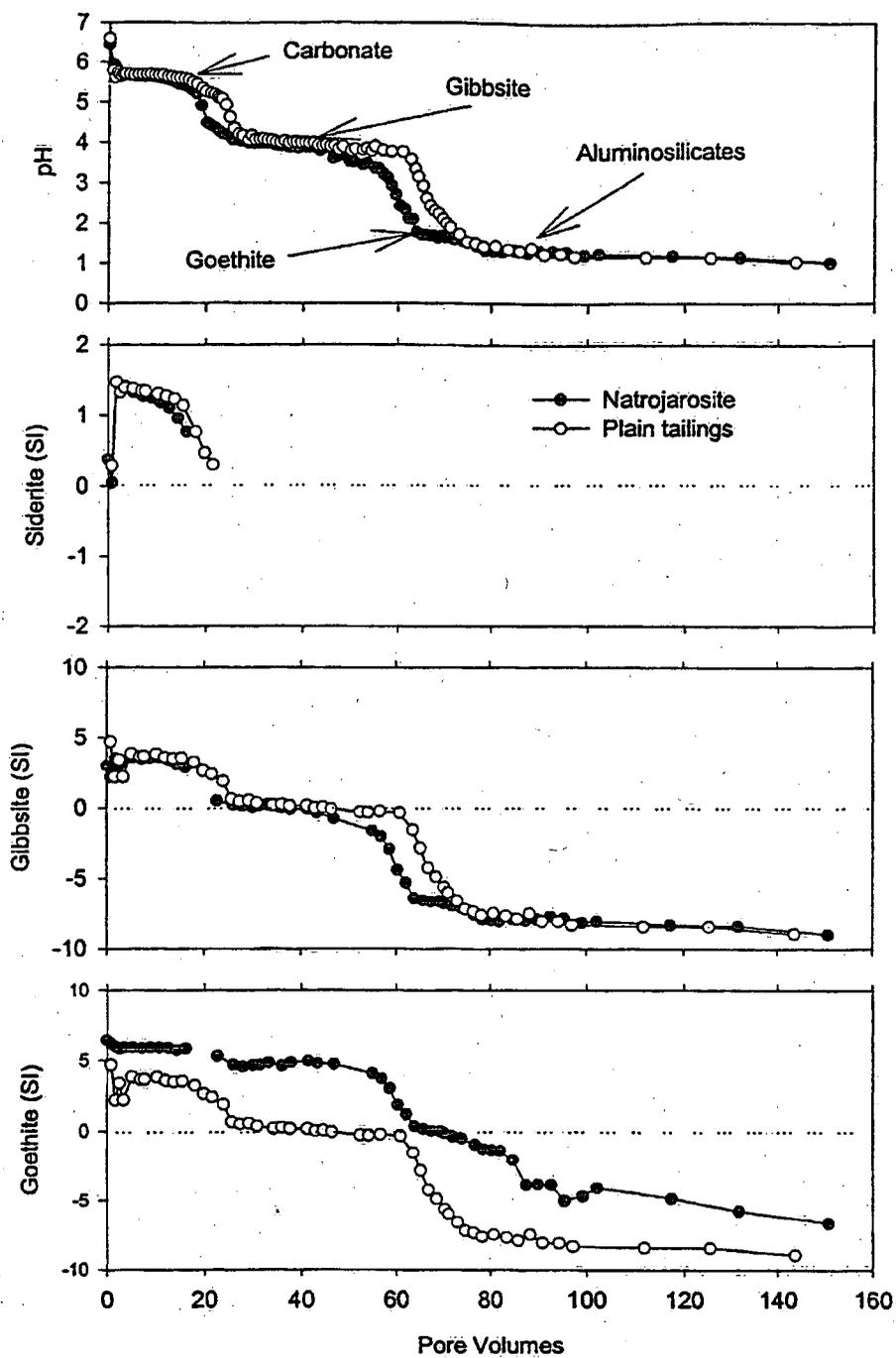
Figure 1 Comparison of saturation indices with the pH of column effluent water.

The concentration of Pb in the plain tailings column increases to 3 mg/l three pore volumes later than in the natrojarosite column (Figure 2). At 40 pore volumes, the concentration of Pb decreases abruptly to below 0.5 mg/l. The only identified source of Pb in the plain Kidd Creek tailings is galena (Jambor et al., 1993).
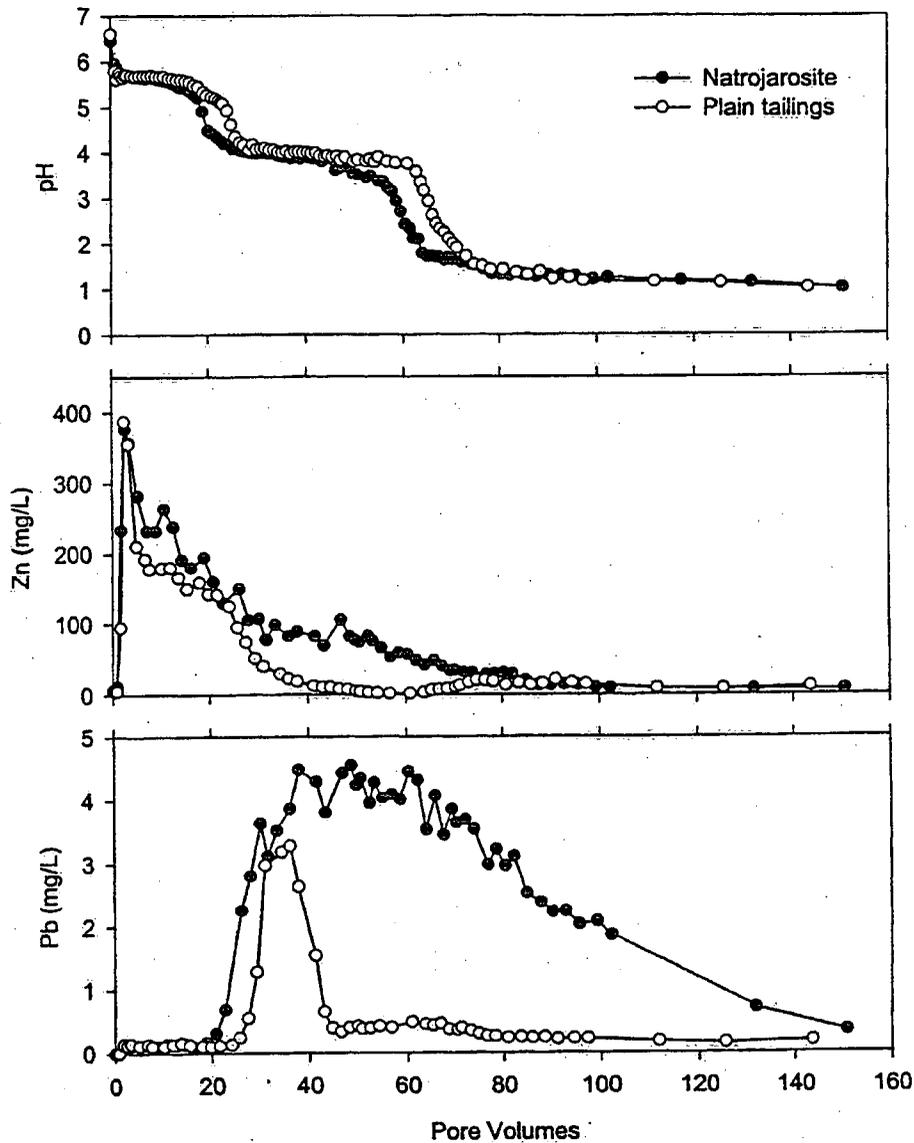

Figure 2 Comparison of Zn and Pb concentrations with the pH

Figure 3 shows the comparison of Cu concentrations and Eh. The concentrations of Cu in the pore water of plain tailings column remain below 1 mg/l throughout the experiment, whereas the concentrations of Cu in the natrojarosite column increase abruptly at 46 pore volumes to 34 mg/l and remain between 15 and 54 mg/l, until 84 pore volumes. At the same time, the Eh in the natrojarosite column increases slightly (30 mV) and remains high for the same duration as high Cu concentrations persist in the column effluent water. An abrupt decrease in dissolved Cu concentration in the natrojarosite column coincides with an abrupt decrease in the Eh. These results suggest that Cu concentrations are controlled by the pore water Eh.

Chemical analysis of solid samples from both experiments show, that Cu was still present in the column materials after the experiments were completed. Mineralogical analyses conducted by Jambor et al. (1993) indicate that Cu is present in trace amounts as secondary covellite and chalcopyrite in the natrojarosite residue. Cu is also present as chalcopyrite in the tailings and natrojarosite residue.
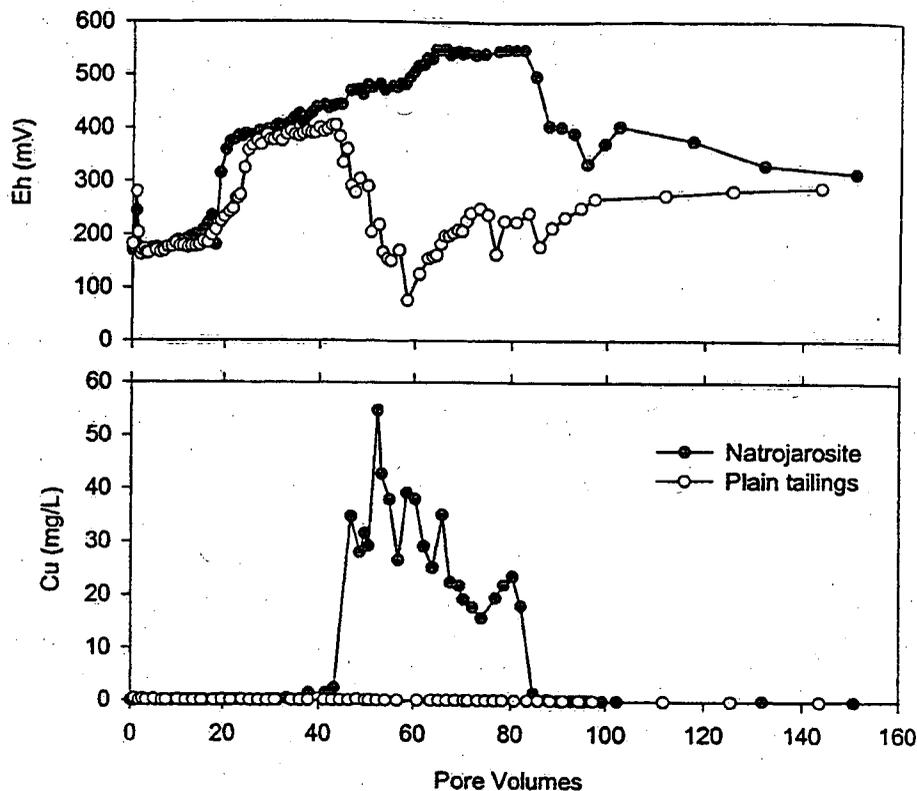

Figure 3 Comparison of Cu concentrations with the Eh.

CONCLUSIONS

Two saturated column experiments were conducted using plain tailings and a mixture of tailings and natrojarosite in the same proportions as at the Kidd Creek metallurgical site. The results of geochemical modeling suggest that the pH of effluent water is controlled by dissolution of a series of minerals, which consists of: an ankerite-dolomite solid solution, gibbsite, and aluminosilicates. In the column that included natrojarosite addition to tailings, an additional pH-plateau develops at pH 1.7, which is probably controlled by goethite dissolution. The observed series of dissolution reactions is similar to the series observed by Morin et al. (1988) and Blowes et al. (1994). Because pH of the pore water affects metal mobility, a detailed understanding of these dissolution reactions is important for understanding metal mobility. The experimental results show that mobility of some metals depends on the pH and Eh of the pore water: Pb is immobile until pH decreases to 4.0, whereas the mobility of Zn is unaffected by pH. The release of Cu seems to be affected by Eh.

still present in the column
:d by Jambor et al. (1993)
pyrite in the natrojarosite

● — Natrojarosite
○— Plain tailings

120   140   160
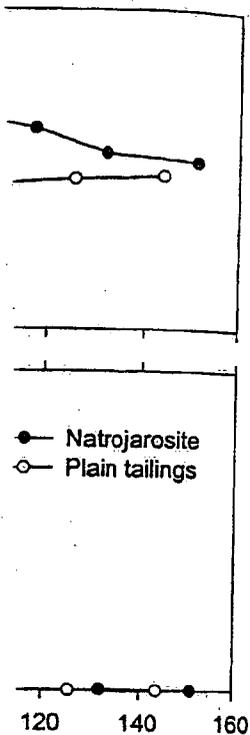
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