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Geochemical behavior of Autoclave-Produced Ferric
Arsenates and Jarosite in a Gold-Mine Tailings
Impoundment

By:

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MANAGEMENT PERSPECTIVE

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EC Priority/Issue: 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. The study was funded by Placer Dome Canada, and the Natural Science and Engineering Research Council Industrial Grants Program.

Current Status: Metal refinery wastes are typically deposited in dedicated impoundments or co-deposited with flotation wastes. The byproducts of Au mining are often arsenical and post-processing deportment of As from these wastes is of considerable environmental interest because of the well-known toxicity of As. This study evaluates the stability of As in wastes derived from an autoclave process.

Next Steps: Future efforts will be directed toward delineating geochemical mechanisms controlling the release of metal-rich wastes derived using other refinery methods.

Abstract

Between 1991 and 1994, metallurgical residues from a pressure-oxidation autoclave at the Campbell Au-quartz mine at Red Lake, northern Ontario, were neutralized with dolomite-rich flotation tailings and were deposited in a polyethylene-lined disposal area. Mineralogical analysis indicates that most of the As occurs as a crystalline ferric sulfarsenate, and some is associated with Fe oxides and with K-H₃O jarosite. Field pore-water geochemical data from 1994 and 1995 showed increases in Fe(II) and As(III) concentrations, suggesting that the sulfarsenate and jarosite are dissolving; none of the discrete As phases included in a thermodynamic database limit dissolved-As concentrations, and these concentrations may continue to increase. These results demonstrate the potential for Fe and As loading through groundwater systems.

Geochemical Behavior of Autoclave-Produced Ferric Arsenates and Jarosite in a Gold-Mine Tailings Impoundment

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ABSTRACT

Between 1991 and 1994, metallurgical residues from a pressure-oxidation autoclave at the Campbell Au-quartz mine at Red Lake, northern Ontario, were neutralized with dolomite-rich flotation tailings and were deposited in a polyethylene-lined disposal area. Mineralogical analysis indicates that most of the As occurs as a crystalline ferric sulfarsenate, and some is associated with Fe oxides and with K-H₂O jarosite. Field pore-water geochemical data from 1994 and 1995 showed increases in Fe(II) and As(III) concentrations, suggesting that the sulfarsenate and jarosite are dissolving; none of the discrete As phases included in a thermodynamic database limit dissolved-As concentrations, and these concentrations may continue to increase. These results demonstrate the potential for Fe and As loading through groundwater systems.

INTRODUCTION

High-temperature roasting of sulfide concentrates has long been used in the mining industry as a method to liberate gold from refractory ores. In recent decades, the roasting process at many plants has been abandoned in favor of biooxidation or autoclave technologies that oxidize the sulfides more efficiently and do not create gaseous S- or As-bearing emissions. In the pressure-oxidation autoclave pretreatment of gold ores, a typical circuit incorporates standard flotation to produce a sulfide concentrate that is fed to an autoclave operating at only moderate temperatures (150–250°C). The oxidized product from the autoclave is treated with cyanide to remove Au, and the resulting residue is commonly codischarged with the flotation wastes to a containment facility.

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Many Au ores are arsenical because of the presence of arsenopyrite [FeAsS] or because of minor solid-solution substitution of As in pyrite [FeS₂]. The post-processing deportment of As derived from these minerals, and their process products, is of considerable environmental interest because of the well-known toxicity of As. The objectives of the current study were to determine the mineral compositions of As-bearing flotation tailings, to determine the mineralogical character of waste products from an operating autoclave, and to assess the in-situ stability of these phases under the saturated, anoxic conditions that prevail in a dedicated waste-storage facility at the gold-producing Campbell mine at Balmertown, northwestern Ontario, Canada (Figure 1).

SITE DESCRIPTION

The Campbell mine is in the Red Lake camp, from which gold has been produced since 1930. The area has a humid continental climate, with annual precipitation averaging 595 mm, average monthly temperatures ranging from -21°C to 18°C, and regional evapo-transpiration of about 380 mm annually.

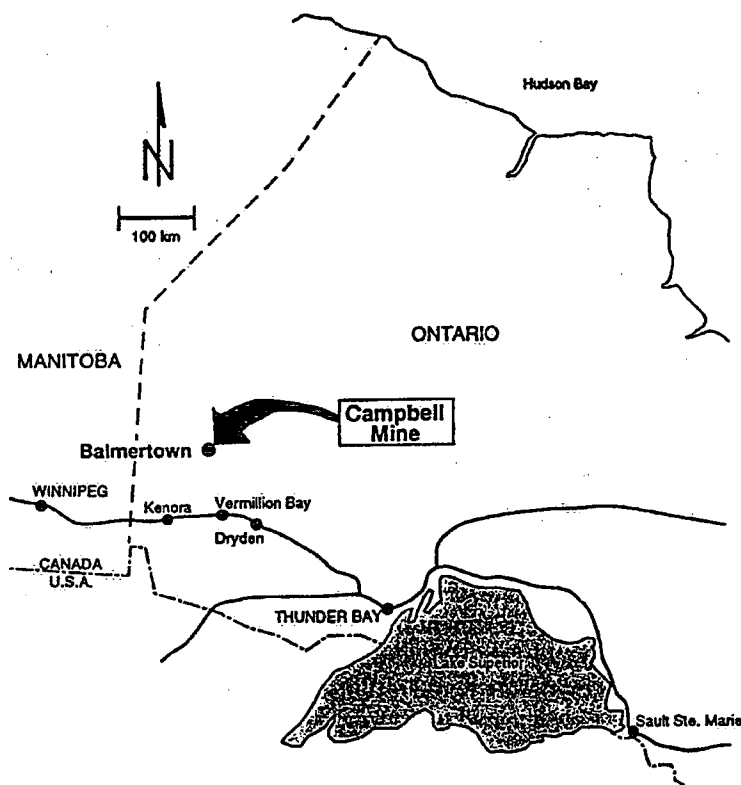


FIGURE 1 Location of the Campbell Mine

The Campbell mine is an underground mining operation producing gold mainly from sheeted swarms of quartz veins and associated silicified-carbonated rocks. Milling began in 1949, and several expansions have increased the rate to the current 1260 tonnes per day. Roasting of sulfide concentrates began in 1951 and was discontinued when an autoclave pressure-oxidation system was commissioned in 1991. A simplified version of the flowsheet is: (1) production of sulfide concentrate by conventional flotation; (2) H_2SO_4 digestion of carbonates in the concentrate, a process referred to as acid pretreatment; (3) autoclave oxidation of the sulfides; and (4) cyanide treatment of the autoclave product to remove gold. The waste streams are thus (1) flotation tailings; (2) acid-pretreatment overflow, which is neutralized with lime or a combination of lime and flotation tailings, and to which $Fe_2(SO_4)_3$ is added as a control for dissolved As; and (3) autoclave products after Au extraction. All of these wastes are codischarged to a containment facility referred to as the current impoundment (Figure 2). Initially, however, it was intended that a lined impoundment (Figure 2) be dedicated to the storage of autoclave wastes and the acid-pretreatment overflow. It was subsequently concluded that a dedicated containment of these wastes would be environmentally inappropriate in the long term, and combined wastes, previously of uncertain type and proportions, were used to fill the impoundment. This paper focuses on the nature of these wastes and the reactions occurring within the dedicated, lined facility.

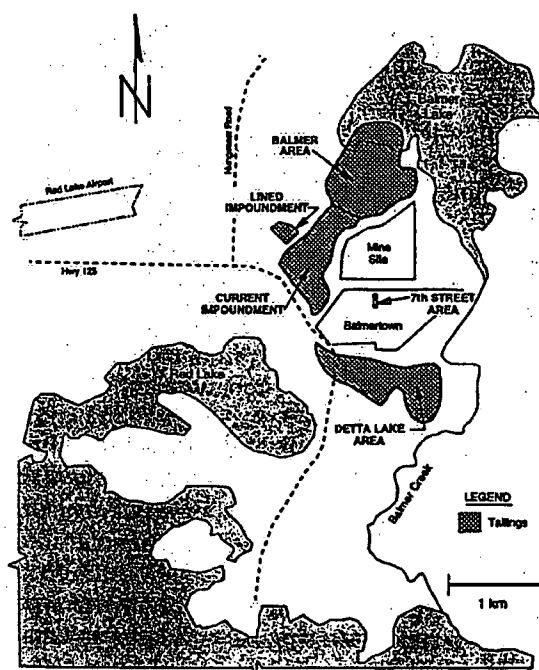


FIGURE 2 Location of the lined impoundment and other tailings-containment facilities at the Campbell Mine

Lined Impoundment

The lined impoundment has a surface area of about 3.6 ha and is about 5 m deep near its center. The impoundment is lined with an 80 mil HDPE geomembrane on the side-slopes and a 60 mil membrane on the bottom. Processing wastes were discharged on the western side of the impoundment forming a beach at this site and a pond on the opposite side. Wastes were deposited from 1991 until full capacity was reached in 1994. Piezometers installed in the impoundment indicate that the vertical gradient is zero. Core C15, obtained from the center of the impoundment, provided a complete vertical section for chemical and mineralogical studies.

METHODS

Tailings Solids

Core C15 was collected in a 5-cm-diameter Al tube. The core was frozen in the field then sawn in half along its length. The frozen split for the mineralogical study was extruded from the barrel and was dried at room temperature. Portions of the dried core were used for bulk-sample X-ray diffractometry and for the preparation of polished sections and polished thin sections for optical microscopy. The sections were also used for scanning electron microscopy (SEM) and for wavelength and energy-dispersion electron-microprobe analyses.

The remaining split of the core was used for particle-density measurements and whole-rock analyses. Particle density was measured in triplicate with an air comparison pycnometer. Analyses for C_{total} and S_{total} were determined by induction furnace, and As, Fe, Yb, and Lu in selected core and mill samples were determined by instrumental neutron-activation analysis. A subset of these samples was also analyzed for Si, Al, Fe, Mg, Mn, Ca, Ti, Na, K, P, Ba, Sr, Y, Zr, Sc, Be, and V by fusion/ICP, and for Ag, Bi, Cu, Ni, Pb, and Zn by four-acid (perchloric, nitric, hydrochloric, sulfuric) digestion/ICP.

Pore Water

Core for squeezing pore water from tailings was collected by the same method as the mineralogy core. The core was immediately cut into 0.25-m lengths and squeezed as described by Patterson et al. (1) and modified by Smyth (2). Each sample was collected in a 60-mL syringe and filtered (0.45- μ m). Measurements of pH and E_H were made in the field in plastic thimbles with a combination pH electrode and a Pt redox electrode. The pH electrode was calibrated in pH 4 and pH 7 buffers and checked at regular intervals. The E_H electrode was checked in ZoBell's solution and Light's solution also at regular intervals. The alkalinity was titrated in the field with methyl red, bromcresol green indicator, and with sulfuric acid using a digital titrator. Samples were collected in pairs: one was acidified with 12N, analytical grade HCl for cation analysis by ICP-AES. An unacidified sample was used for anion analysis. Samples with low As concentrations were also analyzed by AAS after hydride generation. Selected samples were speciated into As(III) and As(V) by an anion exchange method (3) and were analyzed by AAS after hydride generation or by ICP-AES.

Pore-water samples were collected from a piezometer nest after pumping dry the day before sampling. Measurements of pH and E_H were made in a sealed flow-through cell that was maintained near pore-water temperature. Alkalinity was measured in the field by the same method as the squeezed samples. Aqueous sulfide concentrations were determined in the field on selected samples with a colorimetric method (4). Samples from the piezometers were collected with a peristaltic pump and polyethylene tubing and were filtered through 0.45- μm , in-line, cellulose nitrate filters. The same acidification and analysis procedures were followed for the piezometer samples as for the squeezed samples. Additional analytical details are given in (5).

Data Interpretation

The pore-water data were interpreted with the aid of the equilibrium geochemical model MINTEQA2 (6). This program was used to calculate saturation indices of discrete mineral phases, which indicate the tendency of a solid phase to dissolve or precipitate. The thermodynamic database of MINTEQA2 was modified to be identical to that of WATEQ4F (7). The thermodynamic constants for K, Na, and H_3O jarosites were changed to the values recommended by (8). Thermodynamic constants for siderite were added on the basis of work by Ptacek (9).

MINERALOGICAL RESULTS

The flotation tailings consist of quartz, dolomite, chlorite, talc, and variable but minor to trace amounts of amphibole, siderite, calcite, muscovite, pyrrhotite, arsenopyrite, and several other minerals. The sulfide concentrate also contains native gold and minute amounts of various sulfides, including sphalerite, chalcopyrite, stibnite, gudmundite, gersdorffite, argentic-arsenian tetrahedrite, and Pb-Sb sulfosalts.

The mineralogical examination of samples from the mineral-processing plant and from six sites cored in the tailings-storage areas revealed that dolomite is a diagnostic indicator of the presence of flotation tailings. Products from the autoclave are recognizable by the presence of abundant rhombs of hydronium jarosite $(\text{H}_3\text{O},\text{K})\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$ and coexisting iron sulfarsenate that is stellate to spherical in habit and $<20\ \mu\text{m}$ in diameter. The neutralized acid-pretreatment overflow is distinguishable because it consists mainly of gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and minor ettringite $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$, that occur as zoned ovoids resembling oolites.

Lined Impoundment

The mineralogical results indicate that the lined impoundment is filled mainly with flotation tailings and abundant (but minor) autoclave wastes, which are accompanied by small amounts of neutralized acid-pretreatment overflow. The uppermost 0.7 m of the impoundment consists almost wholly of neutralized overflow (Figure 3).

X-ray diffractometry and optical microscopy indicate that autoclave-derived hydronium jarosite and Fe sulfarsenate are common throughout the dolomite-rich (flotation tailings) interval. Pyrrhotite is the main sulfide

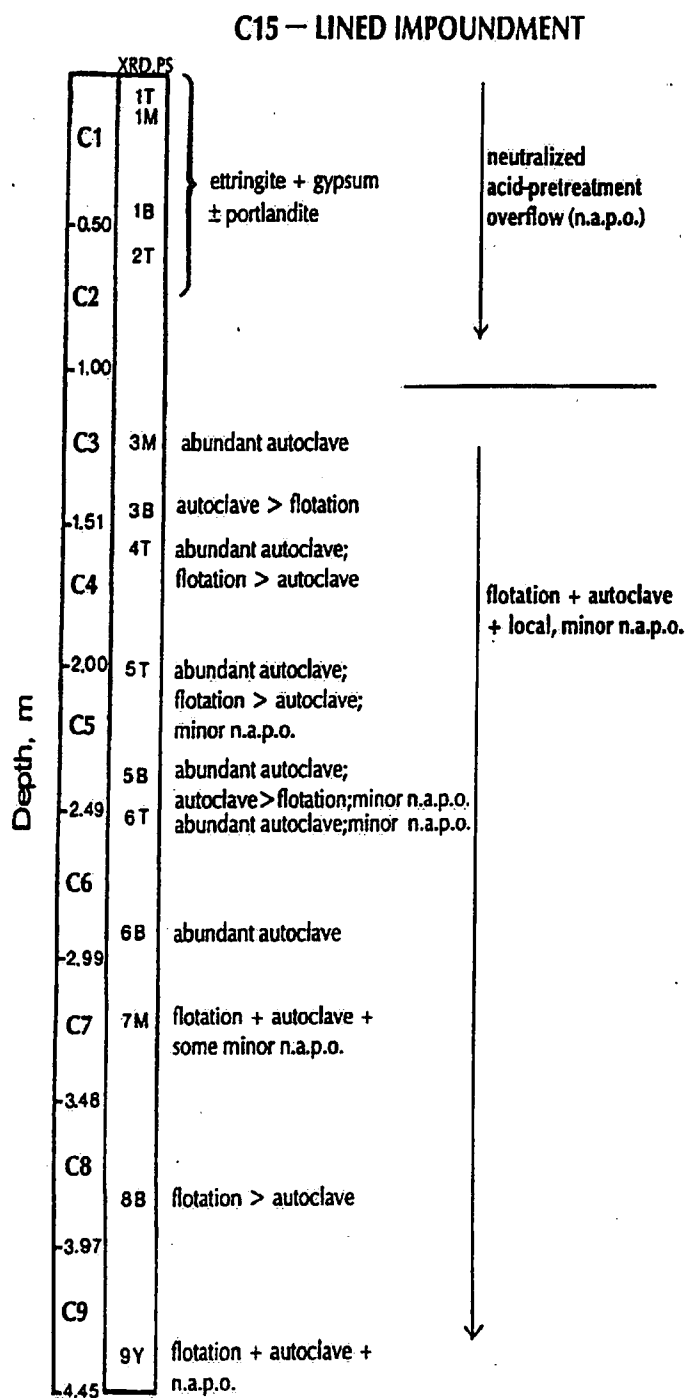


FIGURE 3 Schematic representation of mineralogical results for borehole C15 in the lined impoundment. In the left column, C numbers are core numbers, with depth in meters; right column shows the position and designation of the mineralogical samples.

mineral and is unaltered in all of the samples that were examined. Below 0.7 m, gypsum ovoids characteristic of neutralized overflow occur locally and, except for one 2-mm layer, are dispersed within the other wastes rather than concentrated in discrete layers.

Sources of Arsenic

Potential mineralogical reservoirs for As in the neutralized overflow are sparse. Possibly some As is contained in the sulfate-rich precipitates that make up the bulk of the overflow, but whole-rock analyses confirm that As concentrations in the overflow are low (Figure 4).

Pyrrhotite is the principal sulfide mineral in the Campbell mine flotation tailings in general, as well as in the lined impoundment. The typical proportion of pyrrhotite relative to all other sulfides combined is roughly 90:10, with the latter consisting of arsenopyrite and sphalerite accompanied by minute amounts of pyrite, gersdorffite, chalcopyrite, and other sulfides as noted for the concentrate. Most arsenopyrite in the tailings occurs as fine-grained aggregates locked in quartz. Nevertheless, in terms of potential sources of pore-water As in pristine flotation tailings, arsenopyrite is the only significant source of the element, both because of its common presence and its high As content (46.01 wt% As in FeAsS). The sparseness of arsenopyrite in the lined-impoundment wastes indicates that other sources must be sought to account for the bulk of the As.

The autoclave solids prior to cyanidation consist of quartz, talc, gypsum, anhydrite, hydronium jarosite, and an iron sulfarsenate. Minor to trace amounts of mica, chlorite, porous iron oxide (mainly hematite), magnetite, ilmenite, gold, synthetic chromian spinel, and Fe-Ca-Al silicates are also present. The potential hosts for significant amounts of As are (a) hydronium jarosite, wherein AsO_4 would substitute for SO_4 ; (b) the Fe sulfarsenate, and (c) the porous Fe oxide. The last, however, occurs sparingly relative to the other two.

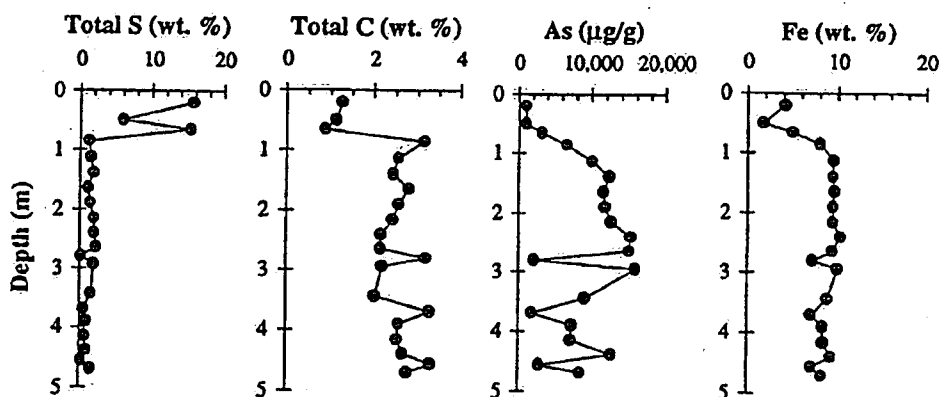


FIGURE 4 Whole-rock profiles for core from the lined impoundment

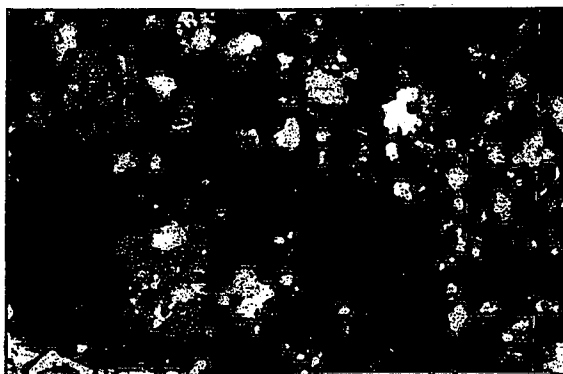


FIGURE 5 SEM backscattered-electron image of Campbell Mine autoclave sample showing two large, well-crystallized grains of hydronium jarosite at the left, with numerous inclusions of Fe sulfarsenate (white). Smaller, somewhat stellate, white grains throughout the matrix are also Fe sulfarsenate. Bar scale represents 10 μm .

Electron microprobe analyses of the jarosite from the autoclave indicate that it is a K-bearing (up to 2.7 wt% K_2O , $n = 6$) hydronium jarosite in which As_2O_5 ranges from 0.0 to 1.8 wt% (average 0.6, $n = 6$). However, high-magnification SEM observations indicate that avoidance of inclusions of Fe sulfarsenate during analysis is difficult (Figure 5); thus, it is not certain that the jarosite is As-bearing.

The Fe sulfarsenate in the autoclave sample is too fine-grained to yield definitive microprobe compositions, but analytical results for six grains ranging from 3 to 6 μm across gave Fe_2O_3 34.7–40.9, Al_2O_3 0.8–1.3, SO_3 8.8–10.5, As_2O_5 27.5–39.7, sum 72.1–89.4 wt%. The sulfarsenate present in the lined impoundment is dark brown, spheroidal, and the spheres typically have diameters $<20 \mu\text{m}$. Microprobe analyses of the spheres showed that some are slightly zoned; the average and range of composition obtained for six spheres are Fe_2O_3 44.56 (43.5–45.9), CaO 0.21 (0.0–0.4), As_2O_5 17.24 (16.1–18.3), SO_3 14.39 (12.5–15.7), for which the simplified formula is $\text{Fe}_2[(\text{SO}_4)_x(\text{AsO}_4)_{4-x}](\text{OH})_x \cdot n\text{H}_2\text{O}$. The sulfate end-member is $\text{Fe}_2(\text{SO}_4)(\text{OH})_4 \cdot n\text{H}_2\text{O}$, with OH decreasing as AsO_4 increases. An X-ray powder-diffraction pattern of the arsenate from the lined impoundment was obtained by hand-picking about 20 grains for a single Debye–Scherrer mount. The phase has been successfully synthesized by J.E. Dutrizac of CANMET, Ottawa, and current experiments are aimed at delineating the limits of the considerable AsO_4 – SO_4 substitution that is accommodated by the compound.

Microprobe analyses of the porous Fe oxide in the autoclave sample (Figure 6) gave low totals and 6–10.6 wt% As_2O_5 ($n = 4$). Hematite, which is the principal component in the porous phase, cannot incorporate such large amounts of As into its structure; the As is therefore assumed to be chiefly absorbed, with some As associated with heterogeneous phases within the pores. Although rich in As, the porous oxide occurs sparingly relative to the Fe arsenate and hydronium jarosite.

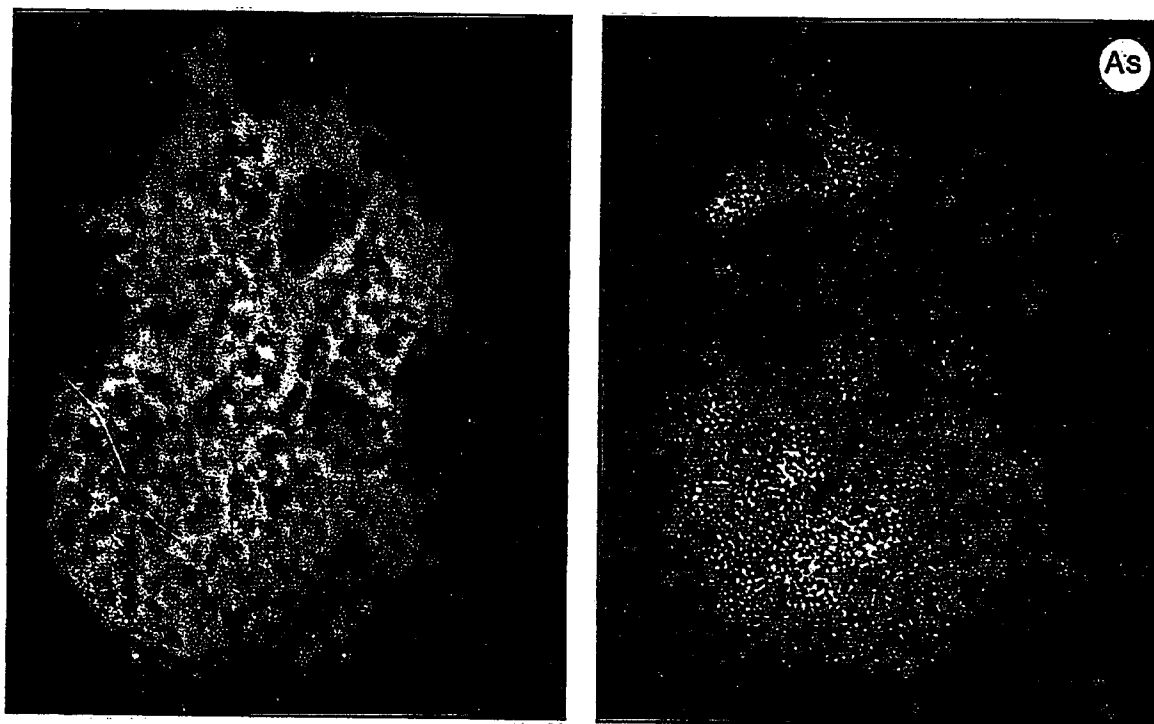


FIGURE 6 SEM backscattered-electron image of heterogeneous, porous iron oxide from the Campbell autoclave. Numerous inclusions (dark) are quartz and silicates. The corresponding X-ray map for As (right) shows that As is associated with the oxide and that concentrations are variable on a micrometer scale. Bar scale represents 5 μm .

GEOCHEMICAL BEHAVIOR

The distribution of tailings types in the lined impoundment is indicated by the whole-rock analytical results for S_{total} and C_{total} (Figure 4), which respectively reflect the presence of sulfates in the acid-pretreatment overflow and carbonates in the flotation tailings. The pore water in the lined impoundment has a characteristic pH of 7 to 8 and a characteristic Eh of 0 to 100 mV (Figure 7). The nearness of the water table to the surface of the tailings limits the ingress of oxygen.

Equilibrium geochemical modeling indicates that the pore water is saturated or supersaturated with respect to calcite, dolomite, siderite, gypsum, and ferrihydrite (Figure 8) and with respect to aluminum hydroxide. Geochemical modeling also indicates that the pore water is undersaturated with respect to jarosite, hydronium jarosite, sodium jarosite, and all of the arsenate phases in the MINTEQA2 database (Figure 8). Iron speciation results from the MINTEQA2 calculations suggest that virtually all of the dissolved Fe occurs as Fe(II).

Large differences in dissolved Fe(II) and As concentrations, and measurable differences in Ca, K, Si, Ni, and Zn concentrations, were observed between 1994 and 1995 (Figure 7). At a depth of 2.5 m, for example, Fe(II) increased from 54 to 155 mg/L; As increased from 0.1 to 6.7 mg/L; Ca decreased from

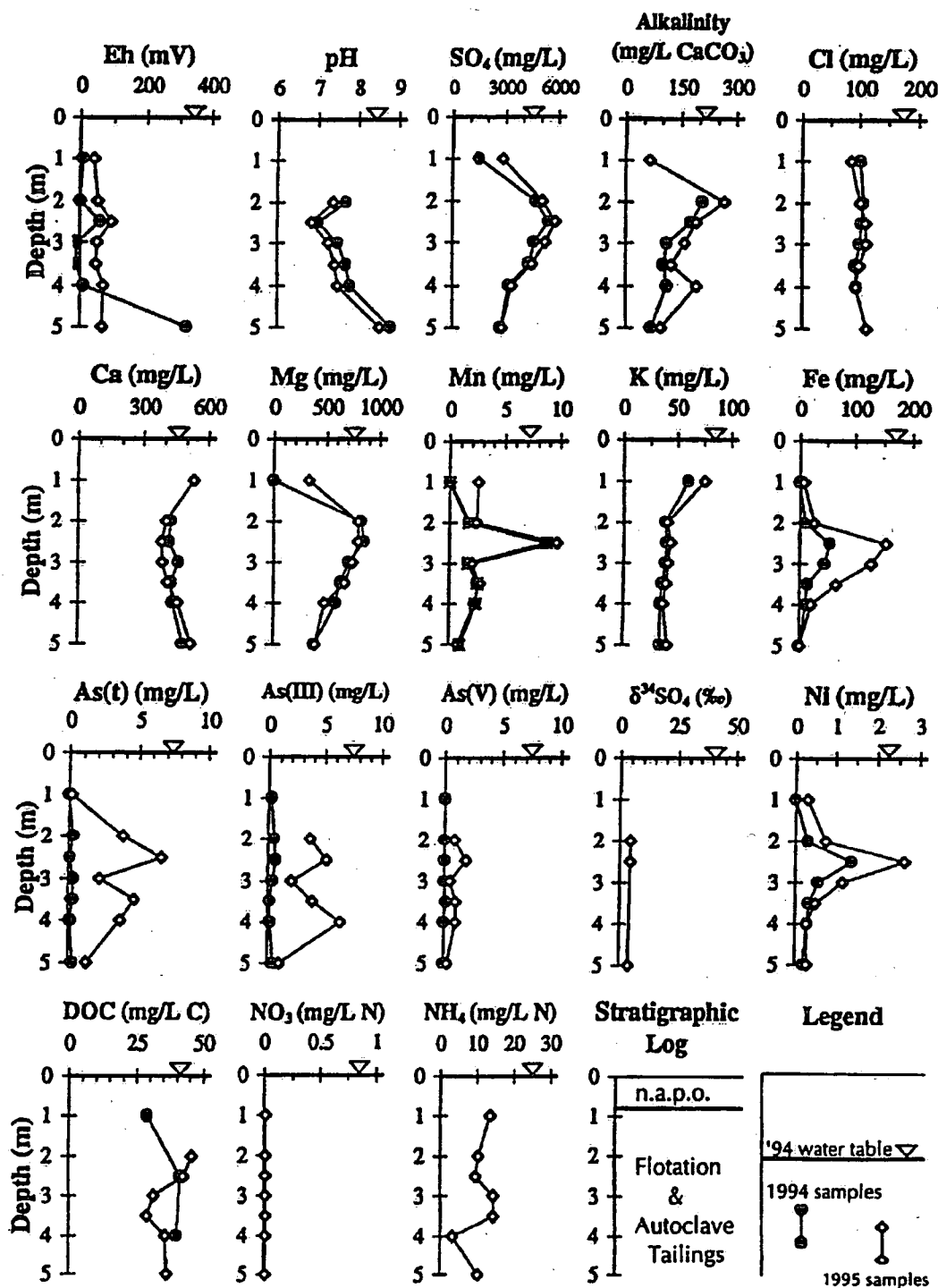
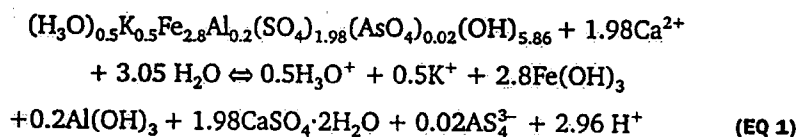


FIGURE 7 Water chemistry profiles for the lined impoundment

420 to 390 mg/L; K increased from 40 to 44 mg/L; Si increased from 7 to 9 mg/L; Ni increased from 1 to 3 mg/L; and Zn increased from 0.1 to 0.3 mg/L. The 1994 Fe concentrations are also higher than the average, influent, unfiltered 1993 process-water concentrations of 6 mg/L. The changes in water chemistry between 1994 and 1995 probably indicate that the hydronium jarosite and ferric sulfarsenate are dissolving. Two dissolution mechanisms are plausible: stoichiometric dissolution and reductive dissolution. Stoichiometric dissolution is a process whereby the solid phase dissolves without any changes in redox state to any of its constituents. Reductive dissolution is a process whereby the solid phase dissolves as a result of one or more of its constituents being reduced to a lower oxidation state.

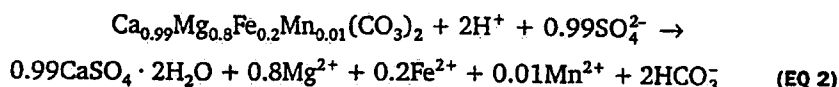
Stoichiometric Dissolution

Geochemical modeling shows that the pore water is undersaturated with respect to both jarosite and hydronium jarosite (Figure 8), suggesting a tendency for (H₃O)-K jarosite to dissolve. Instability of jarosite in saturated tailings has previously been inferred in a study of natrojarosite in the Kidd Creek tailings impoundment (10). Jarosite is the only plausible source of K in the Campbell tailings because muscovite, the only other source of significant K, is unlikely to dissolve fast enough under these neutral-pH conditions. Under the geochemical conditions of the lined impoundment, the chemical equilibrium of jarosite can be described by the reaction



This reaction accounts for increases in K and possibly for increases in As, but does not account for the observed increases in dissolved Fe(II) because the Fe(III) released by this reaction is reprecipitated as Fe(III) oxyhydroxide.

Electron-microprobe analyses indicate that dolomite in the tailings contains up to 0.9 wt% MnO, and from 1.7 to 12.6 wt% FeO; dolomite dissolution therefore provides an alternative source of dissolved Fe(II). Assuming that siderite is not precipitating, dolomite dissolution can be represented by



Although dolomite dissolution is a feasible reaction for supplying Fe(II) to the pore water, the corresponding changes in the concentrations of SO₄, Mg, Mn, and alkalinity are not observed. At a depth of 2.5 m, for example, a decrease in SO₄ of 900 mg/L, and increases in Mg, Mn, and alkalinity of 180, 5, and 550 mg/L would be expected. Increases in the concentrations of Mg and Mn would be expected because the pore water is undersaturated with respect to potentially controlling Mg and Mn phases, and because Mg and Mn derived from dolomite are observed in the pore water of the unsaturated zone in the Balmer Area impoundment. However, the concentrations of Mg and Mn in the lined impoundment did not change between 1994 and 1995 (Figure 7), and

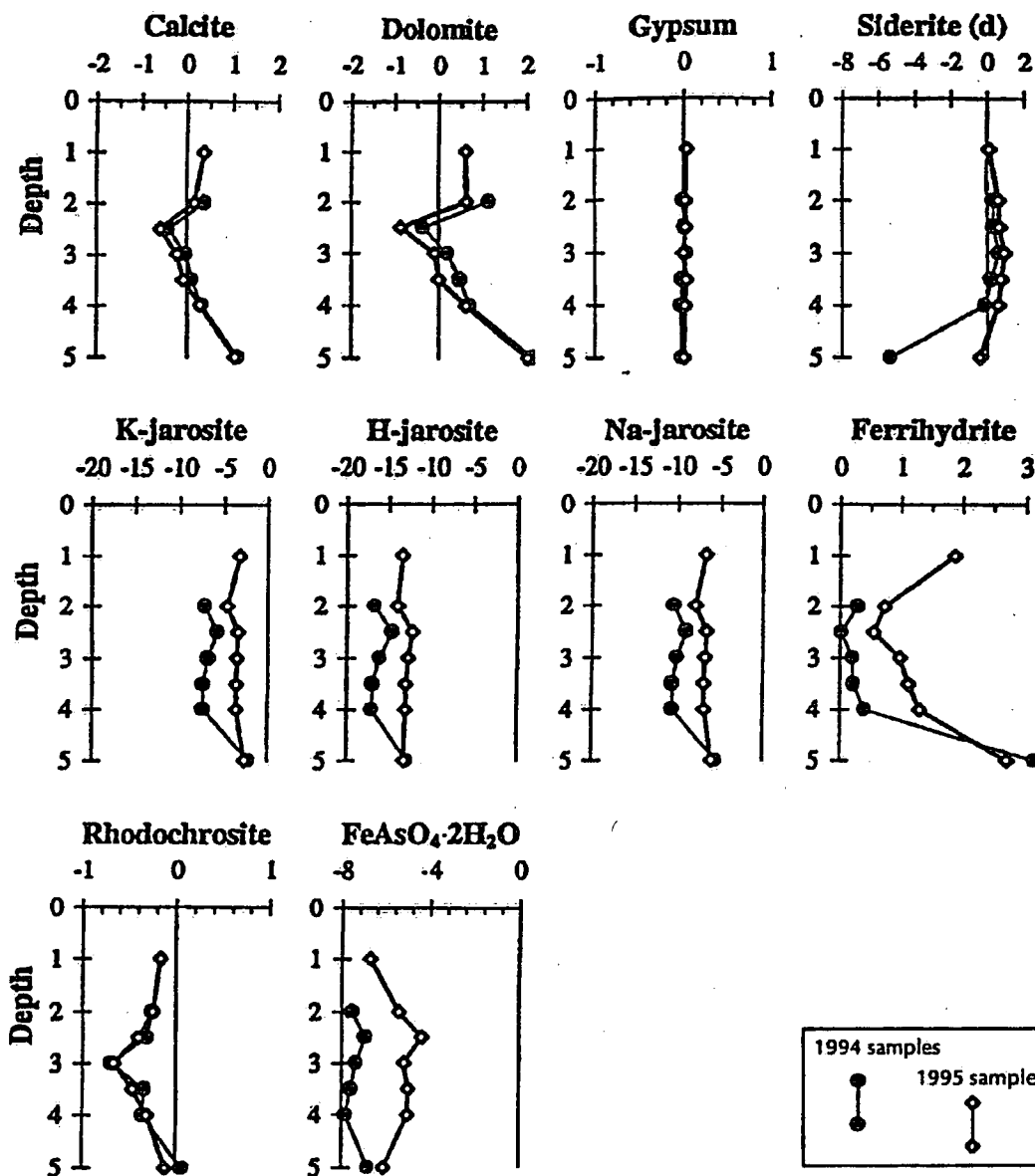


FIGURE 8 Saturation indices for selected phases pertaining to the lined impoundment

the small increase in alkalinity (Figure 7) is probably within the precision of the alkalinity titration. Thus, the stoichiometric analysis suggests that nonreductive dissolution of jarosite does not completely account for the observed increases in dissolved As and Fe(II) concentrations between 1994 and 1995.

The mineralogical character of the ferric sulfarsenate is not yet known in detail, but current indications are that the phase represents at least a partial solid solution between ferric sulfate and ferric arsenate. Assuming that the

phase has a geochemical behavior similar to that of jarosite, dissolution of the sulfarsenate in saturated, neutral-pH mine tailings would be expected. However, a stoichiometric analysis similar to that done for jarosite demonstrates that nonreductive dissolution of the ferric sulfarsenate does not completely account for the observed changes in water chemistry.

Reductive Dissolution

Some of the dissolved Fe(II) that is being released to the pore water in the lined impoundment seems to have been derived from the Fe(III) in the jarosite or ferric sulfarsenate, or both. This interpretation implies that Fe(III) is being reduced. Biotic and abiotic reductive dissolution of Fe(III) phases has been documented in numerous laboratory experiments and field studies (11,12,13,14,15). Similar to Fe, the large increase in dissolved As(III) concentrations and the predominance of the As(III) species (Figure 7) suggest that As(V) in the ferric sulfarsenate (and possibly jarosite) is also being reduced. Biotic reduction of As(V) to As(III) has been observed in field and laboratory settings (16). Cullen and Reimer (17) cited three additional examples of As(V) reduction to As(III) and indicated that observed ratios of As(V)/As(III) are commonly many orders of magnitude lower than those predicted by thermodynamic calculations; biological activity was stated to be of "paramount" influence in this disequilibrium.

The presence of reducing bacteria in the Campbell tailings was inferred by Perry (18), who incubated fresh tailings from the autoclave for 40 days. The control incubation contained only tailings and double-deionized water (DDW), and a simultaneous incubation contained tailings and organic-carbon-enriched DDW. Whereas As and Fe concentrations in the control were consistently less than 0.8 and 0.008 mg/L, respectively, concentrations in the organic-carbon-enriched incubation peaked at 11 mg/L As and 24 mg/L Fe. Differences of this type were also observed for two other tailings mixtures. The relatively high As concentrations in the carbon-enriched incubation suggest either that Fe(III)-reducing bacteria occur in the tailings and are capable of reducing the As-rich phases, or that the organic carbon itself is reducing the As-rich phases.

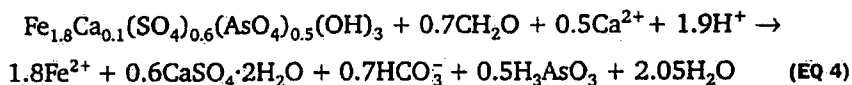
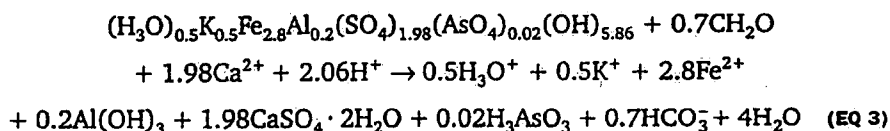
Potential reductants in the tailings and their pore water in the lined impoundment include dissolved NH_4 , sulfide minerals, and dissolved organic carbon (DOC). Dissolved sulfide has been eliminated as a potential reductant because concentrations in the lined impoundment are less than the detection limit of 0.015 mg/L; moreover, ^{34}S - SO_4 ratios are not enriched relative to process water, indicating that dissolved sulfide is not being produced biologically (Figure 7).

Dissolved NH_4 occurs at concentrations of 5 to 18 mg/L throughout the profile (Figure 7) and may be derived from the decomposition of cyanide (19). Although the reduction of both Fe(III) and As(V) by NH_4 is thermodynamically favorable, such reactions have not been documented previously and NO_3 , the oxidation product of NH_4 , was not detected in the pore water of the lined impoundment (Figure 7). Ammonia-oxidizing, chemolithotrophic and heterotrophic bacteria have been isolated from soils and from deep subsurface sediments, but such bacteria have been identified only in oxic environments (20,21).

Sulfide minerals occur throughout the lined impoundment below a depth of 0.8 m because flotation tailings are mixed with the autoclave tailings. Sulfide minerals are effective reductants for a variety of species. At low pH, at which $\text{Fe}(\text{OH})_3$ is soluble, sulfide minerals are known to reduce $\text{Fe}(\text{III})$ to $\text{Fe}(\text{II})$. Wersin *et al.* (22) used Auger electron spectroscopy, X-ray photoelectron spectroscopy, and Fourier Transform Infrared analyses to show that uranyl is reduced on galena and pyrite surfaces. Wersin *et al.* cited four published experimental studies that indicate sulfide minerals can reduce $\text{Au}(\text{III})$, $\text{Ag}(\text{I})$, $\text{Pd}(\text{II})$, and $\text{Cr}(\text{VI})$. Studies of NO_3 reduction by pyrite in aquifers (23) indicate that sulfide minerals are effective reductants. The reduction of dissolved $\text{As}(\text{V})$ on the surfaces of sulfide grains would drive the dissolution of $\text{As}(\text{V})$ -bearing solids such as the ferric sulfarsenate and jarosite in the lined impoundment. Reduction of $\text{As}(\text{V})$ would have the greatest effect on the ferric sulfarsenate because $\text{As}(\text{V})$ accounts for a large proportion of the anions in the sulfarsenate structure.

The reduction of dissolved $\text{Fe}(\text{III})$ on the surface of sulfide minerals is thermodynamically favorable and occurs at high rates when pH is low. At neutral pH, however, $\text{Fe}(\text{III})$ may be preferentially precipitated as $\text{Fe}(\text{OH})_3$ rather than being reduced. Therefore, the sulfide minerals are probably not reducing large amounts of dissolved $\text{Fe}(\text{III})$ in the lined impoundment.

DOC occurs at concentrations of 25 to 45 mg/L throughout the profile in the lined impoundment (Figure 7). Assuming an average DOC concentration of 32 mg/L C and an absence of As-concentration-limiting reactions, DOC has the potential to produce As concentrations of 6 mg/L from jarosite reduction and 140 mg/L As from ferric sulfarsenate reduction according to reactions:



Assuming a porosity of 0.5, which is similar to that in the Balmer Area tailings (Figure 2), 3 mg of As would be released per L of tailings for jarosite reduction and 70 mg/L for ferric sulfarsenate reduction. The high concentrations and large masses of dissolved As that can be produced from reductive dissolution of jarosite and ferric sulfarsenate suggest that DOC is not necessarily a limiting constituent.

The DOC can be attributed partly to the long-chain organic polymers used in the flotation circuit of the mill. The DOC may also be partly derived from the wood chips that are screened out of the mill feed, which are from the timbers in the underground workings, and possibly from the carbon in the carbon-in-pulp Au-extraction circuit. Nonlabile forms of organic carbon can be bacterially decomposed to form labile forms capable of reducing ferric sulfarsenate and jarosite. For the observed changes in dissolved-As concentrations between

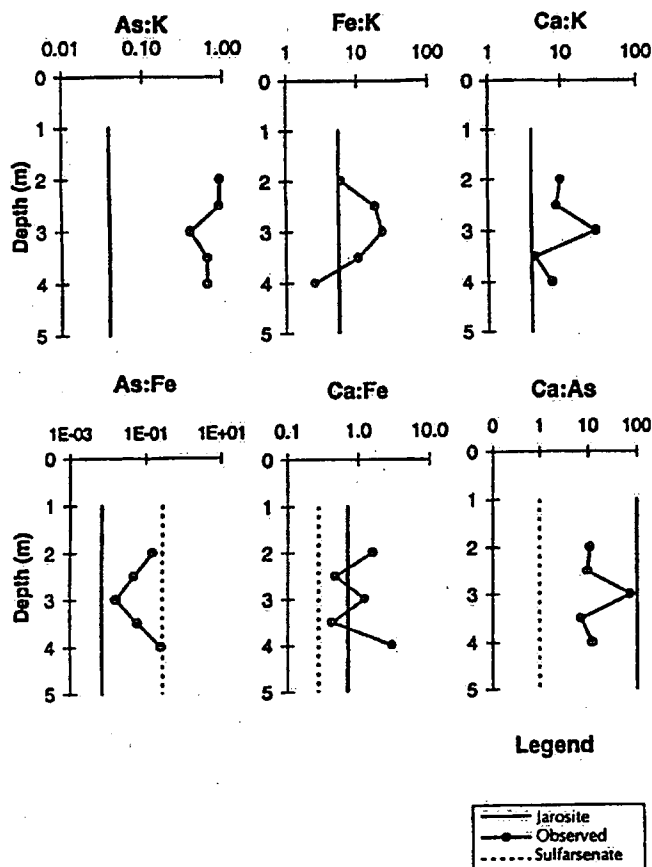


FIGURE 9 Stoichiometric and observed ratios for pore-water samples from tailings of the lined impoundment

1994 and 1995, the reductive dissolution of the jarosite by DOC should consume on the order of 40 mg/L C. In contrast, consumption of C in the reductive dissolution of ferric sulfarsenate should be on the order of 2 mg/L. DOC concentrations measured in 1994 are comparable to those measured in 1995 (Figure 7). The similarity in concentrations may be due to limited precision in the analytical method, to deficiencies in the sampling protocol, to replenishment of DOC from solid carbon sources, or to the assumption that all of the organic carbon is oxidized to CO_2 . The similarity in observed DOC concentrations between 1994 and 1995 suggest that most of the dissolved As is derived from the reduction of ferric sulfarsenate, which consumes much less DOC than the reduction of jarosite.

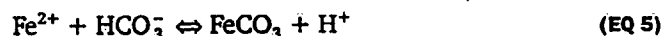
The reduction of jarosite by DOC (reaction 3) releases As and K in a ratio of 0.04:1 (As:K). Observed As:K ratios range from 0.4:1 to 0.9:1 (Figure 9), which are at least an order of magnitude greater than the theoretical ratio. The reduction of jarosite releases Fe and K in a ratio of 5.6:1 (Fe:K).

Observed Fe:K ratios range from 3:1 to 23:1. The high observed ratio suggests that either a large proportion of the K from the jarosite is being consumed by cation exchange or that As and Fe are also being derived from reduction of ferric sulfarsenate (reaction 4).

The reduction of jarosite by DOC (reaction 3) releases As and Fe in a ratio of 0.007:1 (As:Fe) whereas the reduction of ferric sulfarsenate (reaction 4) releases As and Fe in a ratio of 0.3:1 (As:Fe). The observed As:Fe ratios range between these two extremes (Figure 9), supporting the hypothesis that both jarosite and ferric sulfarsenate are dissolving.

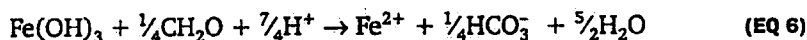
In summary, the observed changes in pore-water chemistry between 1994 and 1995 agree within the bounds posed by assumed reactions (3) and (4). If some of the K released to solution has been consumed by cation exchange, a larger proportion of As may be coming from jarosite dissolution.

The pore water is slightly supersaturated with respect to siderite, suggesting that some Fe(II) and HCO_3^- may be precipitating as siderite (FeCO_3) according to the reaction:



It has been shown (24) that siderite forms in swamp sediments from pore water that is supersaturated with respect to siderite.

An additional reservoir of Fe(III) is the amorphous ferric oxyhydroxides from the neutralized acid-pretreatment overflow. If Fe(III) in the ferric sulfarsenates and jarosites is undergoing reduction, the amorphous ferric hydroxides may also be reduced according to the reaction:



Ferric oxyhydroxides have been identified as strong As adsorbents at near-neutral pH conditions similar to those in the lined impoundment (25,26). However, the ferric oxyhydroxides in these tailings have much lower solid-phase As contents than the ferric sulfarsenate, as is indicated by the low solid-phase As content of the tailings in the upper part of the impoundment, where the ferric sulfarsenate is absent. Dissolution of the ferric oxyhydroxides may release some As to the pore water, but the oxyhydroxide is much less important than ferric sulfarsenate and jarosite as a source of As.

In summary, the differences in 1994 and 1995 pore-water concentrations of Fe(II), As(III), Ca, and K suggest that the ferric sulfarsenate, jarosite, and possibly the ferric oxyhydroxides are unstable in the anoxic zone and will potentially release As to the pore water. Instability of the jarosite is consistent with equilibrium geochemical modeling. Stoichiometric analysis, equilibrium geochemical modeling, calculated Fe speciation, and analytical As speciation suggest that reductive dissolution of ferric sulfarsenate and jarosite is occurring.

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