PERGAMON

Applied Geochemistry 15 (2000) 1245–1263

Applied Geochemistry

www.elsevier.com/locate/apgeochem

A laboratory evaluation of metal release and transport in flooded pre-oxidized mine tailings

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Received 6 May 1998; accepted 30 December 1999
Editorial handling by D. D. Runnells

Abstract

A potential problem in implementing water covers over preoxidized tailings impoundments is the dissolution of oxidation products following flooding, which may result in high concentrations of metals in both tailings pore water and the water cover. To examine metal release phenomena under controlled conditions, a laboratory study consisting of four column experiments of flooded partially oxidized tailings was performed over 2 years. In two of the columns enough water was added to establish a 1-m water cover, while the other two columns were only filled to the surface of the tailings. The columns were kept stagnant for the first half of the study ("static phase") and flushed under constant flow during the second half ("kinetic phase"). Samples of pore water and water cover were collected and analyzed for metals, SO_4, acidity, pH, redox, and dissolved O_2. Mass balance calculations were performed to assess metal release rates. At the end of the experiments the quality of the pore-water (pH 6) within the water covered tailings was better than that of the water cover itself (pH 3). While mineral dissolution released large amounts of Fe during the static phase in all experiments, no substantial dissolution or removal of Fe was detected after 300 days. In the water-covered tailings, Zn was removed from solution during both the static and kinetic phases, apparently through co-precipitation or adsorption with Fe(III) hydroxides. Metal and SO_4 release rates measured in the laboratory were similar to those observed at full-scale field sites. The laboratory observations suggest that while implementing a water cover over pre-oxidized tailings does substantially reduce metal release, long-term treatment of pond effluent and seepage may still be required in some cases. In the field, however, metal concentrations would be influenced by other phenomena, such as dilution due to surface water flow and sediment resuspension through wind, which were not simulated in the laboratory. Thus, the laboratory results cannot be directly extrapolated to the field.

1. Introduction

Many development projects and operating mines with an acid drainage concern are proposing water covers as a method for controlling acid drainage from exposed surfaces and pits and underground workings, and from large volumes of tailings and waste rock. The effectiveness of water covers is due to the low solubility of O_2 ($8.6\ g/m^3$ at 20°C) in water and the rather low O_2 diffusivity of $\sim 2 \times 10^{-9}\ m^2/s$ in water compared to $1.78 \times 10^{-5}\ m^2/s$ in air. These imply that

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0883-2927/00/$ - see front matter
PII: S0883-2927(00)00003-2

O_2 transfer to flooded tailings by molecular diffusion alone is about 10,000 times slower than to uncovered tailings. In addition to reducing the diffusive O_2 flux, a water cover can create a reducing environment suitable for supporting SO_4 and NO_3 reducing micro-organisms in the tailings where soluble metals may precipitate as sulphides. A water cover can also eliminate surface erosion by wind.

In flooded tailings ponds of several tens of hectares, O_2 can enter via several mechanisms including vertical mixing due to the orbital motions caused by wind-induced waves, and turbulent mixing caused by breaking waves. Provided the tailings pond is properly designed to minimize the impact of these mechanisms, a water cover may prevent significant acid generation in subaqueously deposited unoxidized tailings (Yanful and Simms, 1997).

When previously oxidized tailings are flooded, large fluxes of metals into the water cover may occur. One problem the mining industry faces is the uncertainty regarding the amount and rate of dissolution of minerals from flooded pre-oxidized tailings. This paper

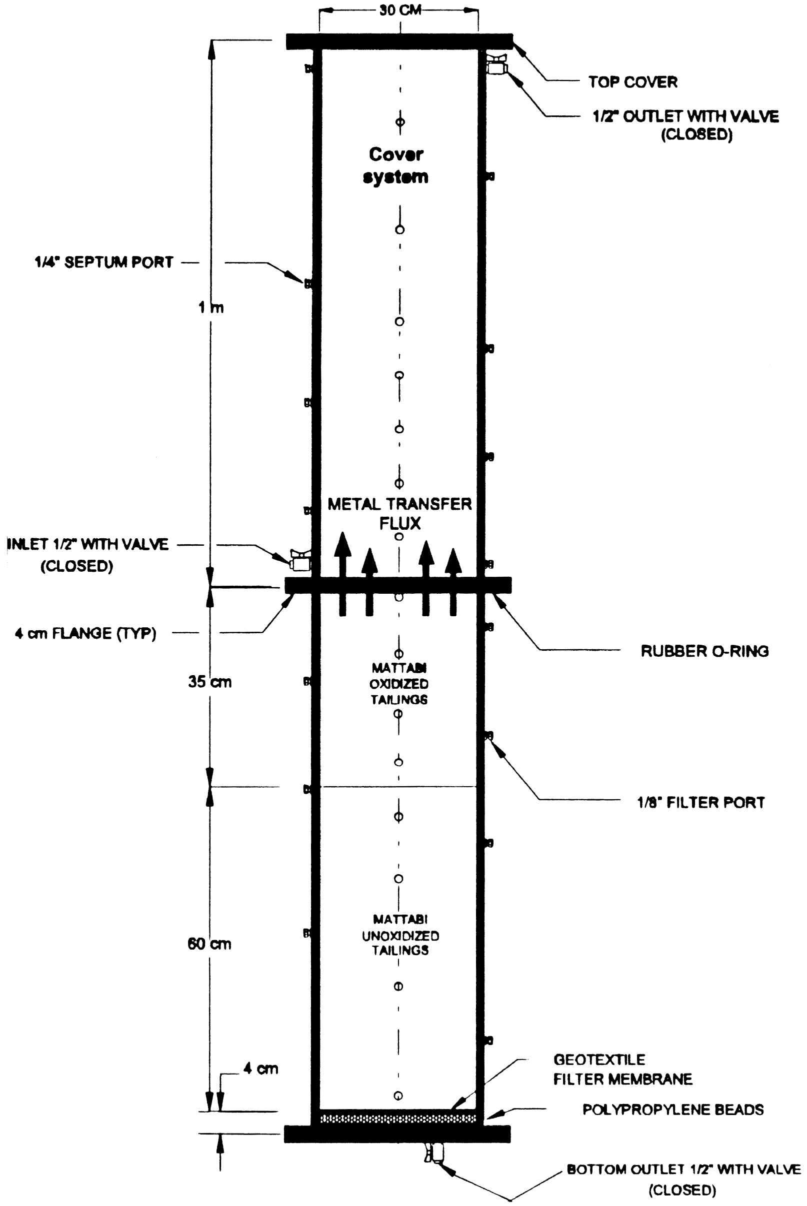

Fig. 1. Schematic of instrumented laboratory column.

presents a laboratory investigation of the rate of dissolution of oxidation products in flooded pre-oxidized tailings. The fluxes of metals and SO_4 observed in the laboratory water covers were compared to those observed at full-scale field sites.

2. Methodology

The experiments consisted of water-covered columns of oxidized and unoxidized tailings from the Mattabi tailings impoundment, near Ignace, Ontario, performed at the Noranda Technology Centre. St-Arnaud and Yanful (1993, 1994) have presented preliminary results from these experiments. Presented in this paper are a detailed description and results of two sets of duplicate columns: one set with a 1-m water cover and another set with saturated tailings but no water cover.

2.1. Experimental methods

Transparent Plexiglas columns, each 2 m high and 0.3 m in diameter, were constructed for the experiments. A schematic of a typical column is shown in Fig. 1. Each column was built with two 1-m sections. The lower section was packed with 0.6 m of unoxidized tailings followed by 0.35 m of oxidized tailings collected from the north portion of the Mattabi tailings disposal site. The two experiments with a 1-m water cover, MTWC-1 and MTWC-2, were constructed first and filled with water from Sturgeon Lake (a lake neighboring the Mattabi tailings site). The two experiments in which the tailings were only flooded to their surface, MTWC-7 and MTWC-8, were constructed almost a year later and filled with distilled water. Each column was equipped with 28 septum ports, 14 to allow sampling of pore water in the tailings, and 14 to monitor water quality with depth in the cover. There was also a bottom outlet that was closed during the static phase and used to sample the effluent when water was allowed to flow through the tailings in the columns. Water samples were preserved and analyzed for a complete metal scan and S by inductively-coupled plasma (ICP) spectrophotometry. Ferric ion was measured independently by colorimetry using a standard method employing a potassium thiocyanate reagent (Furman, 1962; Sandell and Hiroshi, 1978). Ferric iron present in the sample reacts with SCN^- forming a red-brown complex. The amount of Fe(III) is then determined by measuring the absorbance of the solution at 480 nm with a spectrophotometer (Schimadzu UV-VIS model UV-160). Ferrous iron was calculated by subtracting Fe(III) from total Fe. The analyzed constituents are listed in Table 1. Analysis of spiked and blank samples for quality control indicated the analytical results were accurate to within $\pm 2\%$. Acidity was determined by titration and pH was measured at each sampling using a combination electrode and appropriate buffers. Dissolved O_2 (DO) and redox were measured in water samples taken at the end of the experiments, using a calibrated DO meter and a calibrated redox meter connected to an electrode.

2.2. Initial composition and mineralogy

The unoxidized tailings typically contained 35% pyrite, 8% pyrrhotite, 1.5% sphalerite, and 3–4% other sulphide minerals; pyrrhotite was extensively weathered in the oxidized tailings (Freymond, 1994). The elemental composition of the tailings used in the experiments is shown in Table 2. Gypsum (0.2–1.0% by weight) was present in both the unoxidized and oxidized tailings in both columns, and goethite (1.8–3.6%) was observed in the unoxidized tailings (Catalan, 1998).

2.3. Experimental protocol

The experiment was conducted in two phases: a static phase (no flow), and a kinetic phase (flow through) in which 1 l of distilled water was added per week (corresponding to approximately 700 mm of rain per year) to each column to simulate precipitation, and effluent was collected at the bottom. Throughout the experiment, samples of the water cover and pore water were collected at the septum ports. The duration of each phase, in days, and the total volume of effluent collected from each column, in pore volumes, are presented in Table 3. Over the length of the experiment, the flow in each column was fairly constant; Table 4 compares the mean and variability of the flow rates in each column.

At the end of the experiments, MTWC-1 was decommissioned. The tailings were extruded and cut into vertical segments that were sampled and squeezed using a pneumatically driven pore–water squeezer (Yanful et al., 1988) to obtain pore water for chemical analysis. The solid tailings were subsequently leached with de-ionized water and then with dilute H_2SO_4 (pH of 3.5). The leaching and squeezing were performed inside a glove-box, and the leachate and pore water were collected in bottles purged with N_2. The leachates were analyzed to obtain the mass of ions dissolved by each leaching process.

2.4. Geochemical equilibrium modelling

The ion profiles obtained from MTWC-1 prior to its decommissioning, and effluent ion concentrations taken at the end of the kinetic phase for MTWC-1 and MTWC-8, were analyzed using MINTEQ (Felmy et al., 1984), an equilibrium geochemical thermodynamic

Table 1
Measured species in water samples

Method of analysis	Analyzed constituents
I.C.P.	Al As Ca Cd Cu Fe K Mg Mn Na Pb S Se Zn
Colorimetry	Fe^{3+}

speciation model. MINTEQ takes raw pore water concentration, pH, and redox data, and speciates the ions and calculates saturation indices. The charge balance of the speciated ions can be used to assess the completeness, and to some extent, the accuracy of the pore water data. A large charge imbalance usually indicates that an important species was not included in the analysis. Additionally, the program predicts which minerals are likely to precipitate or dissolve, based on ion speciation and the thermodynamic properties of minerals involved in the various dissolution and precipitation reactions. The tendency for a mineral to precipitate or dissolve is represented by its saturation index (SI):

$$SI = \log\left(\frac{IAP}{k}\right) \tag{1}$$

where IAP is the ion activity product and k is the equilibrium constant for the mineral. A positive SI indicates a mineral has the thermodynamic potential to precipitate, and a negative SI indicates that a mineral has the potential to dissolve, if it already exists. MINTEQ is not applicable when the precipitation or dissolution of a mineral is restricted by reaction kinetics, which is commonly revealed by large positive SI values. MINTEQ and similar models have been employed in geochemical assessments of tailings impoundments by Blowes and Jambor (1990), and subaqueously deposited tailings by Drake et al. (1995).

3. Results

3.1. Ion concentration depth profiles

Total Fe, Fe(III), SO_4, and Zn concentration profiles for columns MTWC-1 and MTWC-8 are shown in Figs. 2 through 9. The concentration of SO_4 was obtained from the measured concentration of S by multiplying by three (the ratio of the molecular mass of SO_4 to the molecular mass of S). That is, all S was assumed to be present as SO_4. The results were well-reproduced in each duplicate column. Table 5 shows the change in dissolved mass in the pore water in each column during the static phase, and the amount of dissolved mass measured in the water cover at the end of the static phase.

3.1.1. Water cover columns (MTWC-1)

Figs. 2 and 3 show that in MTWC-1, a substantial increase in the dissolved mass of both total Fe and Fe(III) occurred in the static phase, between 152 and 347 days, apparently in the bottom of the oxidized tailings and the top of the unoxidized tailings. From 0 to 152 days, the change in the average pore water concentration of total Fe (5100 to 5060 mg/l) was insignificant, while by the 347th day the average concentration had increased from 5060 to 6742 mg/l. The percentage of total Fe that was Fe(III) was less than 1%. The pore water concentration of SO_4 (Fig. 4) decreased from an average of 19,500 to 16,900 mg/l by day 152, and then rose to 18,900 mg/l by day 347. The dissolved mass of Zn (Fig. 5) decreased throughout the static phase. As shown in Table 5, sizable increases in con-

Table 2
Elemental composition of oxidized tailings obtained from unsaturated zone and relatively un-oxidized tailings obtained from saturated zone

Element (% weight)	MTWC-1 and 2 oxidized	MTWC 7 and 8 oxidized	MTWC-1 and 2 un-oxidized	MTWC-7 and 8 un-oxidized	Mean and coefficient of variation
Al	2.72	3.93	3.14	2.85	3.16 (0.17)
Ca	0.31	0.12	0.42	0.1	0.24 (0.65)
Fe	22.1	24.1	19.9	26.5	23.2 (0.12)
S	20.3	19.6	18.4	26.4	21.1 (0.17)
Si	14.0	14.3	16.6	12.1	14.3 (0.13)
Zn	0.60	0.33	0.54	0.18	0.41 (0.47)

Table 3
Experimental protocol

Column[a]	Static phase duration (days)	Kinetic phase duration (days)	Kinetic phase pore volumes
MTWC-1	348	605	2.43
MTWC-2	348	605	2.59
MTWC-7	227	424	1.72
MTWC-8	227	424	1.69

[a] MTWC-1 and 2 have a 1-m water cover over the tailings; MTWC-7 and 8 are flooded to the surface of the tailings.

Table 4
Time-averaged means and standard deviations of effluent flow rates

Column	Mean (l/day)	Standard deviation (l/day)
MTWC-1	0.142	0.0042
MTWC-2	0.153	0.0041
MTWC-7	0.133	0.044
MTWC-8	0.134	0.029

centration of all species except Zn and Fe(III) were detected in the water covers.

During the kinetic phase, total Fe, Fe(III), and Zn were quickly flushed out of the pore water. Sulphate was also initially rinsed out, but there was no appreciable change between the SO_4 profiles at 1.4 and 2.34 pore volumes. This implies that the removal of SO_4 from the pore water by flushing was balanced by its release from the solid phase (probably gypsum). Fig. 5 shows that nearly all the Zn was removed from the pore water during the kinetic phase. However, only 87% of the dissolved mass at the beginning of the static phase was collected in the effluent, implying that 13% either precipitated or adsorbed onto the tailings.

3.1.2. Columns with no water cover (MTWC-8)

In column MTWC-8 (saturated tailings without cover), the dissolved ion concentrations of Fe and SO_4 measured in the static phase (Figs. 6 and 7), were substantially higher than in the columns with a water cover. Conversely, the concentrations of Zn (Fig. 8) were much lower. The average pore water concentration of total Fe, shown in Fig. 6, increased from 8400 to 16,400 mg/l by day 97, and remained more or less the same for the rest of the static phase. Both the

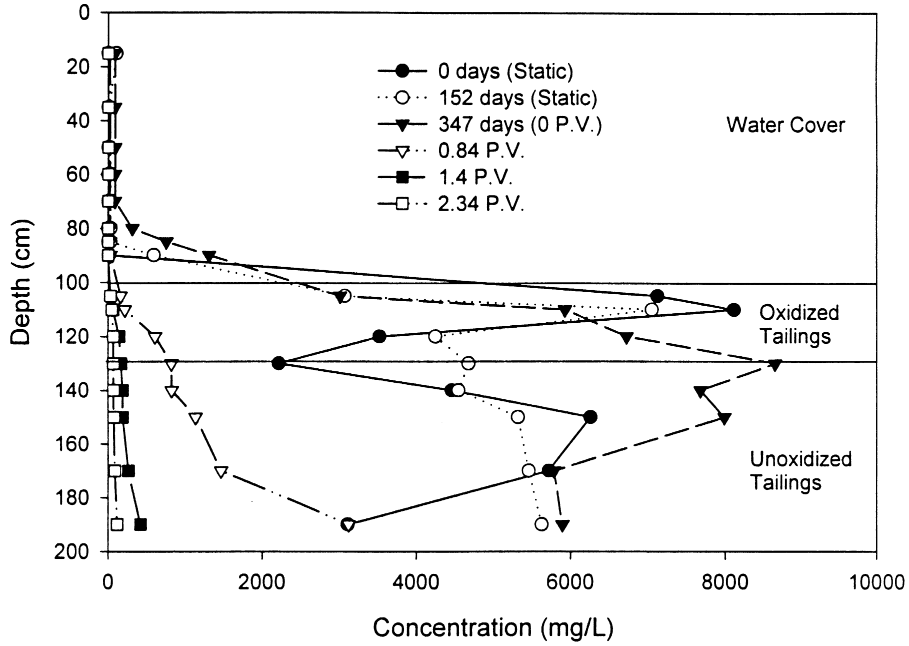

Fig. 2. Total Fe concentration profiles in column MTWC-1 (zero pore volume (0 P.V.) denotes the start of the kinetic phase).

Table 5
Changes in dissolved mass during static test (g)

MTWC♯	Initial mass	Net mass increase	Final mass in water cover[a]	Final mass in water cover and pore water
Fe				
1	160	61.6	17.3	222
2	159	45.7	38.6	205
7	298	257	N/A	596
8	309	212	N/A	521
Zn				
1	76.0	−38.7	0	37.2
2	88.6	−33.1	0	55.4
7	2.38	1.72	N/A	4.1
8	2.55	1.76	N/A	4.31
Fe(III)				
1	0	7.63	0	7.63
2	0	8	0	8
7	129	−96.8	N/A	32.2
8	122	−98.6	N/A	23.4
SO_4				
1	632	8	0.189	639
2	654	−28.9	0.131	625
7	782	293	N/A	1080
8	717	238	N/A	955

[a] N/A indicates not applicable as there is no water cover in columns MTWC-7 and 8.

dissolved masses of SO_4 (Fig. 7) and Zn (Fig. 8) also increased between 0 and 97 days, but changed only slightly between 97 and 163 days. The concentrations of total Fe and SO_4 followed the same trend with depth and were very close in molarity (approximately 30 mmol/l at the end of the static phase). The average

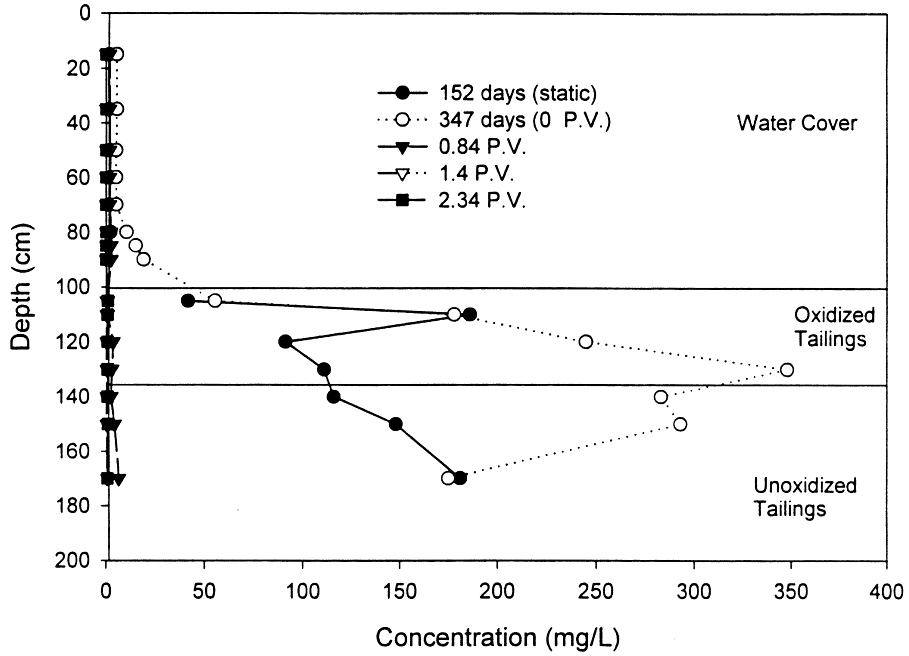

Fig. 3. Ferric iron concentration profiles in column MTWC-1 (zero pore volume (0 P.V.) denotes the start of the kinetic phase).

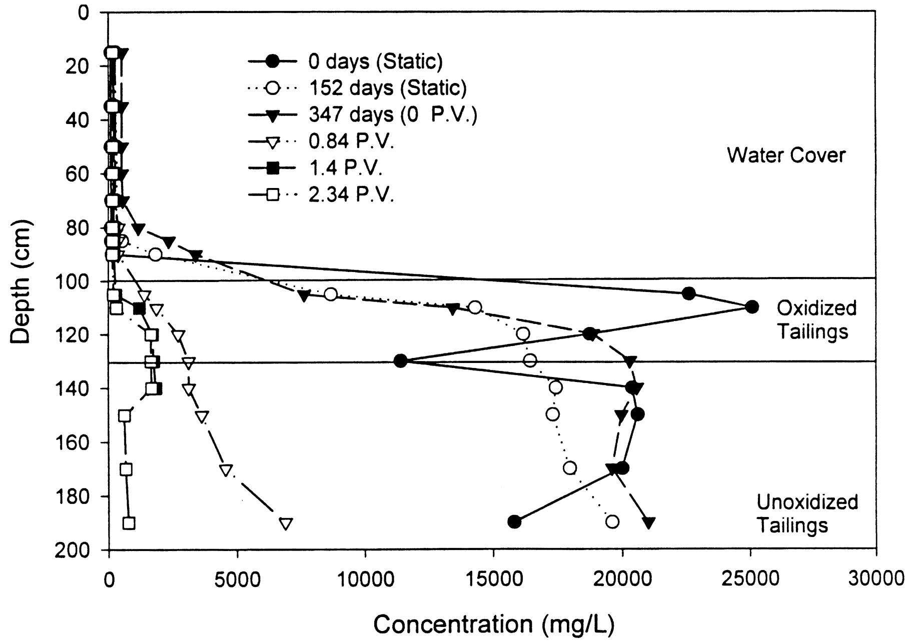

Fig. 4. Sulphate concentration profiles in column MTWC-1 (zero pore volume (0 P.V.) denotes the start of the kinetic phase).

pore water concentration of Fe(III) (Fig. 9) decreased from 3360 mg/l (40% of total Fe) to 740 mg/l (5% of total Fe) during the static phase, and continued to decrease in the kinetic phase. At the end of the kinetic phase the pore water concentrations of total Fe, SO_4 and Zn remained high, with average values of 500 (Fig. 6), 1000 (Fig. 7), and 15 (Fig. 8) mg/l, respectively.

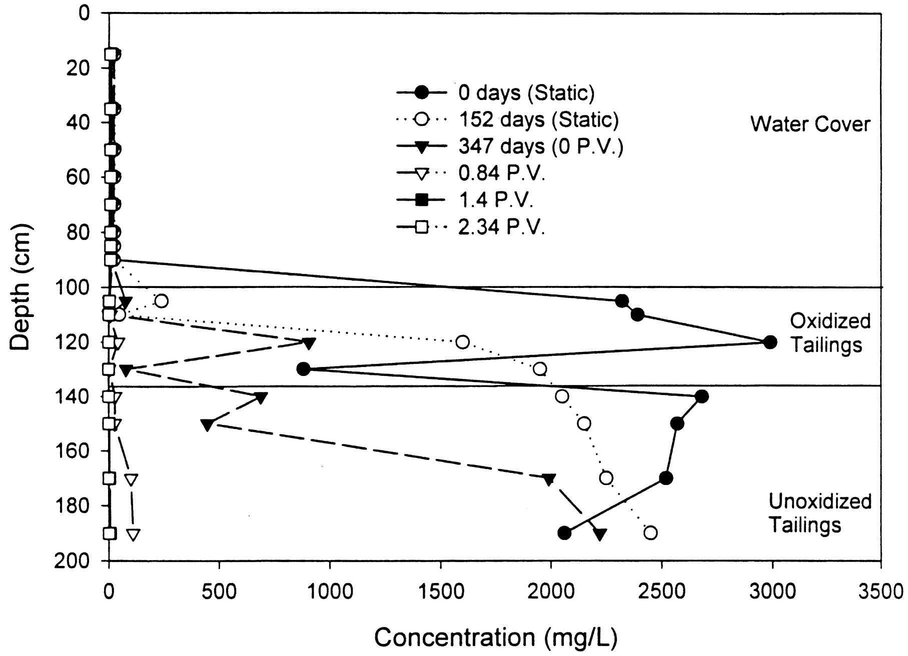

Fig. 5. Zinc concentration profiles in column MTWC-1 (zero pore volume (0 P.V.) denotes the start of the kinetic phase).

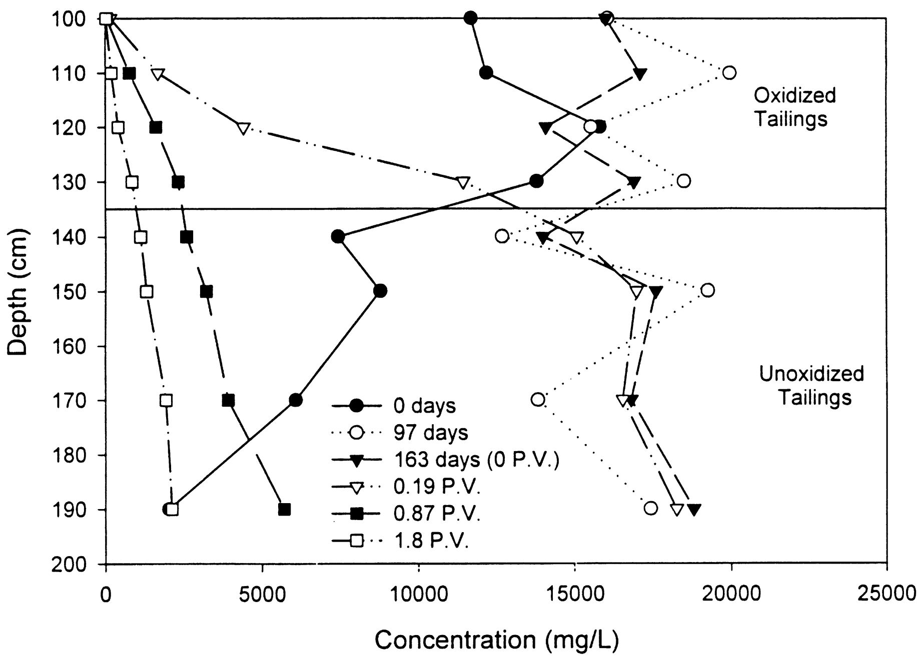

Fig. 6. Total Fe concentration profiles in column MTWC-8 (zero pore volume (0 P.V.) denotes the start of the kinetic phase).

3.2. *Effluent concentration profiles*

The effluent from the base of each column was regularly analyzed during the kinetic phase. The effluent profiles for total Fe, SO_4, Zn, Ca, and Mg for MTWC-1 and MTWC-8 and Al for MTWC-8 are shown in Figs. 10 and 11. As noticed in the concentration-depth profiles, the Fe and SO_4 trends in these columns were nearly identical, and were very close in molarity. The effluent Zn concentrations were lower in

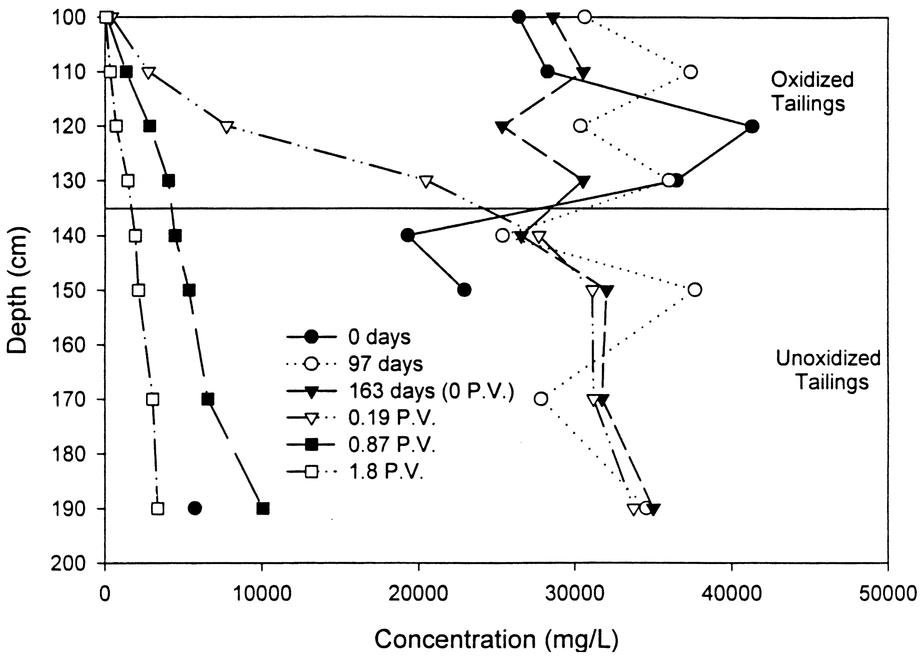

Fig. 7. Sulphate concentration profiles in column MTWC-8 (zero pore volume (0 P.V.) denotes the start of the kinetic phase).

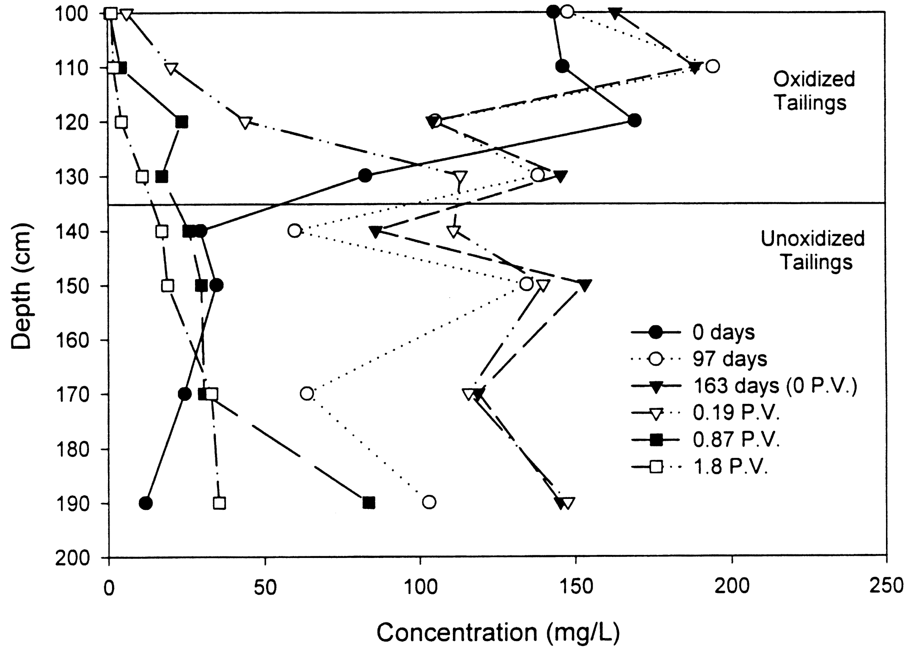

Fig. 8. Zinc concentration profiles in column MTWC-8 (zero pore volume (0 P.V.) denotes the start of the kinetic phase).

MTWC-8 than in MTWC-1. Also in MTWC-8, Al concentrations were initially high, but decreased quickly, while only trace quantities of Al were detected in MTWC-1. In MTWC-1, the molar concentrations of Ca and SO_4 converge towards the end of the kinetic phase, which suggested gypsum dissolution.

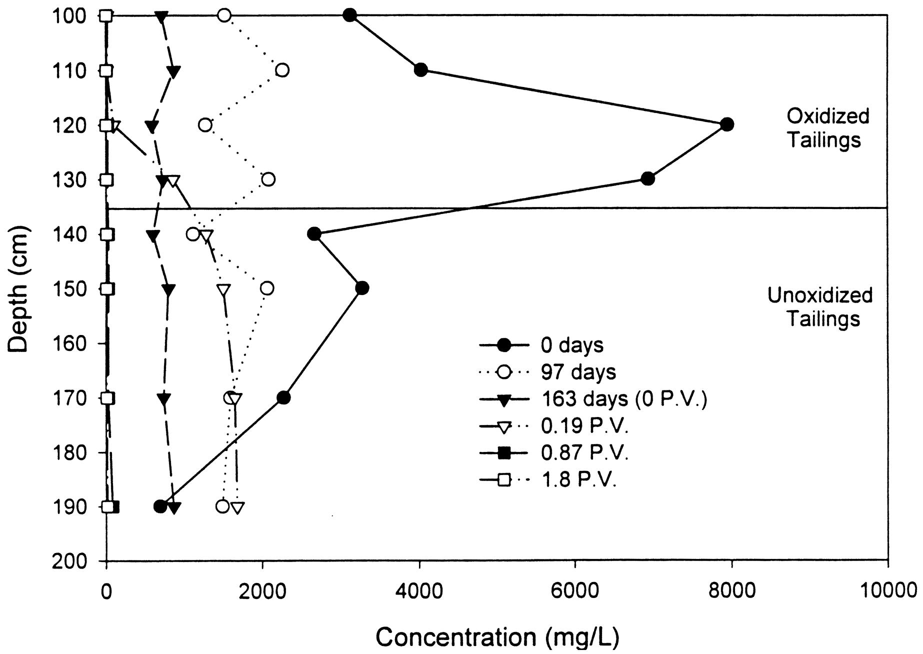

Fig. 9. Ferric iron concentration profiles in column MTWC-8 (zero pore volume (0 P.V.) denotes the start of the kinetic phase).

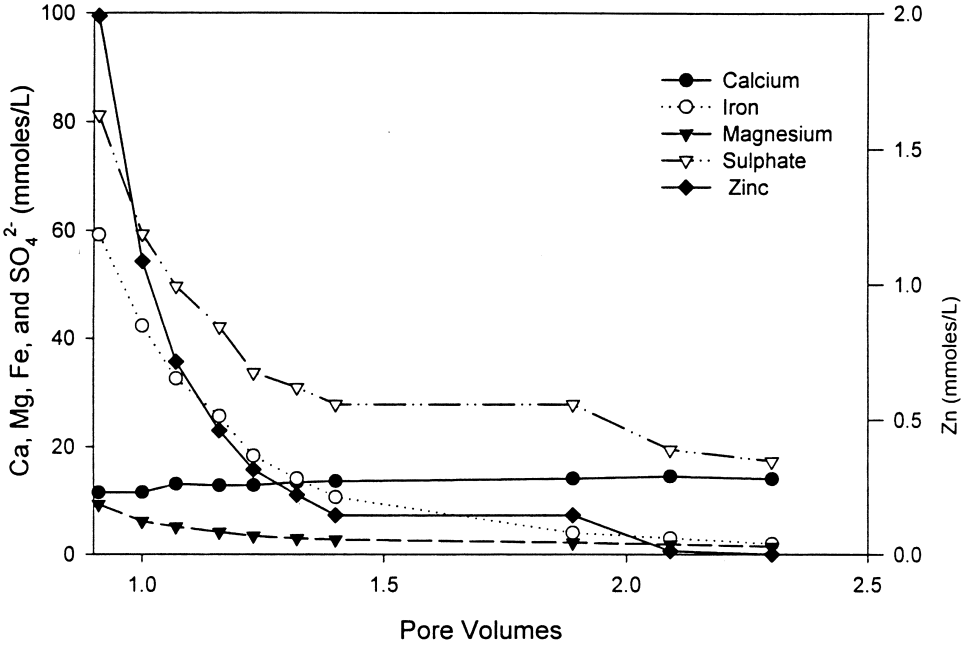

Fig. 10. Effluent species concentrations in column MTWC-1.

3.3. Final dissolved oxygen, pH, and redox after termination of the kinetic phase

Profiles of pH, dissolved O_2, and redox potential were obtained for the water cover and pore water in each column at the conclusion of the kinetic phase. There was little difference observed in the profiles between duplicate columns. Profiles for a water-covered (MTWC-1) and saturated tailings columns (MTWC-8) are shown in Figs. 12–14.

Surprisingly, the pH profile in MTWC-1 suggests the quality of the cover water was worse than that of

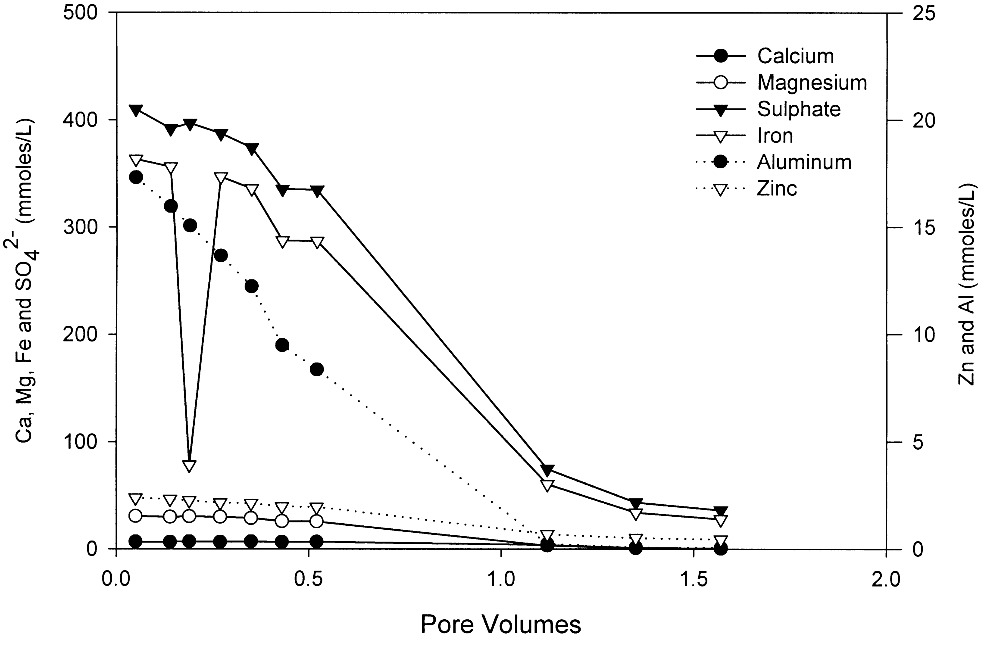

Fig. 11. Effluent species concentrations in MTWC-8.

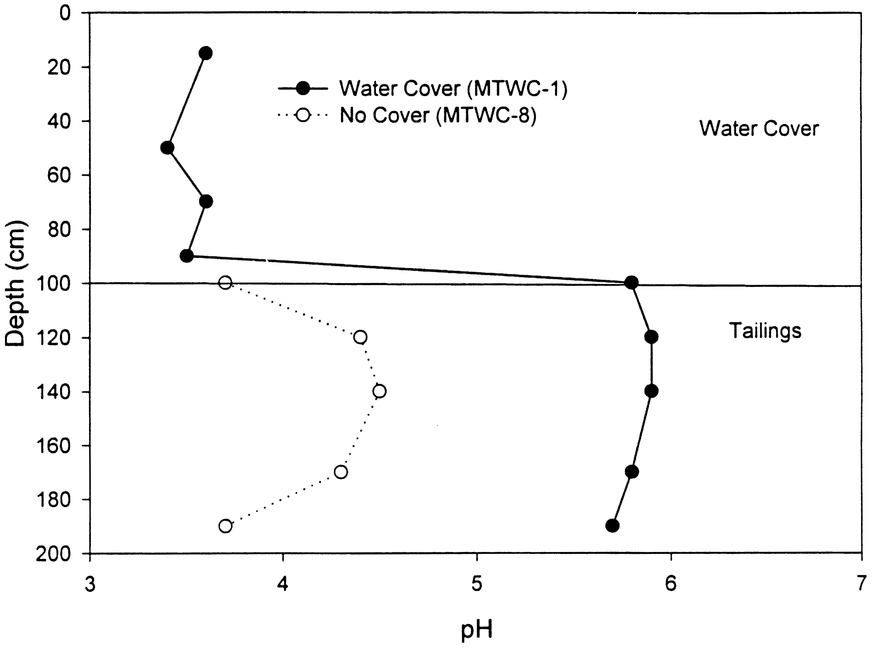

Fig. 12. pH profiles in Mattabi columns at end of kinetic phase.

the pore water. The redox potential profile indicates conditions in the water cover were oxidizing, but moderately to strongly reducing in the pore water (Fig. 14). The quality of the water cover may be controlled by the precipitation/dissolution of Fe(III) oxyhydroxide minerals and other secondary minerals. The dissolved O_2 concentrations in both sets of columns were similar (Fig. 13). The redox potential was higher (Fig. 14) and

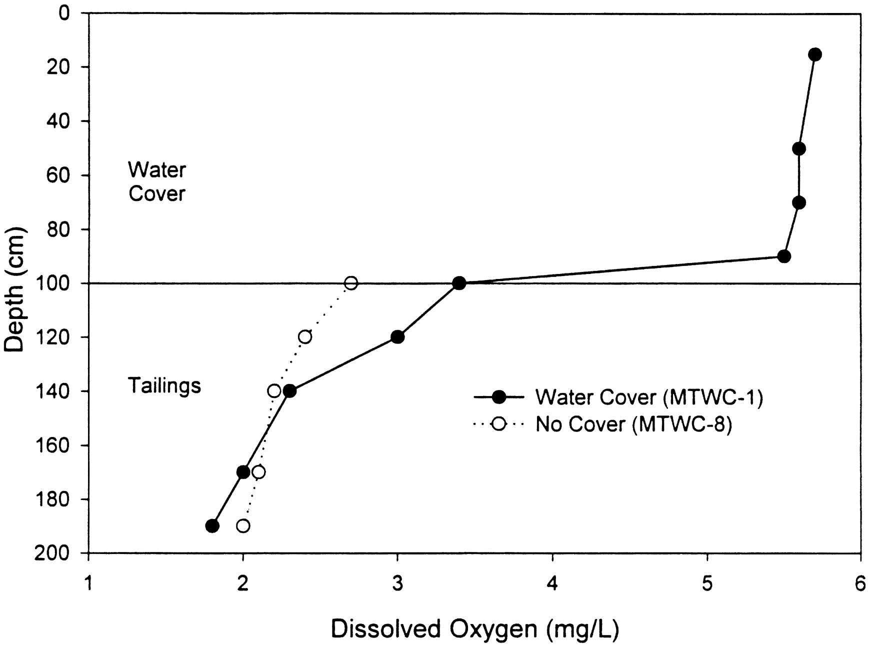

Fig. 13. Dissolved O_2 profiles in Mattabi columns at end of kinetic phase.

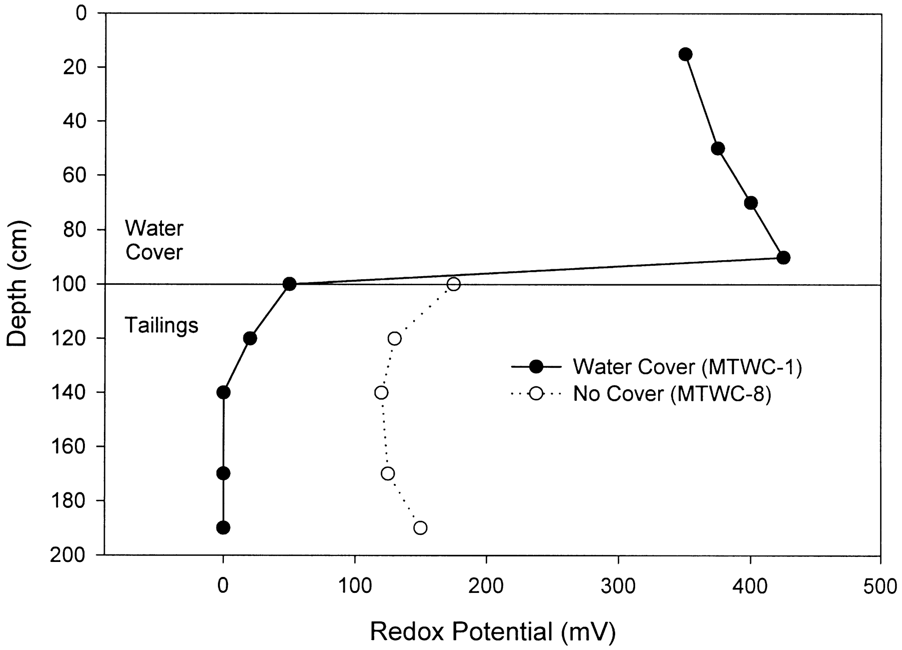

Fig. 14. Redox profiles in Mattabi columns at end of kinetic phase.

pH was lower (Fig. 12) at the surface of the columns without a water cover than at the surface of the covered columns.

3.4. Decommissioning and mass-balance in column MTWC-1

The masses of Fe and Zn removed by flushing during the kinetic phase, by pore water squeeze and by water and acid leaching are presented in Table 6. The mass of Fe removed by squeezing and acid leaching (1.5 g) is small compared to the mass removed by flushing (215 g). In contrast, 87% of the initial mass of Zn was removed by flushing, and a significant amount of Zn was removed through water and acid leaching. The total mass of Zn removed, 38,100 mg, which comprises Zn removed by flushing (32,315 mg), by pore water squeezing (3160 mg), and by leaching (2668 mg) was 103% of the initial amount. Apparently, the adsorption or precipitation of Zn was reversed during the pore-water squeeze and the water and acid leaching.

3.5. Geochemical modelling

MINTEQ analysis of the final ion concentration profiles, and of the squeezed pore water of MTWC-1 showed that the saturation index of gypsum was close to zero (Fig. 15). It was, therefore, possible that SO_4 and Ca concentrations were largely controlled by gypsum towards the end of the experiment, as suspected from effluent (Fig. 10) and depth (Fig. 4) concentration profiles.

Fig. 16 shows the saturation indices of possible Fe-bearing secondary minerals calculated from the effluent ion concentrations. Eh was determined from the rela-

Table 6
Dissolved mass removed by flushing, pore water squeeze, and leach tests

Ion	Dissolved mass at end of static test	Removed by flushing	Pore water squeeze	Leach tests	Total mass removed[a]
Fe (total)	219 g	215 g (98.1%)[b]	1368 mg	166 mg	217 g (98.8%)[b]
Zn	37.1 g	32.3 g (87%)[b]	3160 mg	2668 mg	38.1 g (103%)[b]

[a] Total mass removed = sum of masses removed by flushing, pore water squeezing, and leaching.

[b] Percent of the dissolved mass at the end of the static test.

tive concentrations of Fe(II) and Fe(III) and ranged from 450 to 600 mv in both columns. In MTWC-1, ferrihydrite was near equilibrium by the end of the kinetic phase, and in MTWC- 8 lepidocrocite and goethite were near equilibrium. It appears that melanterite was near equilibrium at the beginning of the kinetic phase in both experiments. All Fe_xS_x minerals were excessively unsaturated, having saturation indices less than −30.

4. Discussion

In existing tailings impoundments, the oxidation of Fe sulphides initially results in the formation of soluble Fe–SO_4 minerals, such as melanterite (Nesbitt and Myercroft, 1994). The Fe–SO_4 minerals may subsequently weather, releasing Fe(II) that is then oxidized to Fe(III), which commonly precipitates in the form of amorphous Fe hydroxides such as ferrihydrite. These hydroxides may in turn weather and reprecipitate or recrystalize into more stable forms such as goethite and lepidocrocite (Bingham et al., 1992).

Field studies of existing tailings impoundments (Blowes and Jambor, 1990; Yanful et al., 1990) and laboratory studies of tailings oxidation (Yanful et al., 1999) have shown that long term pore water concentrations are controlled by the precipitation/dissolution of secondary minerals. The field studies, which were conducted on tailings from the Waite Amulet site near Rouyn-Noranda, Québec, showed that Fe concentrations were principally controlled by Fe(III) hydroxide minerals. However, in the present experiments, the similar molarity of the initial pore water concentrations for Fe and SO_4 in the water-covered and saturated (no water cover) tailings suggest that the principal source of Fe was an Fe–SO_4 mineral. MINTEQ analysis of the effluent concentrations gave saturation indices for melanterite from 0 to −2.5 for both columns. The higher Fe sulphide content of unoxidized Mattabi tailings (35% and 8% pyrrhotite) compared to the Waite Amulet tailings (15% pyrite) and relative shallowness of the unsaturated zone are probably responsible for the long-term stability of Fe–SO_4 minerals. During initial oxidation, large amounts of Fe(II) and SO_4 would be flushed down below the capillary fringe of the tailings before oxidation of Fe(II) to Fe(III) could occur. The upper part of the saturated

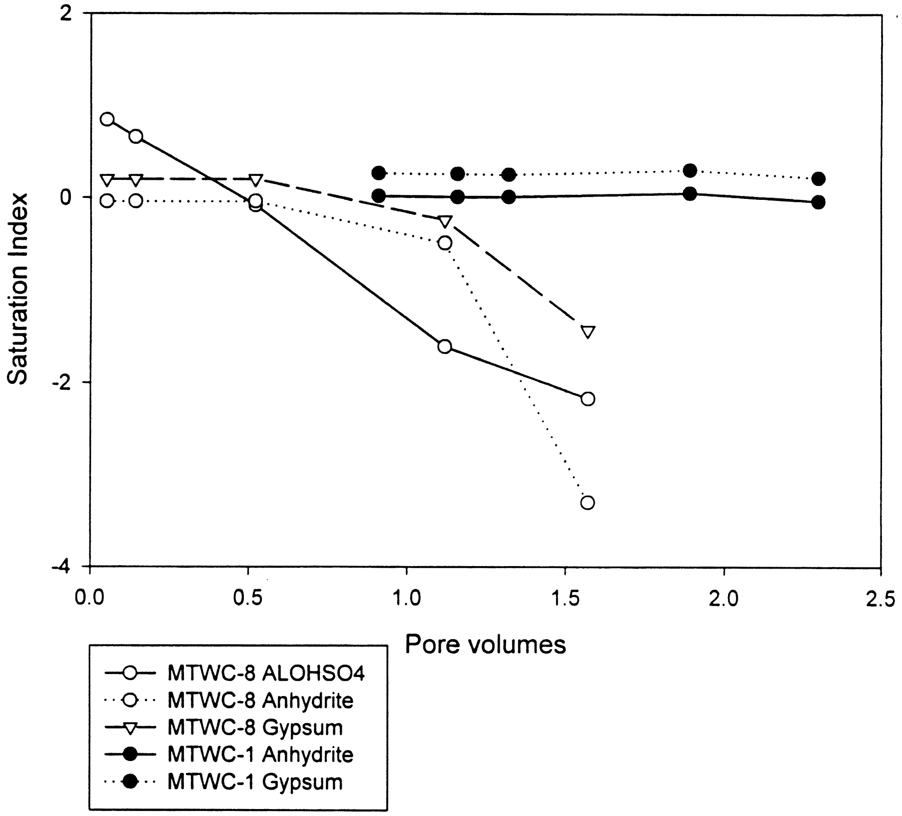

Fig. 15. Saturation indices for gypsum, anhydrite, and $AlOHSO_4$ in MTWC-1 and 8 calculated from effluent ion concentrations.

zone and the lower part of the unsaturated zone of tailings deposits typically contain high concentrations of Fe(II) and SO_4 ions (Yanful et al., 1990).

4.1. Mass transport to the water cover and mass balances

4.1.1. Static phase

The flooding of tailings results in mass transport from the pore water to the water cover through

1. Mixing of the pore water with the water cover during flooding
2. Subsequent transport due to diffusion, or other transport mechanisms.

The mixing and dilution of the pore water by flooding in the present experiments likely increased the pH sufficiently to allow for precipitation of Fe(III) hydroxides. In the water cover experiments, the formation of Fe precipitates at the surface of the tailings was observed during the first day of the experiment (St-Arnaud and Yanful, 1993). Table 5 shows that virtually no Fe(III) was measured in the water cover columns immediately after flooding; however 122 and 129 g of Fe(III) were initially present in each of the saturated columns. The initial dissolved mass of Fe(II), 160, 159, 169, and 187 g in MTWC-1, 2, 7, and 8, respectively, was similar (< 17% difference by mass) in all the columns. The difference between the average concentration of the water cover experiments with the saturated columns was not (16%) substantially different from the difference in concentration between MTWC-7 and 8 (11%).

During the first half of the static phase, the dissolved mass of Fe(II) and SO_4 in the unprotected columns (MTWC-7 and 8) increased substantially, by approximately 350 g (Fig. 17) and 500 g (Fig. 18), respectively. Conversely, the masses of Fe(II) and SO_4 in the water cover columns (MTWC-1 and 2) changed only slightly, Fe(II) concentrations increasing by about 50 g and SO_4 concentrations decreasing by 20–50 g. The shape of the ion concentration profiles (Figs. 2 and 4) indicates that substantial transport of Fe and SO_4 into the water cover occurred. Possible transport mechanisms include molecular diffusion, thermal diffusion, and

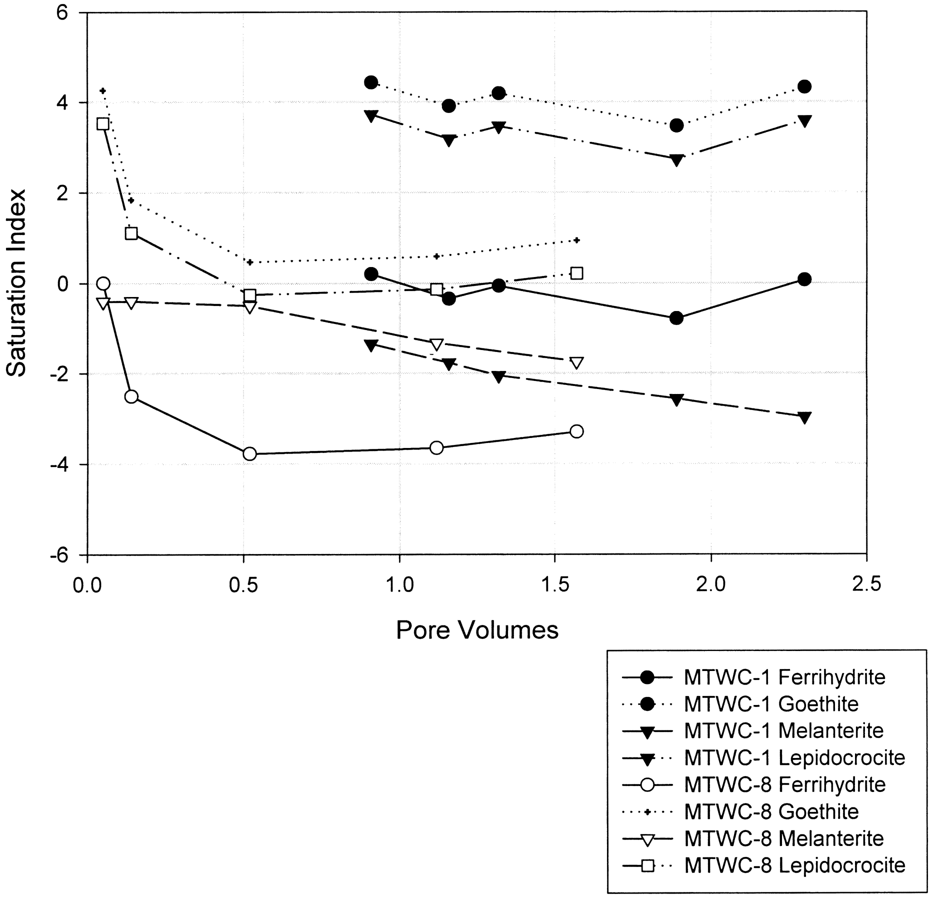

Fig. 16. Saturation indices of Fe bearing minerals in MTWC-1 and 8 calculated from effluent ion concentrations.

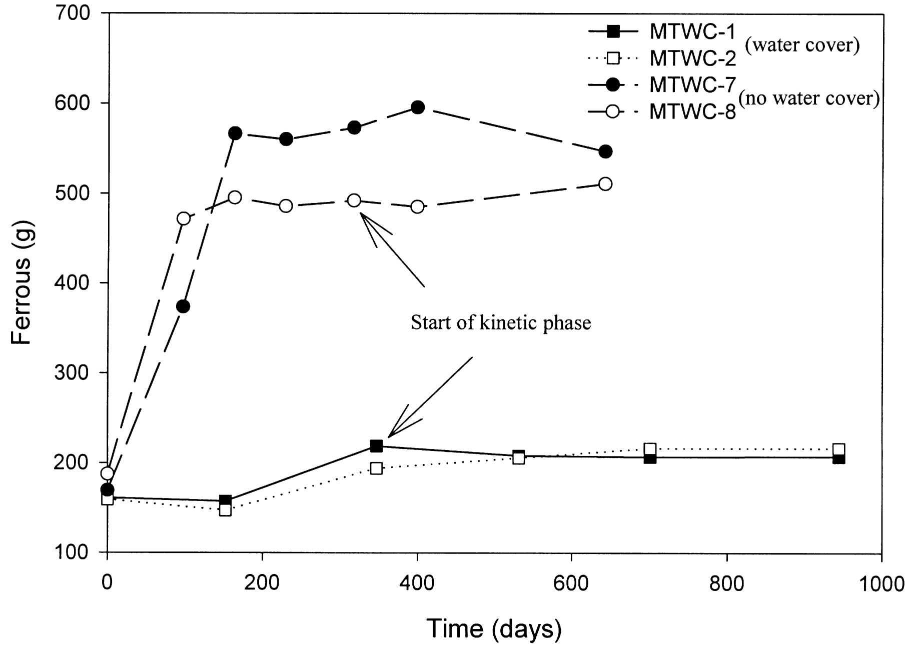

Fig. 17. Total dissolved mass of Fe(II) in water cover, pore water and effluent.

flow induced by consolidation of the tailings (St-Arnaud and Yanful, 1994). Transport of ions to the water cover and subsequent oxidation and/or precipitation are likely to have offset the increase in mass due to mineral dissolution during the first 150 days of the experiments.

4.1.2. Kinetic phase

Essentially, the mass of total Fe and SO_4 during the kinetic phase is conserved in all four columns; it would appear that detectable release of Fe to the pore water ceased by 300 days after flooding (Fig. 17). The total dissolved mass of Fe and SO_4 in the water cover col-

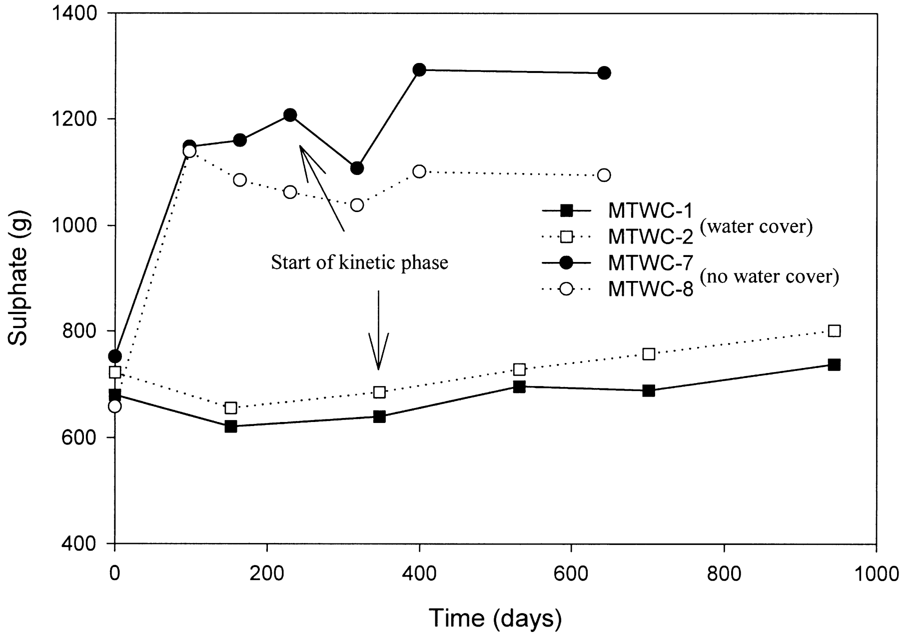

Fig. 18. Total dissolved mass of SO_4 in water cover, pore water and effluent.

umns was much smaller than in the uncovered columns, respectively 400 and 500 g lower in each case. The decline of Fe(III) concentrations in the uncovered column at the beginning of the static phase (Fig. 19) is likely due to Fe(III) precipitation. The saturation of the tailings would have slightly increased the pH through dilution, allowing for some precipitation of Fe(III).

The dissolution and re-precipitation of Fe(III) secondary minerals in different forms may explain the low pH (about 3.5) of the water cover at the conclusion of the experiments, as shown in Fig. 12. This pH falls within the general range characterizing the threshold between Fe hydroxide precipitation and dissolution (Evangelou and Zhang, 1995). Other investigations, including field studies of mine waste impoundments (Blowes and Jambor, 1990; Yanful et al., 1990) and laboratory leaching tests on tailings (Jeffrey et al., 1988, Yanful et al., 1999) have shown that the dissolution of secondary minerals and their subsequent precipitation in more stable forms provide a long-term source of acidity in unsaturated pre-oxidized tailings.

In the water cover columns Zn was being removed from solution (Fig. 20). This could not be attributed to the precipitation of Zn minerals, as MINTEQ analysis predicted that Zn-bearing minerals would dissolve. Zinc, however, is believed to co-precipitate with or be adsorbed by Fe(III) oxyhydroxide minerals (Blowes and Jambor, 1990) at tailings sites. Laboratory experiments by Kinneburgh et al. (1976), and Kooner (1993) showed that significant adsorption of Zn occurs on ferric hydroxides for pHs greater than 4 and 5 respectively. These conditions would have occurred in the water cover at the start of the static phase, and during the kinetic phase as the flushing front progressed through the tailings. In the present experiments, Zn was found in semi-soluble precipitates detected in the decommissioning of MTWC-1, St-Arnaud and Yanful (1994) reported the presence of Zn in precipitates formed at the tailings/water interface. Additionally, MINTEQ analysis predicted that ferrihydrite was favoured to precipitate in MTWC-1. Though Fe(III)–hydroxide precipitation would have affected the mass balance of total Fe, the amount of Zn removed from solution (3 g) was very small compared to the mass of Fe (220 g). Zinc concentrations were therefore probably controlled by adsorption or co-precipitation with Fe hydroxide minerals in MTWC-1 and MTWC-2.

The mass of Zn in the uncovered columns (MTWC-7 and MTWC-8) was much lower than in the covered columns (Fig. 20). This may be partially due to the low initial elemental composition of Zn in the former columns (approximately half of that in water covered columns). Other explanations for the low dissolved mass of Zn in MTWC-7 and 8 are not apparent to the authors.

4.2. Comparison with full-scale field sites

The control of SO_4 concentrations by gypsum solu-

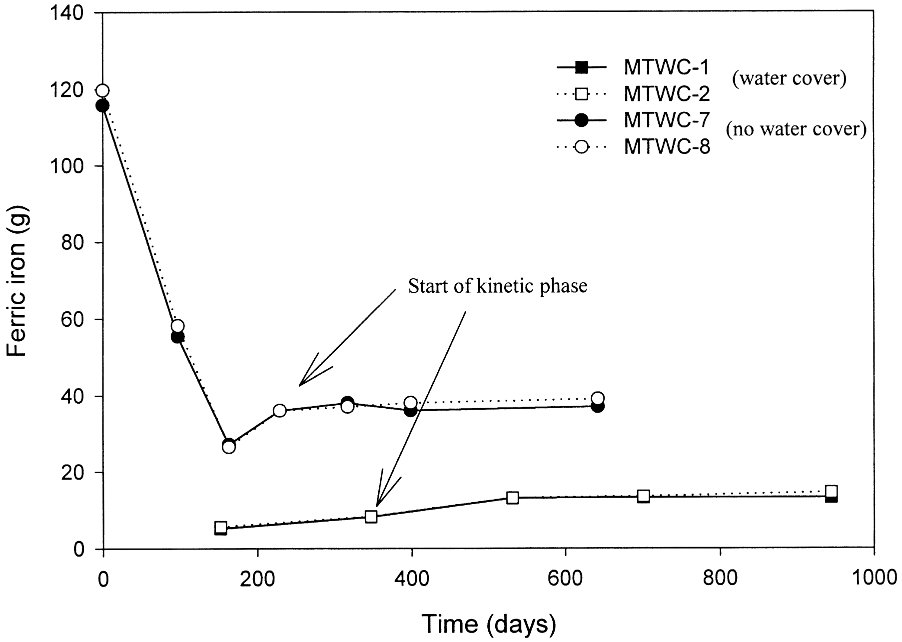

Fig. 19. Total dissolved mass of Fe(III) in water cover, pore water, and effluent.

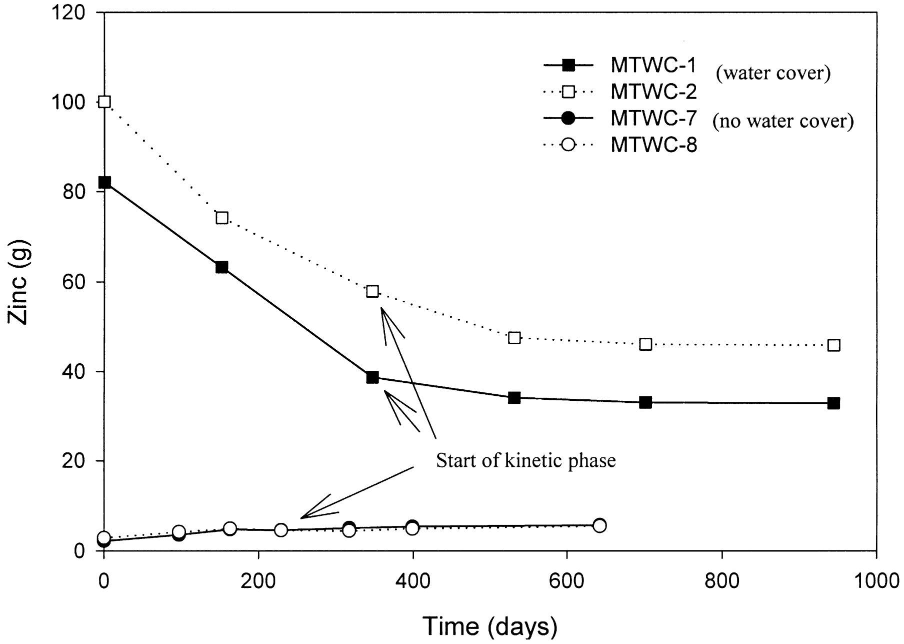

Fig. 20. Total mass of dissolved Zn in water cover, pore water and effluent.

bility, inferred in the water covered tailings in the present laboratory study, has been observed in water covered tailings at field sites, including the Løkken and Hjerkinn tailings ponds in Norway. Water cover effluent concentrations from these sites are shown in Fig. 21 (Yanful and Simms, 1997). The adsorption of heavy metals (for example, Zn) by Fe hydroxides has been proposed to explain data from field evaluations of uncovered tailings impoundments (Blowes and Jambor, 1990), analysis of river sediments (Calmano et al., 1994), and subaqueous tailings deposits (Drake et al., 1995; Pelletier, 1991).

Table 7 compares the fluxes of SO_4, Zn and Fe into the water cover at other sites (Yanful and Simms, 1997) and in the present study (MTWC-1). The Mattabi laboratory columns produced a SO_4 flux similar to fluxes observed at the Løkken and Hjerkinn sites, while the SO_4 fluxes for the Stekenjokk and Quirke sites are similar but an order of magnitude lower than the laboratory flux. With the exception of Løkken, Zn fluxes observed at all the sites are lower than 0.1 mg/m^2. The differences in the magnitude of the fluxes may be attributed to differences in initial tailings mineralogy, degree of oxidation in the tailings impoundment before flooding, and hydrology.

The similarity between field and laboratory fluxes in Table 7 is surprising, as many field conditions are not simulated in the experiments. Firstly, the water cover is not likely to remain under static conditions for long periods of time, as it is usually flushed by surface water flow. Secondly, the laboratory study did not simulate the effects of wind. Remobilization of the tailings by wind-induced turbulence may provide a significant control on water cover quality (Yanful and Simms, 1997). Calmano et al. (1994) have noted that resuspension of river sediments controls heavy metal concentrations.

Table 7
Comparison of fluxes into water cover from tailings (mg/m^2/day)

Site	SO_4	Fe[a]	Zn
Hjerkinn, Norway	6.9	N/A	0.015
Løkken, Norway	5.2	0.32	1.5
Stekenjokk, Sweden	0.25	N/A	0.017
Quirke Lake, Canada	0.16	0.0027	0.00013
Laboratory (MTWC-1)	2.1	0.6	0.053

[a] N/A: data not available.

5. Summary and conclusions

The results of the laboratory experiments showed that flooding of pre-oxidized tailings and subsequent diffusion of ions into the water cover improved the quality of the tailings pore-water, but that the quality of the water cover has remained poor for the duration of the experiment (600 days). It is likely that the formation of Fe-bearing minerals at the tailings/water

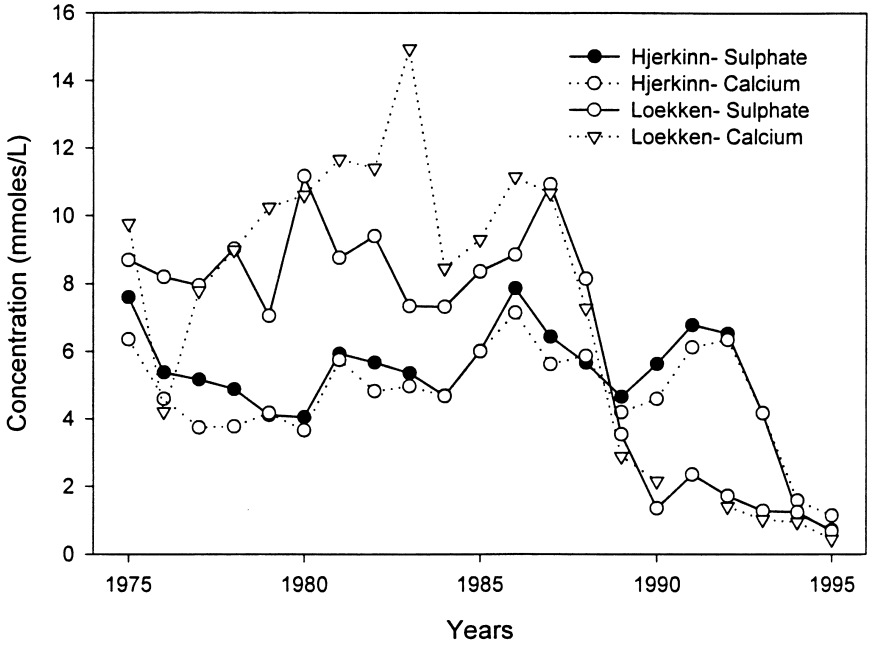

Fig. 21. Outflow concentrations of SO_4 and Ca. From Løekken and Hjerkinn water covers in Norway (adapted from Yanful and Simms, 1997).

interface and their continual dissolution and re-precipitation or re-crystallization into more stable forms, kept the pH low and maintained metal concentrations at high values. These results suggest that long-term treatment of pond effluent and seepage may still be required following flooding of pre-oxidized tailings; however, it should be noted that in the field, water cover quality may be influenced by other hydrogeochemical processes, such as precipitation, surface water flow, and sediment resuspension, which were not simulated in the laboratory. Thus the laboratory results cannot be directly extrapolated to the field.

Iron dissolution in the solid tailings stopped by the 300th day. Flushing during the kinetic stage readily reduced metal concentrations and, in fact, improved the quality of the pore water above that of the water cover. While no substantial leaching or attenuation of Fe was observed, mass-balance calculations showed that Zn was being substantially removed from solution. Mineralogical analyses of tailings in the laboratory, MINTEQ analysis, and experience at other tailings sites suggested that Zn was adsorbing and/or co-precipitating with Fe(III) hydroxides. By the end of the test, gypsum dissolution apparently controlled SO_4 concentrations, a phenomenon commonly observed in the field.

The quality of the pore water of the uncovered tailings was substantially poorer than the pore water of the covered tailings, as there was no water cover to serve as a sink for metals and acidity. The activity of secondary minerals in these tailings would delay improvement of the pore water quality for quite some time. The total ion loading of the uncovered tailings considerably exceeded that of the water covered tailings by the end of the experiments. Thus, this study suggests flooding pre-oxidized tailings would, in the long-term, reduce metal release to the environment.

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