Mine Water Environ (2014) 33:241–255
DOI 10.1007/s10230-014-0264-x

TECHNICAL ARTICLE

Laboratory Study of Highly Pyritic Tailings Submerged Beneath a Water Cover Under Various Hydrodynamic Conditions

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Received: 22 April 2013 / Accepted: 5 March 2014 / Published online: 22 March 2014

Abstract Many studies have examined the efficiency of water covers for control of acid mine drainage, but few have addressed underwater deposition of highly pyritic tailings with low neutralizing capacity. This study simulated the effects of various hydrodynamic conditions on water quality when tailings containing 80 % pyrite were deposited beneath a water cover. The tailings were placed at the bottom of laboratory columns and covered with deionized water. The applied hydrodynamic conditions were: stagnant, stagnant with downward intermittent infiltration, continuously stirred with low tailings resuspension (130–180 mg/L), and continuously stirred with high tailings resuspension (2,910–3,100 mg/L). A continuously stirred water cover with a sand layer placed over the tailings was also studied. Water cover and pore water samples were analyzed monthly to determine variations in the geochemical parameters over monitoring periods ranging from 338 to 840 days. With stagnant water covers, the pH remained near neutral and concentrations of dissolved metals were generally low compared to columns with tailings resuspension. The addition of a layer of inert material significantly prevented pyrite oxidation. Zn was the dissolved metal with the highest concentration (except for Fe) in all of the column leachates, although the tailings contained only 0.38 % Zn.

Keywords Acid mine drainage · Underwater deposition · Chemical stability · Tailings resuspension · Water cover geochemistry · Geochemical modeling

Introduction

Pyritic tailings can oxidize in the presence of oxygen and water and generate acid mine drainage (AMD). Reducing the oxygen supply to the tailings appears to be one of the most effective ways to prevent AMD generation in humid climates (e.g. Aubertin and Chapuis 1991; Collin and Rasmuson 1990; Elberling and Damgaard 2001; Holmström and Öhlander 1999; Nicholson et al. 1989). This can be achieved by depositing the tailings beneath a water cover. The efficiency of this technique is due to the limited availability of dissolved oxygen (DO) and the low DO diffusion coefficient in the water cover. The DO concentration and diffusion coefficient in water (8.6 mg/L and 2×10^{-9} m^2/s at 25 °C, respectively) are low compared to those for oxygen in air (285 mg/L and 1.8×10^{-5} m^2/s at 25 °C, respectively) (Davé et al. 2003; Romano et al. 2003; Yanful and Verma 1999).

DO concentration and resuspension of submerged tailings can affect the effectiveness of a water cover. DO concentration in the water cover depends on the transfer of oxygen from air to water (which is influenced by wind speed) and DO transport through the water cover to the tailings. DO transport through the water cover depends on the DO concentration gradient between the air–water and water-tailings interfaces, the oxidation rates of resuspended tailings (if present) and of tailings at rest, the DO diffusion coefficient in the tailings, and the water infiltration rate, if applicable (Li et al. 1997). DO transport in the water cover has been studied in the field, in the laboratory, and using

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mathematical and numerical models (Berg et al. 1998; Elberling and Damgaard 2001; Vigneault et al. 2001). Generally, measured vertical DO profiles are used to determine the DO flux at the water-tailings interface using Fick's first law. Laboratory testing and interpretation procedures were developed to determine the reaction rate coefficient K_r of tailings submerged under water, with cell tests that can be used to estimate the flux (Awoh 2012; Awoh et al. 2013a).

Resuspension is generally caused by wind-induced waves and return currents. The hydrodynamic conditions for resuspension in shallow water covers have been previously studied (Adu-Wusu et al. 2001; Catalan and Yanful 2002; Mian 2004; Mian and Yanful 2004, 2007; Mian et al. 2007; Peacey and Yanful 2003; Samad and Yanful 2004; Yanful and Catalan 2002). Most of these studies focused on determining wave—and return current-induced shear stresses and the critical shear stress above which resuspension begins. Resuspension exposes the tailings to greater contact with DO in the water cover. Resuspended particles can more easily oxidize, and thus increase the acidity of the water cover and the release of dissolved metals.

The efficiency of the water cover in terms of oxidation control has been evaluated in situ (e.g. Awoh et al. 2013b; Holmström and Öhlander 1999; Mbonimpa et al. 2008; MEND 2001; Peacey and Yanful 2003; Vigneault et al. 2001; Yanful and Simms 1997) and in the laboratory (Davé and Paktunc 2003; Davé et al. 1997; Doepker and Drake 1991; Yanful et al. 2000). A brief literature review focusing only on laboratory studies is presented below. Given the huge amount of results presented in each of these studies, only general conclusions are presented below.

Doepker and Drake (1991) studied the dissolution of metals from two lead and one copper mine tailings using a series of submerged tailings batch tests at a U.S. Bureau of Mines laboratory. The lead mine tailings contained dolomite [$CaMg(CO_3)_2$], with trace amounts of sphalerite (ZnS), pyrite (FeS_2), and galena (PbS). The copper mine tailings contained abundant free pyrite with minor amounts of chalcopyrite ($CuFeS_2$). Dissolved metal release was greater in tests with aerated water close to DO saturation than metal dissolution from stagnant waters. Metal mobilization also increased with contact time, which varied from 76 to 156 days. For a given contact time, the contact surface area, leachate exchange rates (dilution effects), and dissolved oxygen, as well as the geochemical characteristics of the tailings themselves, were the most important factors affecting dissolution from submerged tailings.

Davé et al. (1997) evaluated the oxygen diffusion and metal release characteristics of four reactive tailings deposited underwater using laboratory column lysimeters. The materials used were fresh pyrrhotite with 3 % S, low-sulphide with 10 % S, and partially oxidized tailings with 4 % S. The molecular diffusion of oxygen from the water surface to underwater reactive tailings was measured under three test conditions: unmixed water covers with depths of 0.5 and 1.0 m and a mixed water cover with a depth of 1.0 m. The tests lasted for approximately 1 year after reaching equilibrium conditions. The main findings were that tailings submersion did not completely prevent oxidation or metal release. Unexpectedly, neither the height of the water cover above the tailings nor mixing had any effect on oxygen diffusion or leaching characteristics.

Yanful et al. (2000) performed laboratory experiments to examine the impact of resuspension on dissolved metal release from submerged unoxidized mine tailings obtained from the Falconbridge Strathcoma Mine, near Sudbury, Ontario, Canada. The tailings contained 75 % pyrrhotite and 0.14 % chalcopyrite. Column tests using different water cover depths (45–80 cm) with and without resuspension were monitored for 126 days. Tailings resuspension was induced by a stirrer placed 10 cm from the water cover surface. The stirred water covers were not fully oxygen-saturated. In the columns, a 10–cm thick tailings layer was sandwiched between an 80 cm water cover and a 15 cm bottom water layer. Results indicated that tailings at rest oxidized less and released less acidity and lower metal concentrations than resuspended tailings. Acidity and metal release increased with increasing mixing energy.

Davé and Paktunc (2003) studied the surface reactivity of copper mine tailings under shallow water cover conditions using aquarium-type diffusion lysimeters containing 30 cm of tailings at the bottom and 26 cm of saline sea water and natural lake fresh water covers. The tailings used were acid generating with a sulfide content of 18–20 %, a negligible neutralization potential of approximately 0–2 kg $CaCO_3$/tonne, and a negative net neutralization potential in the range of −600 to −700 kg $CaCO_3$/tonne. The water was recirculated to create well-mixed and oxygenated water cover conditions without turbulence and tailings resuspension. Variations in the cover and pore water quality with time were measured for a study period of 1.5 year. The dissolution and release of previous oxidation–reaction products present in the tailings influenced the pore water chemistry.

Laboratory studies (e.g. Davé et al. 1997; Yanful and Simms 1997) and theoretical calculations (Li et al. 1997) have also shown that adding a layer of inert or non-acid-generating reactive material above the reactive tailings could limit tailings oxidation. The materials used were mostly sand, compost, and peat. Awoh et al. (2013a) investigated the impact of placing such a protective layer on the dissolved oxygen flux consumed by the tailings (see also Awoh 2012). DO flux decreased from 608 to 5.2 mg O_2/m^2/days (by 99 %) when a 5 cm-thick protection layer was placed over the tailings used in this study (described subsequently).

Although water covers have been investigated for years, few studies have addressed water covers placed over extremely pyritic tailings (>80 % pyrite) with very low neutralizing capacity. The purpose of the present study was to contribute to the understanding of the behaviour of such water covers. The objective was to investigate the geochemical evolution of such water covers when subjected to different controlled hydrodynamic conditions for a long period. The study was performed using laboratory column tests with stagnant water covers with and without infiltration, aerated water cover without tailings resuspension, continuously stirred water covers with low and high tailings resuspension, and a continuously stirred water cover with a layer of inert granular material placed over the tailings. Variations in the chemistry of the cover and pore water were monitored for 338–840 days.

Materials and Methods

Tailings Characteristics

Particle size was determined using a Malvern Mastersizer laser particle size analyzer. The lower limit reported by the device was 0.0582 µm. Details on the techniques of grain–size distribution measurements were given by Merkus (2009). The results showed that 85 % of the particles in the tailings were smaller than 80 µm and 5 % were smaller than 2 µm. The grain–size distribution curve showed particle diameters $D_{10} = 4.9$ µm, $D_{30} = 18.5$ µm, $D_{50} = 36.5$ µm, $D_{60} = 47.3$ µm, and $D_{90} = 109.3$ µm, corresponding to 10, 30, 50, 60, and 90 % of particles passing on the cumulative curve, respectively. The coefficients of uniformity ($C_U = D_{60}/D_{10}$) and of curvature [$C_C = (D_{30})^2 (D_{10}D_{60})^{-1}$] were 9.6 and 1.5, respectively.

The relative density of the tailings was determined with a Micromeritics Accupyc 1330 helium pycnometer (±0.03 % accuracy), which gave a result of 4.58. This result was close to the density of solid grains of pure pyrite at 5.01 (Landry et al. 1995).

Mineralogical analysis performed by X-ray diffraction (Bruker A.X.S. Advance D8) using the quantitative Rietveld method (relative precision of ±0.5 %) with TOPAS software (Young 1995) showed that the tailings were 83 % pyrite (theoretically, 83 % pyrite by weight should give 44.4 % of S), 9 % chlorite, 6 % quartz, and 2 % muscovite and traces of carbonate. Carbon/sulfur analysis with an ELTRA CS2000 Carbon Sulphur determinator (±0.5 % of carbon and sulfur present) showed 47 % sulphur and 0.13 % carbon.

The chemical analysis of the tailings was carried out by complete digestion in $HNO_3/Br_2/HF/HCl$ followed by inductively coupled plasma atomic emission spectrometry (ICP-AES, Perkin-Elmer Optima 3100 RL, relative precision of 5 %; Villeneuve 2004). The precision was verified with materials certified by the Canadian Certified Reference Materials Project (CCRMP). The results showed a strong dominance of Fe and S contents at 48.9 and 38.7 %, respectively, and the presence of Zn (0.38 %) and other trace elements, such as Ni (0.001 %), Cu (0.05 %), Pb (0.07 %), and Ca + Mg + Mn (0.53 %).

The presence of Zn was confirmed by a scanning electron microscope (SEM) (Hitachi S-3500 N) equipped with an energy dispersive spectrometer (Silicon Drift Detector, Oxford X-Max 20 mm^2) with INCA software (450 Energy). The detection limit is approximately 1 % (Çubukçu et al. 2008). The result showed three forms of sphalerite: free sphalerite, sphalerite attached to pyrite, and sphalerite as an inclusion in pyrite. The first two forms of sphalerite were more available for oxidation than the sphalerite included within pyrite, which could also release Zn. In addition to sphalerite, the optical light microscopy analysis also highlighted trace amounts of other minerals such, chalcopyrite ($CuFeS_2$), galena (PbS), graphite (C), and magnetite ($Fe^{2+}Fe_2^{3+}O_4$).

Laboratory Column Tests

Column Test Setup

Four water cover configurations were simulated using PVC columns with an inner diameter of about 13 cm and an internal height of about 128 cm. To avoid interaction with light, black PVC was used. Six water sampling ports (ports 1–6) were placed along the column at heights of 110, 70, 40, 30, 20, and 10 cm from the bottom of the column, respectively. Ports 1–3 were designed to be located in the water cover, while ports 4–6 were designed to collect pore water from the tailings. An overview of the column setup is shown in Fig. 1.

The pore water sampling system consisted of three white horizontal PVC tubes perforated and covered with a geotextile mesh to prevent tailings from entering the tube. The volume of the tube was approximately 40 mL. The ends of each sampling tube were connected to valves used for sampling, as described below. Initially, a syringe was inserted through plastic vials for sampling. Each vial was closed with a septum stopper on the air side and the extremity inserted into the tailings was covered with a geotextile mesh to prevent solid particles from entering the vial. Sampling pore water using a syringe was unsuccessful. After sedimentation and consolidation, the tailings were very dense, so very little water was collected, even when a high suction was applied.

A lid screwed to the top of each column was used to support an AC motor (model 103, Talboys Laboratory) to

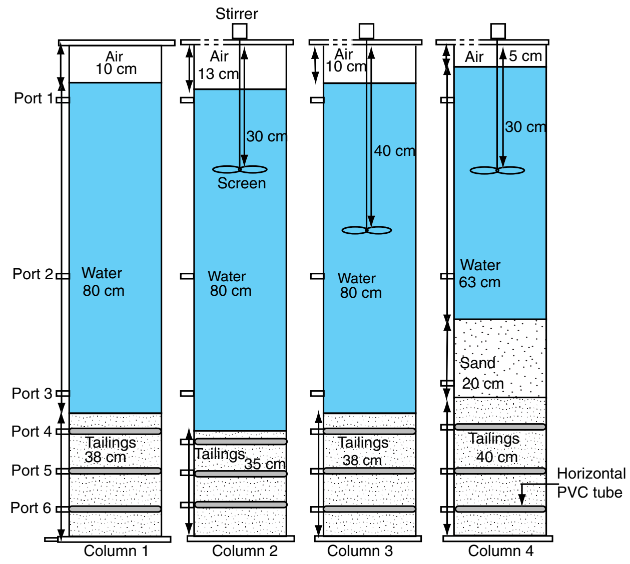

Fig. 1 Experimental setup in the laboratory

control the water cover stirrer, when applicable. The stirrers had three 2.5 cm long wings. The stirrer extended to a depth of about 30 cm in columns 2 and 4 and about 40 cm in column 3. The lid was perforated to allow introducing DO and temperature probes into the water cover.

Before filling the column, tailings were first homogenized with a mixer. The volume of pulp tailings required for a 30 cm thick tailings layer was estimated and gradually poured into the column through a funnel. When the pulp reached the level of the first horizontal sampling tube (Port 6), the tube was filled with deionized and deoxygenated water to prevent air pockets from forming in the tube. Pulp filling then continued until the level of port 5 was reached. The above-described procedure was repeated until reaching the top pore water sampling tube (Port 4). Once the entire tailings volume was poured into the column, the pulp was allowed to settle and consolidate for several days until equilibrium was reached. The thickness of the tailings in columns 1, 2, 3, and 4 was respectively 38, 35, 38, and 40 (see Table 1). For column 4, a 10 cm sand layer was initially placed over the tailings. Despite precautions taken to avoid mixing of the sand and tailings, fine particles of tailings were later observed in the stirred water cover. An additional 10 cm sand layer was added to form a 20 cm thick layer of inert granular material. This scenario was used to study the impact of adding a layer of sand on the water cover effectiveness.

The supernatant water above the tailings was replaced by deionized water (not deoxygenated) while minimizing tailings resuspension. The thickness of the water covers over the tailings was approximately 80 cm for columns 1–3 and approximately 63 cm for column 4.

After allowing the column to rest for 4 days, the hydrodynamic conditions (Table 1) were then applied to each column. These conditions were applied from April 2009 to July 2011 (840 days) for column 3 and from Oct. 2009 to July 2011 (650 days) for column 4 (delay due to problems with placement of the sand layer over the tailings). The water cover was continuously stirred in column 3, with high resuspension of tailings, and continuously agitated in column 4, without resuspension of tailings (but possible sand resuspension). For columns 1 and 2, these conditions were implemented in two phases. In the first monitoring phase, from April 2009 to July 2010 (471 days), the water cover was stagnant (no stirring) in column 1 and continuously stirred with low resuspension of tailings in column 2. A stagnant water cover was used to simulate ideal conditions for water cover and to provide a basis for comparison with other scenarios. A continuously stirred water cover was used to study the impact of tailings resuspension on water cover quality. Column 2 was stirred at 53 revolutions/min (RPM), with low tailings resuspension (130–180 mg/L of suspended solids SS), at about 87 RPM in column 3, with high tailings resuspension (2,910–3,100 mg/L of SS), and at 53 RPM in column 4, without tailings resuspension. High tailings resuspension was used to study the worst case scenario.

None of the tailings were flushed to eliminate pre-existing sulphates and dissolved metals in the pore water prior to monitoring, though in hindsight, this would have

Table 1 Column configurations and applied hydrodynamic conditions

Column	Tailings depth (cm)	Water depth (cm)	Phase 1	Phase 2
1	38	80	Stagnant water	Bottom seepage
2	35	80	Continuously mixed water with low resuspension (130–180 mg/L of SS)	Continuously mixed water without resuspension + aeration
3	38	80	Continuously mixed water with high resuspension (2,910–3,100 mg/L of SS)	*
4	40 (+20 cm sand)	63	Continuously mixed water without resuspension	*

* Not defined

been a good thing to do. It should also be mentioned that the water cover in columns 2 and 3 were initially planned to be continuously mixed, with and without low tailings resuspension. For that purpose, preliminary stirring tests were performed using transparent Plexiglas cylinders. During these tests, there was no resuspension at 53 RPM in a column with the same configuration as column 2 and very low resuspension at 87 RPM in a column with the same configuration as column 3. These stirring tests lasted for approximately 1 h. These stirring conditions were then applied to the true tests. Further monitoring of the suspended tailings concentrations revealed, however, an unexpected effect of stirring time that increased the concentrations to the values given above.

In a second phase, which ran from Aug. 2010 to July 2011 (338th days of monitoring), the hydrodynamic conditions applied to columns 1 and 2 were modified (no change was made to columns 3 and 4). For column 1, the cover water was rapidly replaced with 80 cm of fresh deionized water. Downward infiltration was applied monthly to column 1 by opening a valve at the base of the column for 24 h. This valve was connected to a plastic U-tube to prevent air flow into the base of the column. Water was drained from the column at a flow rate of about 37.5 mL/h. This downward infiltration was used to study the impact of forced contact between the tailings and DO from the water cover. Without infiltration, DO penetration was limited to a few mm into the tailings, as mentioned in the introduction. Deionized water was added to compensate the drained water.

For column 2, the water cover was also rapidly replaced with deionized water. Water stirring was replaced by aeration without tailings resuspension using three crossed horizontal plastic tubes perforated on the upper surface placed about 10 cm above the tailings. The horizontal tubes were linked to a vertical tube fixed to the top of the column. Clean, dry, dust-free and oil-free compressed air was sent into the vertical tube at a flow rate just sufficient to create upward aeration of the water cover without resuspending the tailings. The objective was to evaluate the influence of aeration without resuspension on the oxidation of mine tailings compared to oxidation in stirred water cover with low resuspension.

For convenience, columns 1 and 2 are designated hereinafter by 1–1 and 2–1 for the first monitoring phase and 1–2 and 2–2 for the second phase. The first water sampling in phase 2 was performed after 31 days (502nd day of monitoring).

Water Sampling and Analysis

Before each sampling of the cover water, the vertical DO concentration profile was measured downwards from the top of the water cover at 20 cm intervals using a fiber-optic oxygen sensor type PSt3 (0–100 % oxygen; accuracy ±0.4 % O_2 at 20.9 % O_2) combined with an oxygen reading system (OXY10, PreSens GmbH, Germany). This probe provided a DO reading within 60 s. Cover water samples were then collected from each column using sampling ports 1–3 (starting from the top) and stored in 150 mL HDPE bottles. After geochemical analysis, part of each sample was returned to the water cover. A small amount of deionized water (about 20 mL) was also added to the column to compensate for the quantity used for the elemental analysis. Hence, the water cover was maintained at a constant height above the tailings. The dilution effect was assumed to be negligible.

The pore water in the tailings was sampled using ports 4–6. While the amount of water (about 15 mL) needed for ICP-AES analysis was sampled from one side of the horizontal tube, deionized and deoxygenated water was added to the opposite side. The column was slightly inclined to allow sampling and replacing the water in the pipe without disturbing the system (preventing oxygen inflow). It was assumed that different dissolved ions were exchanged between pore water and water in the horizontal tubes by molecular and ionic diffusion, and that equilibrium was established between two successive sampling campaigns. The time required to reach equilibrium was previously determined (results not shown here). For that purpose, a 20 cm layer of saturated tailings was placed at the bottom of a large bucket. Two tubes similar to those installed in the columns for pore water sampling were placed on this layer and covered by a top 20 cm layer of saturated tailings. The tubes were flushed and filled with deionized and deoxygenated water. Water samples were simultaneously collected from inside the two tubes and tailings and analyzed over time. Chemical analysis showed that the water in the tubes was representative of the pore water after less than 1 month. Based on these results, the sampling frequency in the columns was set at 1 month.

The pH, redox potential (Eh), and electric conductivity (EC) of the water cover samples were promptly measured. The pH determinations had a relative precision of ± 0.01 pH (Orion Triode sensor coupled with a bench-top pH/ISE meter Orion model 920A). The Eh was measured with a Pt/Ag/AgCl combined electrode (relative precision ±0.2 mV) and subsequently corrected for a standard hydrogen electrode. The EC had a ±0.5 % precision (OAKTON Acorn Series CON 6 conductivity meter with two platinum electrodes).

All water cover and pore water samples were filtered through a Fisher Scientific nylon filter with a 0.45 μm pore diameter. Samples were then acidified to 2 % v/v HNO_3 for preservation. The acid quality met the requirements of the American Chemical Society. Samples were subsequently chemically analyzed by ICP-AES (relative precision of ±5 %; Villeneuve 2004).

Concentrations of suspended solids (SS) in the stirred water covers for columns 2–1 and 3 were measured by filtering through a 0.45 µm capsule filter (CEAEQ 2004) on monitoring days 248, 361, and 471. The suspended tailings collected from column 3 after 471 days were dried at a temperature between 40 and 50 °C and subjected to laser particle size analysis to examine the size of tailings particles affected by resuspension. XRD mineralogical and ICP-AES analyses were performed to investigate the impact of oxidation on these particles.

Post-testing Analysis

Columns 1 and 2 were dismantled after a period of 809 days; column 3 was dismantled after 840 days and column 4 after 650 days (post-testing analysis was not performed for column 4). Water-tailings interfaces were analyzed visually and tailings samples were collected. Mineralogy was determined by optical reflected light microscopy on polished sections using a Zeiss Axio Imager M2 m microscope. Scanning electron microscopy (SEM) using backscattered electrons imaging (BSE) was performed on a Hitachi S–3500 N microscope equipped with an X-ray energy dispersive spectrometer (Silicon drift detector X-Max 20 mm^2) and INCA software (450 Energy). The aim was to characterize secondary mineral precipitates.

Results and Interpretation

Given the large amount of data collected, only the most representative and pertinent results are presented here. Vertical DO profiles in the water covers are first presented, followed by temporal variations in pH, sulphate, and dissolved Zn in water samples from port 3, located at 2 cm above the water-tailings interface for columns 1–1, 1–2, and 3, at 5 cm for columns 2–1 and 2–2, and at 70 cm above the sand-tailings interface for column 4. Port 3 in column 4 was located in the sand layer (20 cm), making gravity sampling difficult. Comparison of sulphate and dissolved metals in cover and pore water is also presented followed by vertical profiles of pH, sulphate, and Zn. Finally, results of the characterization of resuspended tailings in column 3 and of post-testing tailings are presented.

Vertical DO Profiles in the Water Cover

Vertical DO profiles determined after 471 days of monitoring (arbitrarily chosen date) in columns 1–1, 2–1, 3, and 4 are given in Fig. 2. The DO profiles determined after 127 days of monitoring for columns 1–2 and 2–2 are also presented. In stirred columns 2–1, 3, and 4, DO concentrations were generally homogeneous from the top to the bottom of the water cover. In the aerated column 2–2, DO seems to decrease towards the top slightly from 8.24 to 8 mg/L, but this difference is not statistically significant, given the precision of ±0.4 %.

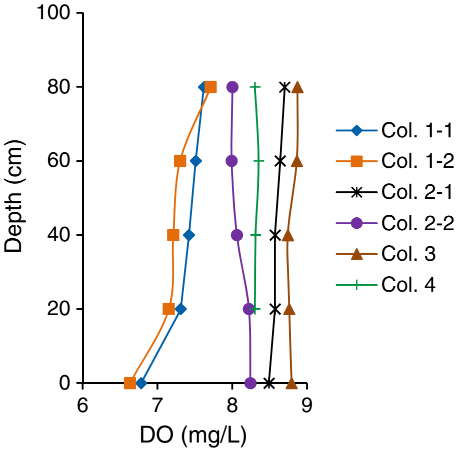

Fig. 2 Vertical DO profiles in cover water after 471 days for columns 1–1, 2–1, 3, and 4 and after 127 days for columns 1–2 and 2–2

DO concentrations in these columns (2–1, 2–2, 3, and 4) ranged from 8 to 9 mg/L. Water temperature during measuring ranged from 19.2 to 20.9 °C. Saturated DO concentrations in water at this temperature range varied from 9.3 to 8.9 mg/L (Benson and Krause 1984). These results indicate that DO in the water cover in these columns was close to saturation. The DO in the aerated water cover for column 2–2 was less than in the stirred water cover for columns 2–1, 3, and 4. Mixing the water favoured greater oxygen solubility than water aeration.

In columns 1–1 and 1–2, DO concentrations decreased from 7.6–7.7 mg/L at the top of the water column to 6.6–6.8 mg/L at the water-tailings interface for temperatures from 19 to 20 °C. DO concentration at saturation for these temperatures is 9.3–9.1 mg/L (Benson and Krause 1984). Thus, DO concentrations in the stagnant columns 1–1 and 1–2 were less than saturation. The natural transfer of oxygen at the water–air interface (without agitation or aeration) and the diffusion of DO through the water column could not saturate the water cover. The decreased DO could also be related to the formation of the iron oxy-hydroxides observed at the water tailings interface.

Variations of pH

Figure 3 shows the temporal variation in pH. For columns 1–1 and 4, pH evolves in a more rugged manner but

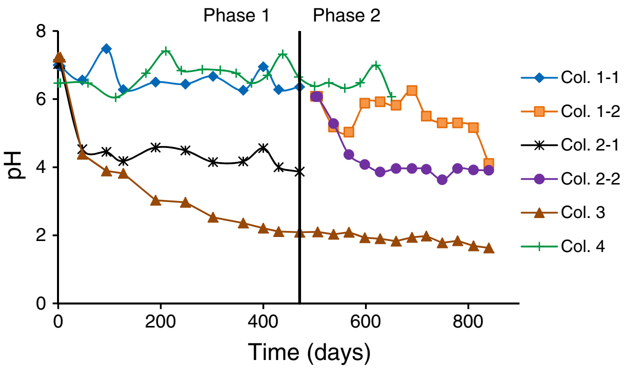

Fig. 3 Temporal change in pH of the cover water at port 3 for columns 1–1, 1–2, 2–1, 2–2, and 3 and at port 2 for column 4

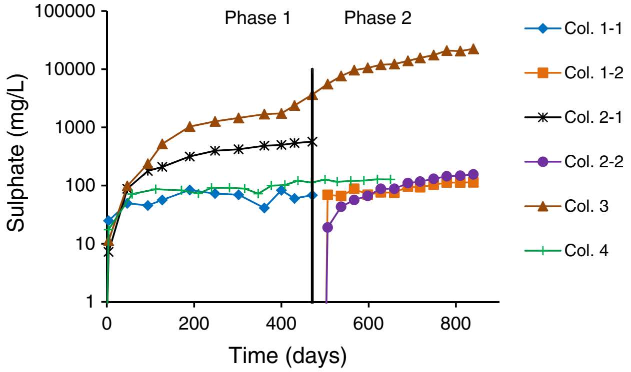

Fig. 4 Temporal change in sulphate concentrations in the water covers at port 3 for columns 1–1, 1–2, 2–1, 2–2, and 3 and at port 2 for column 4 (logarithmic scale for the vertical axis)

remained approximately neutral (from 6 to 8) in the water cover. Indeed, a water cover at neutral pH contains fewer ions in solution and so is more prone to pH variations than an acidic water cover. Thus, the uncertainty of a pH measurement at neutral pH is more important than the uncertainty at acidic pH.

For column 1–2 with 24-h monthly downward infiltration, the water cover pH decreased with time, from 6 to 4. This drop was attributable to the infiltration, which induced contact between the tailings and water with a greater DO.

In the cover water in column 2–1, pH decreased from 7 to 3.8 during the first 471 days of monitoring (phase 1). The replacement of the water by deionized water at the beginning of phase 2 (column 2–2) increased the pH to 6. The pH decreased thereafter and stabilized at around 3.9 at the end of phase 2. This pH was close to that reached at the end of phase 1. These results suggest that continuously stirring with low resuspension (column 2–1) has the same effect on tailings oxidation than continuous aeration (column 2–2). These results suggest that as tailings resuspension in column 2 was stopped (phase 2), oxidation of unsuspended tailings and possible diffusion from the pore water was responsible for the observed decrease in pH in column 2–2.

In column 3, which was continuously stirred for 840 days without changing the hydrodynamic conditions, pH dropped from 7.2 to 1.6. This decrease was due to oxidation of suspended and unsuspended tailings in contact with the DO-saturated water.

Sulphates and Dissolved Metals

The generally high redox potentials of the water samples (not shown, between ≈300 and ≈900 mV), as well as the relatively high DO concentrations in the waters, suggest oxidative conditions consistent with sulfate being the predominant form of sulphur in solution. Under these conditions, the sulphate content was calculated from the concentration of total sulphur (S) measured with ICP-AES, using the ratio of molecular weights and assuming all sulphur was sulphate.

The analysis showed that the deionized (not deoxygenated) water used to fill the columns (at time 0) contained very little sulphate (0.27 mg/L) or Zn (0.009 mg/L). The first water sampling was performed 4 days after filling the columns. After the 4 days, sulphate (from 7 to 69 mg/L) and Zn (from 0.015 to 3.9 mg/L) were present in water samples from all water covers. Sulphate (350–1,000 mg/L) and Zn (0.06–2.4 mg/L) were present in the pore water in each column; therefore, the presence of these ions in the water covers were probably mostly due to molecular diffusion of ions from the tailings pore water. The difference in ions concentrations across the columns was because they were filled with tailings pulp at different times (although the same homogenized pulp was used).

From Day 4 to the end of monitoring, sulphate and Zn concentrations increased in all water covers to different degrees (Figs. 4, 5). The detection limit for Zn is 0.009 mg/L. Figures 4 and 5 show the temporal variation in sulphate and Zn concentrations in the water covers. Zn variation is presented because it was the metal with the highest dissolved concentrations (except for dissolved Fe in column 3).

In columns 1–1, 1–2, and 4, concentrations of sulphate and Zn are generally lower than in other columns. They increase significantly in column 3, particular after approximately 400 days, which can be explained based on the rate of sulphate loading in the water cover, as discussed below. Concentrations of sulphate and metals were higher in columns 2–1 and 3 than in the other columns for two reasons: first, the water covers in these columns were DO saturated, causing the tailings to oxidize and release metals. In addition, the covers in columns 2–1 and 3 were stirred, with low and high tailings resuspension, respectively, so that suspended particles in the DO saturated water were more easily oxidized.

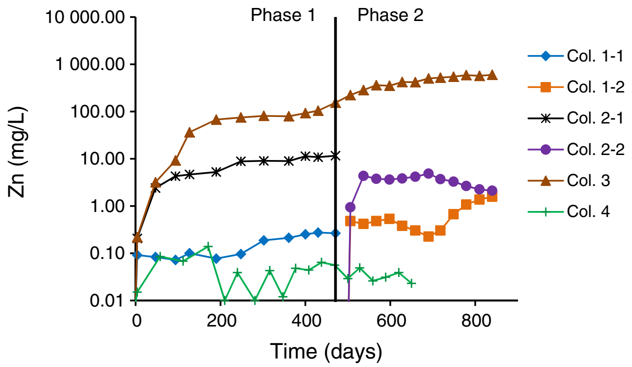

Fig. 5 Temporal change in Zn concentrations in the water covers at port 3 for columns 1–1, 1–2, 2–1, 2–2, and 3 and at port 2 for column 4 (logarithmic scale for the vertical axis)

The presence of Fe and Zn was due to the oxidation of sulphide minerals (i.e. pyrite and sphalerite). The concentrations of dissolved Fe may be underestimated due to precipitation of iron oxides, as observed from SEM analyses at column dismantling and from geochemical modeling using VMinteq (Felmy et al. 1984, see results below). The Al presence was mainly due to the dissolution of silicates, such as muscovite ($KAl_2(AlSi_3O_{10})(OH)_2$) and chlorite ($(Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2 \cdot (Mg,Fe)_3(OH)_6$) present in the tailings in respective proportions of approximately 2 and 9 %. The presence of Cu is due to the dissolution of chalcopyrite ($CuFeS_2$), which was detected by SEM in the tailings. Elemental analysis of the tailings showed 0.05 % Cu content. Ni (0.001 %) and Pb (0.068 %) were also detected in the the tailings, which explain their presence in the water cover.

Comparison of Sulphate and Dissolved Metals in Cover and Pore Waters

The sulphate and Zn content were compared for the water covers (for samples from port 3 for columns 1–1, 1–2, 2–1, 2–2, and 3, and port 2 for column 4) and the pore waters (sample from port 5 located 20 cm from the bottom of the column). Sulphate concentrations were lower in the water cover than in the pore water in columns 1–1, 1–2, 2–1, 2–2, and 4 (Fig. 6). A secondary vertical axis was used in Fig. 6c (for column 3) to make comparison easier. In columns 1–1, 1–2, 2–1, and 2–2, tailings oxidation close to the water tailings interface did not produce enough sulphate, so concentrations remained lower in the water cover than in the pore water. In column 4, the presence of the sand layer prevented DO from oxidizing the underlying tailings; the sulphate in the water cover may have diffused from the pore water. In column 3, with a DO-saturated water cover and strong tailings resuspension (2,915–3,100 mg/L), much higher sulphate concentrations were observed in the water cover than in the pore water. Downward diffusion may have occurred.

Figure 7 shows the Zn concentrations in the water covers and pore waters (a secondary vertical axis was used in Fig. 7c). For columns 1–1 and 4, Zn concentrations were generally lower in the water cover than in the interstitial water for the same reasons as for sulphate. In columns 1–2, 2–1, 2–2, and 3, Zn concentrations in the water covers were higher than in interstitial water. In these scenarios, sphalerite oxidation was the main generator of Zn. In column 1–2, downward infiltration of water cover with greater DO content favoured the oxidation of the tailings close to the interface, which were continuously exposed to DO. However, Zn content did not increase in the pore water, probably because the DO introduced during the 24 h/month period was rapidly consumed.

In all columns, sulphate and Zn concentrations in the pore water fluctuated. It is difficult to explain these fluctuations. However, sulphate and Zn concentrations in the interstitial water in columns 1–1, 1–2, 2–2, and 4 generally decreased over time. Sulphate decreased from 705 to 348 mg/L in column 1–1 after 471 days, from 348 to 172 mg/L in column 1–2 after 338 days, from 1,041 to 861 mg/L in column 2–2 after 338 days, and from 757 to 414 mg/L in column 4 after 650 days. Similarly, Zn concentrations decreased from 0.6 to 0.1 mg/L in column 1–1, from 0.19 to 0.12 mg/L in column 1–2, from 2.4 to 2.07 mg/L in column 2–2, and from 0.4 to 0.12 mg/L in column 4.

In columns 2–1 and 3, sulphate and Zn concentrations in the pore water increased over time. Sulphate ranged from 780 to 1,062 mg/L in column 2–1 and from 496 to 840 mg/L in column 3. Zn increased from 0.5 to 2.36 mg/L in column 2–1 and from 0.6 to 68 mg/L in column 3. Since sulphate and Zn were higher in the water cover than in interstitial water, these ions may have been released by molecular diffusion to the pore water, causing the increased concentrations.

Vertical pH, Sulphate, and Zn Profiles

Vertical pH, sulphate, and Zn profiles were used to highlight the vertical distribution of the cover and pore water chemistry. Vertical pH profiles in the water covers (pH was not measured in the pore water, as explained earlier) for columns 2–1, 2–2, 3, and 4, were almost constant. The pHs were around 4 for columns 2–1 and 2–2, around 2 for column 3, and around 7 for column 4. Column 4 showed the highest pH and column 3 (highly mixed) the lowest. For columns 1–1 and 1–2, a very low pH gradient was found in the water covers because the water was not mixed and the DO was consumed by tailings close to the water-tailings interface. The pH

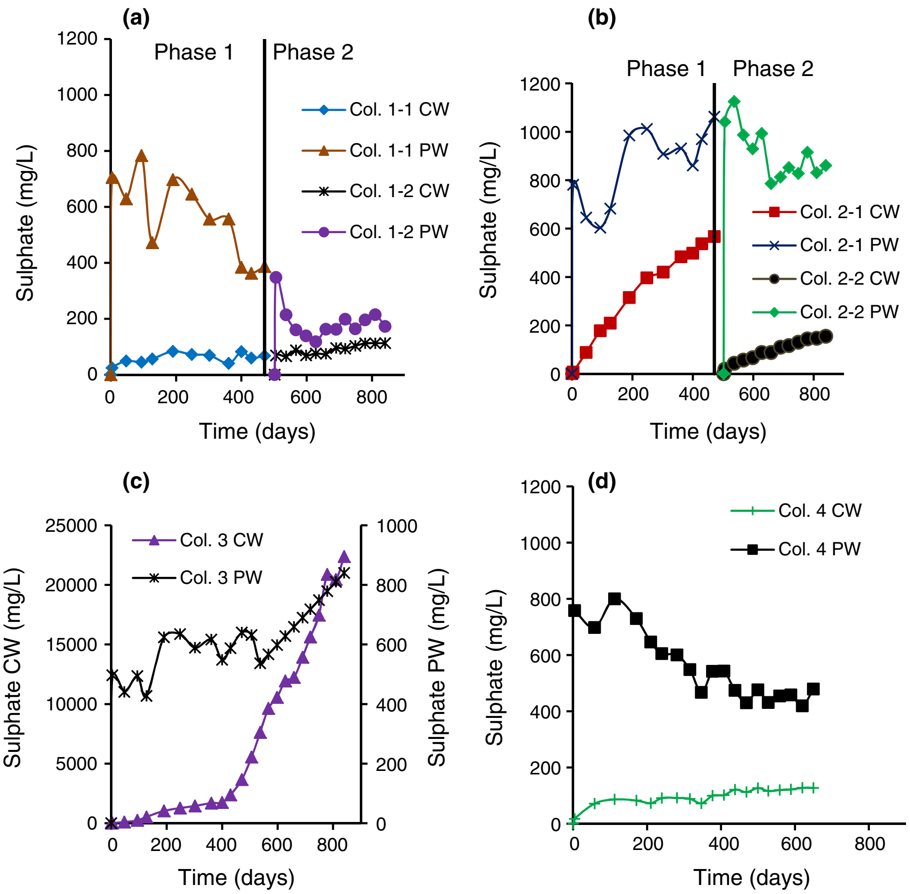

Fig. 6 Comparison of temporal change in sulphate concentrations in cover water (CW) at port 3 for columns 1–1, 1–2, 2–1, 2–2, and 3 and at port 2 for column 4 and in pore water (PW) at port 5 (a secondary vertical axis is used in Fig. 6c)

decreased very slightly from the top of the water cover to the water-tailings interface (from 6.7 to 6.4 for column 1–1 and from 6.2 to 5.8 for column 1–2).

Figure 8 shows the vertical profiles for sulphate and Zn for July 2010 (after 471 days of monitoring) for columns 1–1, 2–1, 3, and 4, and in Nov. 2010 (after 127 days of monitoring) for columns 1–2 and 2–2. These profiles were representative of results obtained for other dates. Even if presented in the same figure, only profiles for the same date should be compared. For the vertical profiles, depth 0 corresponds to the water-tailings interface, except for column 4, where depth 0 is the sand-tailings interface. Positive and negative values correspond to depths above and below the interface, respectively. Sulphate concentrations remained almost constant throughout the water covers, ranging from 50 to 68 mg/L in column 1–1. Sulphate concentration ranged from 58 to 69 mg/L in column 1–2, from 567 to 585 mg/L in column 2–1, around 66 mg/L in column 2–2, around 3,500 mg/L in column 3, and around 92 mg/L in column 4. Sulphate increased with increasing depth in pore water within tailings in all columns, except for column 3.

Dissolved metal concentrations were higher in pore water than in the water covers, as it is generally expected when pre-oxidized tailings are stored under a water cover (MEND 2001; Peacey et al. 2002). In this study, the tailings were not handled under anaerobic conditions, so dissolved metals and sulphate may have formed during handling. Tailings were exposed to dissolved oxygen during storage, homogenization, and column filling. Consequently, sulphate and dissolved metals (Fe and Zn) were observed in pore waters immediately after the columns were set up.

Zn concentrations were uniform throughout the water covers: around 0.3 mg/L for column 1–1, from 0.4 to 0.5 mg/L for column 1–2, around 12 mg/L for column 2–1, 3.6 mg/L for column 2–2, 153 mg/L for column 3, and 0.03 mg/L for column 4. These profiles are logically consistent with the applied hydrodynamic conditions. Unlike the sulphate profiles, Zn concentrations generally decreased with increasing depth in the pore waters. These profiles correspond to the expected vertical profiles for dissolved metals when unoxidized tailings are stored beneath a water cover: concentrations of dissolved metals may be higher in the water cover than in the pore water within the tailings (MEND 2001).

In column 3, sulphate and Zn concentrations in the water cover were higher than in the pore water, as expected when

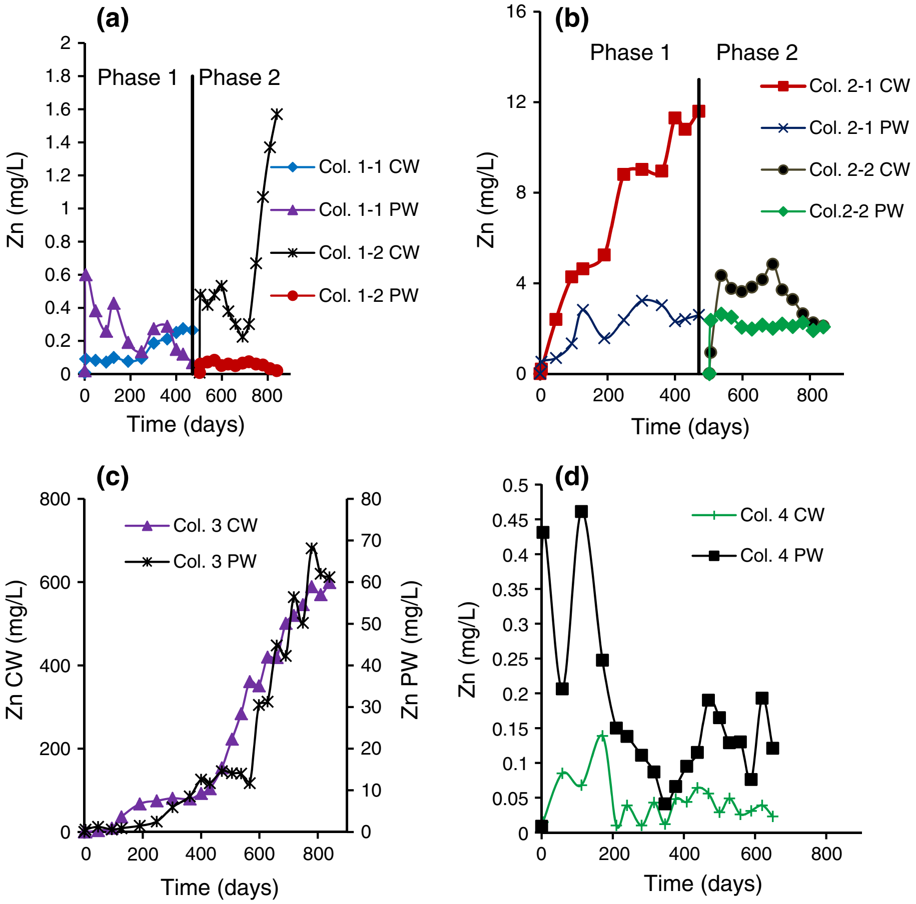

Fig. 7 Comparison of temporal change in Zn concentrations in cover water (CW) at port 3 for columns 1–1, 1–2, 2–1, 2–2, and 3 and at port 2 for column 4 and in pore water (PW) at port 5 (a secondary vertical axis is used in Fig. 7c)

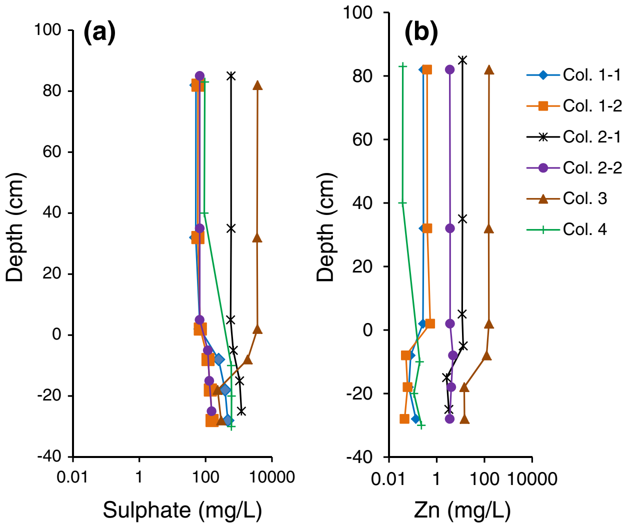

Fig. 8 Vertical sulphate (**a**) and Zn (**b**) profiles in columns (after 471 days for columns 1–1, 2–1, 3, and 4; and after 598 days for columns 1–2 and 2–2, logarithmic scale for Zn horizontal axis)

a water cover is placed over unoxidized tailings. This profile was probably due to tailings oxidation induced by the strong agitation of the water cover, which caused tailings resuspension. Exposing the tailings to DO-saturated water accelerated oxidation and produced large quantities of sulphate and dissolved metals, exceeding those of the interstitial water.

The profiles presented in Fig. 8 were consistent with the pH profiles. In columns 1–1, 1–2, and 4, where pH was around neutrality, sulphate and dissolved metal concentrations were generally lower than in columns 2–1, 2–2, and 3, which were in the range of acidic pH.

Properties of Suspended Tailings in Column 3

The strong tailings resuspension in column 3 (approximately 3,000 mg/L of suspended solids) allowed for sampling enough suspended solids (SS) for characterization. The parameters determined on the sample collected after 471 days of monitoring are described in Section "Tailings Characteristics" . Laser particle size analysis showed that 98 % of the particles in the SS were smaller than 80 μm and 16 % were smaller than 2 μm. For the total tailings (before resuspension), 85 % of the particles were smaller than 80 μm and 5 % were smaller than 2 μm. The D_{10}, D_{30}, D_{50} and D_{60} were 0.9, 3.6, 6.2 and

Table 2 Elements (%) obtained by the chemical analysis of suspended solids in column 3 and the initial tailings

Sample	Fe	S	Al	Zn
Suspended particles	43.9	26.2	3.2	0.22
Initial tailings	48.9	38.7	0.91	0.38

8.0 μm for the SS and 4.9, 18.5, 36.5 and 47.3 μm for the total tailings, respectively. D_x corresponds to x % volume on the cumulative grain-size distribution curve. These results suggest that finer tailings fractions were resuspended.

Mineralogical analysis of SS by XRD showed a decrease in pyrite content from 83 % in the original tailings to 53 % in the SS, and an increase, from 7 to 27 % for chlorite and from 4 to 6 % for muscovite. Table 2 compares the main elements obtained by chemical analysis using ICP-AES in SS and initial tailings. Fe decreased from 49 to 44 % and S from 39 to 26 %. As Fe, S and Zn decreased in the SS, the Al content increased from that of the initial tailings. The increase in Al may also be due to silicates containing Al (ex. chlorite and muscovite) being lighter than other minerals and preferably resuspended. Assuming that most of the sulphur is derived from pyrite, 26.2 % sulphur corresponds to approximately 49.1 % pyrite, which is in accordance with the XRD results.

Post-testing Mineralogical Analysis of Tailings

Visual observation when the columns were dismantled revealed orange–yellow precipitates of different intensities at the water-tailings interface in columns 1–1, 1–2, 2–1, 2–2, and 3 (analysis not performed on column 4). These precipitates were more pronounced (almost reddish) in columns 2–1 and 3. SEM analysis of tailings samples collected at the water-tailings interface showed signs of different degree of oxidation. As expected, tailings in columns 2–1, 2–2, and 3 were more oxidized than tailings in columns 1-1 and 1-2. There were many iron oxide crusts and aggregates (see Fig. 9). In columns 1–1 and 1–2, the mineral particles (pyrite, quartz, and silicates) embedded in the aggregates were not coated with iron oxides, unlike in columns 2–1 and 3. Column 1–1 showed the lowest oxidation; only small quantities of agglomerates were observed and microscopic observation revealed that the tailings remained very similar to the initial tailings for that column. The chemical analysis of precipitation products of pyrite oxidation in the different columns using SEM indicated that the minerals were generally composed of iron oxyhydroxides.

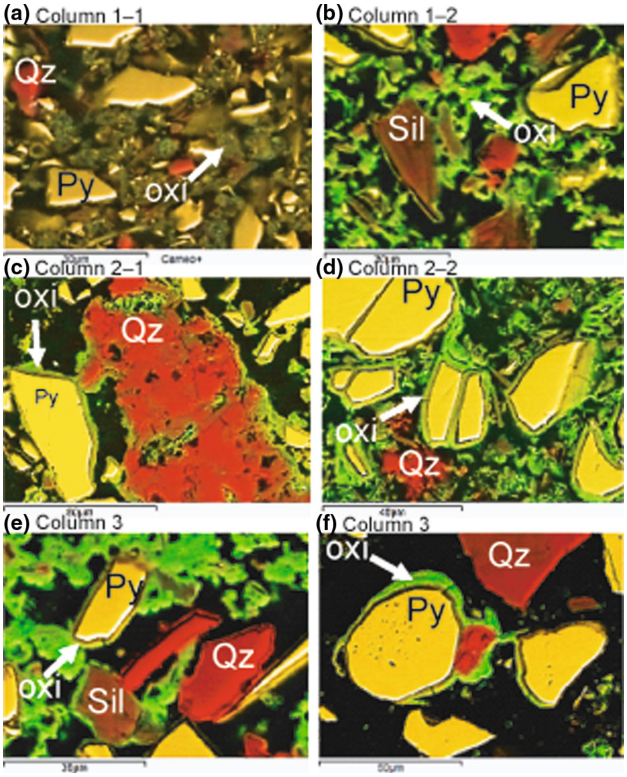

Fig. 9 SEM BSE/X-mapping overlapping images showing detailed aspects of pyrite oxidation (*Qz* quartz, *Sil* silicate, *Oxi* oxide, *Py* pyrite)

Discussion

Rate of Sulphate Loading in the Water Cover

To compare the different scenarios tested, the average daily sulphate loading rate in the water covers was determined from the slope of the curve of the temporal variation in average sulphate concentrations. Average concentration was defined as the sulphate load per unit volume of the water cover. A linear variation in concentration was assumed between two neighboring ports in the water cover. For columns 2 and 3, with almost homogeneous sulphate concentrations throughout the water cover depth, the average sulphate concentration was close to that measured at the different ports (1–3). In columns 1 and 4, where sulphate concentrations were higher in the pore water than in the cover water, upward sulphate diffusion and tailings oxidation may explain the water cover concentration variations. In columns 2 and 3, where sulphate concentrations were higher in the cover water than in the pore water, downward diffusion and tailings oxidation may explain the net variation in water cover concentrations. For this reason, the daily rate of sulphate loading (RSL) was used instead of the commonly used rate of sulphate production (Fig. 10).

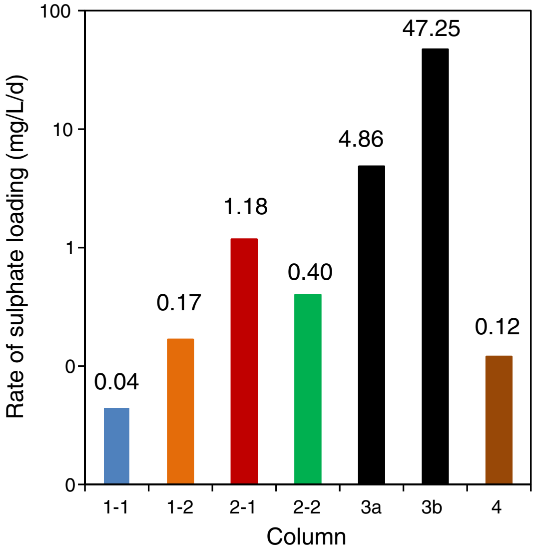

Fig. 10 Rate of sulphate loading in the water cover

Two RSL rates are given for column 3, which was stirred with strong resuspension and presented the highest RSL. The slope of the curve of average sulphate concentration in column 3 showed an inflection point after 400 days (see Fig. 4 for measurements at port 3). From t = 0 to t = 400 days, the RSL was 4.86 mg/L/days (column 3a in Fig. 10). Thereafter, the RSL jumped to 47.25 mg/L/days (column 3b in Fig. 10). There was also a rapid increase in dissolved metals, coinciding with an increase in sulphate after 400 days. This increase may be due the depletion of neutralizing minerals in the suspended tailings after 400 days (the neutralization rate decreased from 0.21 to 0.005; see section below). Also, after approximately 400 days, the pH of the water cover in column 3 was ≈2.2. At this pH, Fe^{3+} remains in solution and becomes an oxidizing agent that can oxidize pyrite (e.g. Aubertin et al. 2002; Evangelou 1995; Holmes and Crundwell 2000; Jambor and Blowes 1994; Zheng et al. 1986). Qualitative tests indicated that acidophilic and neutrophilic bacteria that can influence sulphide oxidation (Silverman 1967; Holmes and Crundwell 2000) were present in the tailings in this study. For example, *Thiobacillus thioparus* is a neutrophilic bacterium that is active within an optimal pH range between 6 and 8 at a temperature of 10–37 °C, where it can oxidize sulphide, thiosulphate, and other reduced sulphur species (Blowes et al. 2003; Bussière et al. 2005). *Acidithiobacillus thiooxidans* is an acidophilic bacterium that oxidizes sulphur and thiosulphates (Blowes et al. 2003; Bussière et al. 2005) at pHs ranging from 1 to 6 at temperatures from 10 to 37 °C. These pH and temperature conditions were present in column 3. Consequently, these bacteria probably contributed to accelerated tailings oxidation.

Column 2–1, stirred with low resuspension, had the second highest RSL, followed by column 2–2 (aerated without resuspension), column 1–2 (monthly downward infiltration), column 4 (with a sand layer above the tailings), and column 1–1 with a stagnant cover water. The RSL was about 4 times lower for column 1–1 (RSL = 0.04 mg/L/days) than for column 1–2 (RSL = 0.17 mg/L/days), indicating that intermittent downward infiltration lowers the pH as it brings DO-rich water in contact with the tailings. A comparison of columns 2–1 (1.18 mg/L/days) and 2–2 (0.40 mg/L/days) shows that tailings resuspension helped increase sulphate production compared to aeration of the water cover without resuspension. The RSL in column 4 (0.12 mg/L/days), stirred with a layer that prevents tailings oxidation, was higher than in the stagnant column 1–1. Stirring in column 4 led to homogeneous sulphate distribution throughout the water cover, and appears to have favoured diffusion from the tailings.

Oxidation–Neutralization Curves in the Water Cover

The concept of oxidation–neutralization curves used by Benzaazoua et al. (2004) to predict acid generation from kinetic tests was extended to the water covers in the different columns. The species used are sulphate, which is the main sulphide oxidation product, and the sum of dissolved Ca + Mg + Mn + Al + Si, which represent the main neutralization products from carbonate and silicate dissolution. The cumulative mass of sulphate measured in the water cover is plotted versus the cumulative amount of Ca + Mg + Mn + Al + Si. Sulphate results are presented in Fig. 11 for columns 1–1, 1–2, 2–1, 2–2, and 4, and Fig. 12 for column 3. In columns 1–1, 1–2, 2–1, 2–2, and 4, the minerals (Ca + Mg + Mn + Al + Si) generally show very good linear correlation with sulphate (0.73–0.99 coefficient of determination R^2). The slopes of the curves are, respectively, 0.33; 0.37; 0.41; 0.41; and 0.42 for columns 1–1, 1–2, 2–1, 2–2 and 4. These results indicated dissolution of neutralizing minerals as acidity is produced.

In column 3, the oxidation–neutralization curve shows the two stages discussed above. Up to 400 days, the acidity produced by pyrite oxidation was neutralized. The slope was 0.23 with a R^2 of 0.98, close to 1. Thereafter, sulphate rose very quickly whereas Ca + Mg + Mn + Al + Si increased slowly; the slope changed abruptly from 0.23 to 0.014, which indicates that the produced acidity was less controlled by neutralization. This could be due to depletion of neutralizing minerals: the initial tailings contained 83 % pyrite and only 9 % chlorite, 2 % muscovite, and trace amounts of carbonate. A second explanation is the hydrodynamic conditions applied to column 3, with strong tailings resuspension. As discussed above, direct oxidation of

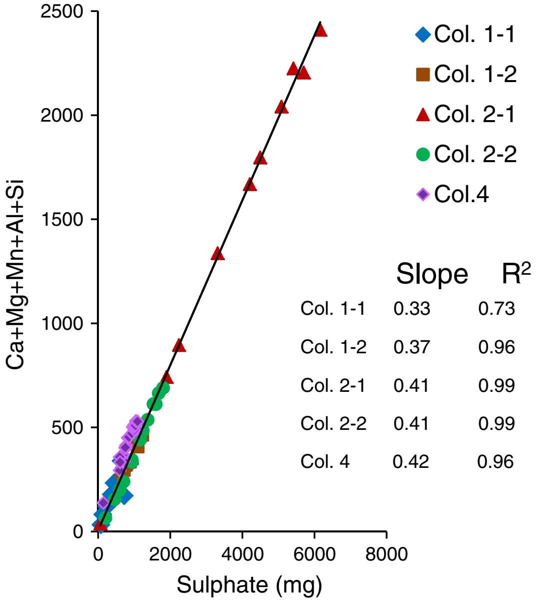

Fig. 11 Oxidation–neutralization curves of water covers in columns 1–1, 1–2, 2–1, 2–2, and 4

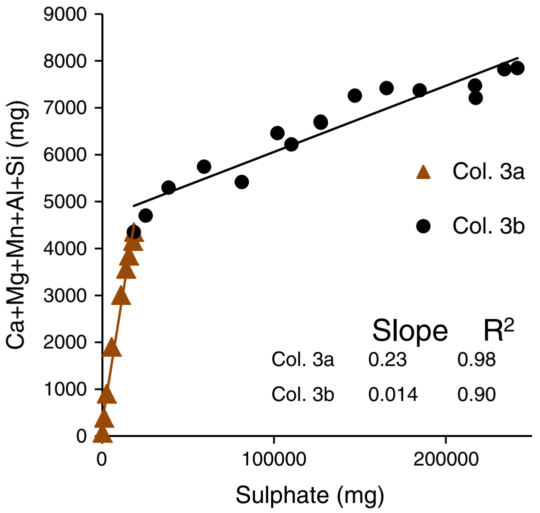

Fig. 12 Oxidation–neutralization curves of water cover in column 3

the SS and the tailings that were close to the water-tailings interface, combined with indirect oxidation by Fe^{3+} and bacterial action, would have significantly increased the water's acidity.

Geochemical Modeling Results

Geochemical modeling with VMinteq (Felmy et al. 1984) was used to calculate aqueous mineral saturation indices for various minerals in the columns (except for column 4) at different monitoring periods, taking into account the water quality (including the Eh and DO results) and the pCO_2 in the gaseous phase (ambient CO_2 380 ppm or 0.00038 atm). A positive saturation index suggests supersaturation (possible precipitation) of the mineral. In all samples, geochemical modelling with VMinteq at day 471 of monitoring for column 1–1 and 2–1 and at day 840 of monitoring for columns 1–2, 2–2, and 3 suggest that iron oxyhydroxides such as ferrihydrite, goethite, and lepidocrocite, are suspected to precipitate. Iron oxyhydroxides were also identified by chemical analysis using SEM.

Future Work

The following recommendations are proposed:

Geochemical modeling of water quality would be interesting to assess the long-term performance of water covers.

During resuspension of tailings under water, the finest particles are most easily resuspended. The equations of critical shear stress, which currently make use of the mean diameter of the initial tailings to estimate the minimum water cover height, should be adapted to better consider this aspect.

It would be appropriate to determine the chemistry of different fractions of submerged tailings to learn how the particle size and chemistry of suspended particles affects the geochemical behavior of water covers.

A thorough study of the influence of microbiological processes on the oxidation of submerged tailings would better explain the geochemical behavior of water covers.

Conclusions

The main conclusions that can be drawn from this study are:

Resuspension greatly enhanced the production and release of sulphate and metals from tailings into the water cover. In the water cover with more tailings resuspension, the neutralizing minerals were depleted after a 400 day monitoring period, leading to an increase in sulphate and dissolved metals.

Intermittent downward infiltration promotes contact between the tailings and water cover with high DO, leading to oxidation of mine tailings, lower pH, and the production of sulphate and dissolved metals, compared to a stagnant water cover without infiltration.

Adding a layer of inert material (in this case, a 20 cm sand layer) significantly reduced pyrite oxidation in extremely pyritic tailings.

Dissolved metal and sulphate concentrations increased in the following order of hydrodynamic conditions: a stagnant water cover, a stagnant water cover with bottom seepage, a continuously mixed water cover with a layer of inert material, a continuously mixed water cover with a low degree of resuspension, and a continuously mixed water cover with a high degree of resuspension.

In these tests, Zn was the main dissolved metal (after Fe), with the highest concentration in all columns under the tested conditions, even though the tailings contained only 0.38 % Zn (as free sphalerite, attached to pyrite, and included within pyrite).

Pyrite oxidation in all columns except the one with the sand layer showed precipitation of iron oxyhydroxides at the water-tailings interface, which agreed with geochemical modeling using VMinteq.

Finally, field measured data at several sites in Canada have shown that resuspension cannot be eliminated, even with a deep (up to 2 m) water cover (Adu-Wusu et al. 2001; Kachhwal and Yanful 2010). For highly pyritic tailings, placing a protective layer of inert granular material would virtually eliminate tailings resuspension and greatly improve the efficiency of a water cover.

Acknowledgments The authors thank the Research Institute on Mines and the Environment at UQAT-Polytechnique, the NSERC, for a Discovery Grant provided to the second author, and the URSTM staff for their help in the laboratory. Special thanks to Thomas Genty, who carried out the water sampling during the first author's maternity leave.

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