Long-term Storage of Sulfide-rich Tailings under a Shallow Water Cover

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Abstract
The oxidation of sulfide-minerals in subaerial tailings deposits generates acid and releases sulfate and metals to pore water. Discharge of this metal-rich water can lead to severe degradation of water quality in receiving lakes and streams. Subaqueous disposal of tailings is a common method for limiting sulfide-mineral oxidation in tailings. Numerous short-term studies have demonstrated that shallow water covers are effective at limiting oxygen diffusion to submerged tailings; however, long-term studies are lacking. The former Sherritt-Gordon Zn-Cu mine, located in Sherridon, Manitoba, Canada, deposited sulfide-rich tailings into Fox Lake during 1951. Surface water, pore water and core samples were collected in 2001 and 2009 to examine long-term biogeochemistry of tailings submerged in approximately 1 m of water. A narrow zone of extensive sulfide-mineral alteration was observed within the upper 6 cm of the tailings, suggesting that sulfide-mineral oxidation occurred shortly after deposition. However, subsequent inputs of organic matter at the tailings-surface water interface likely promoted growth of sulfate-reducing bacteria. Pore water within the tailings was characterized by circumneutral pH conditions, increased H_2S concentrations, and low sulfate and metal concentrations, which are indicative of dissimilatory sulfate reduction. Secondary sulfide-minerals were observed as coatings on primary sulfides in the original zone of oxidation.

Keywords: subaqueous, oxidation, bacteria, pyrite, sulfate reduction, sulfur isotopes

Introduction
Subaqueous disposal of tailings is commonly proposed for limiting sulfide-mineral oxidation. The O_2 ingress into the tailings is limited by the low diffusion coefficient of the water cover. For example, the diffusive flux of O_2 to water covered tailings may decrease by up to 10000 times relative to uncovered tailings (Robertson et al., 1997). Suppression of sulfide-mineral oxidation therefore may be accomplished by disposal of tailings into deep lakes or marine environments (Pedersen et al., 1993), or by the construction of wet covers on existing tailings impoundments (Robertson, 1992). A number of studies have investigated the short-term storage of tailings under a shallow water cover (Vigneault et al., 2001; Samad and Yanful, 2005), but few studies have considered the reactivity of tailings that have been submerged over long times (Jacob and Otte, 2004). The objective of this study was to characterize the biogeochemical processes that have occurred within sulfide-rich mine tailings subjected to nearly six decades of storage under a 1 m water cover. This study involved detailed analyses of mineralogy, pore water geochemistry and microbial populations within the tailings.

Background
The former Sherritt-Gordon Mine is located in Sherridon Manitoba, ~800 km northwest of Winnipeg, Manitoba, Canada (Figure 1). From 1927–1990, this area was characterized by mean annual precipitation of 485 mm (Environment Canada, 2011) and evapotranspiration of 350 mm (Hydrological Atlas of Canada, 1978). Average monthly temperatures in the area ranged from –21 ^{o}C in January to 18 ^{o}C in July with a mean annual temperature of 0.5 ^{o}C (Environment Canada, 2011).

Two Zn-Cu volcanogenic massive sulfide ore bodies were exploited to produce Zn and Cu concentrates with minor amounts of Au and Ag. Each ore body was about 5 m thick and occurred as lenticular layers of

massive and disseminated sulfides, and as irregular remobilized masses (Goetz and Froese, 1982). The ore averaged 2.45 wt. % Cu, 2.97 wt. % Zn, 0.62 g/t Au and 19.9 g/t Ag (Farley, 1949). Ore-zone sulfides were, in decreasing order of abundance, pyrite [FeS_2] and pyrrhotite [$Fe_{(1-x)}S$] (2:1 ratio), chalcopyrite [$CuFeS_2$], sphalerite [ZnS], and accessory cubanite [$CuFe_2S_3$]. Farley (1949) reported rare arsenopyrite [FeAsS] occurring as small grains within pyrrhotite, native gold, and irregular occurrences of galena [PbS] in veinlets and disseminations within hanging-wall shear zones in the gneiss host rock. During the life of the mine, a total of 7.7 Mt of pyritic ore was milled producing 0.17 Mt of Cu, 0.14 Mt of 50 % Zn concentrate, and minor amounts of Ag (91320 kg) and Au (2867 kg) (Mineral Resources Branch, 1978).

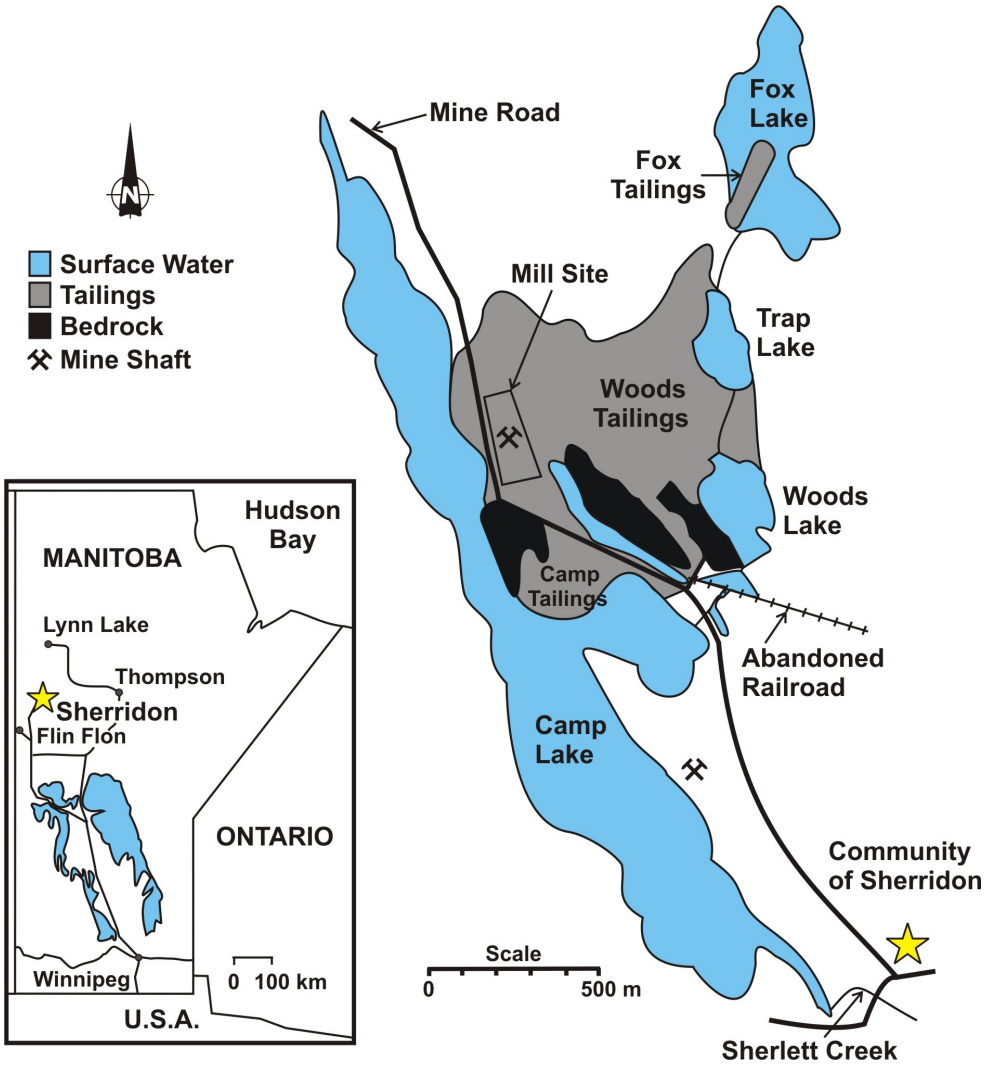

Figure 1. Location of Sherridon, Manitoba, Canada.

The mine operated from 1931–1951, but mining was suspended in 1932 due to depressed metal markets. Sphalerite was not recovered by the concentrator during the early years of operation because of interferences from fast-floating pyrrhotite (Walker, 1930). Mining and milling resumed in 1937, however Zn concentrates were not produced until 1942. Sulfide-rich tailings from the mining operations were discharged into three separate tailings impoundments containing a combined 7.4 Mt and occupying an area of 47 ha (Figure 1). The Camp Tailings were deposited between 1931 and 1932 and the Woods Tailings were deposited between 1937 and 1951. Tailings were deposited into Fox Lake at the end of mining in 1951.

Fox Lake is a small (700m by 300m) lake situated in a semi-closed basin with only an outflow. The lake overlies Precambrian Shield rock of the Sherridon Group, consisting of both metasedimentary and metavolcanic rock (Goetz and Froese, 1981). A geologic contact transects through the western 1/3 of the lake, with fine- to medium-grained quartz-rich gneiss underlying the western portion of the lake and a fine- to medium-grained layered amphibolite underlying the eastern portion of the lake. The quartz-rich gneiss is composed of quartz, oligoclase-andesine, K-feldspar, biotite and almandine. The amphibolite unit consists of hornblende, garnet and granoblastic aggregates of quartz, andesine, with traces of biotite, cummingtonite and anthophyllite (Goetz and Froese, 1981). Chemical composition of the quartz-rich gneiss and layered amphibolite are shown in Table 1.

Table 1. Average composition (%) for the quartz-rich gneiss and layered amphibolite units. Number of samples analysed is represented by n. Table modified after Goetz and Froese (1981).

Unit	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	CO_2	H_2O
Gneiss (n=25)	74.39	0.21	12.08	0.36	3.10	0.09	1.62	2.50	1.74	2.34	0.08	0.50	1.05
Amphibolite (n=15)	52.07	0.56	16.09	1.84	9.25	0.19	5.43	8.86	2.56	0.60	0.14	1.17	1.49

The 60 year old Fox Tailings form a number of small exposed islands of tailings with the majority of tailings submerged underwater, extending outward into Fox Lake as a series of lobes (Figure 2). The exposed tailings were visually oxidized and much of the submerged tailings were overlain by naturally established vegetation.

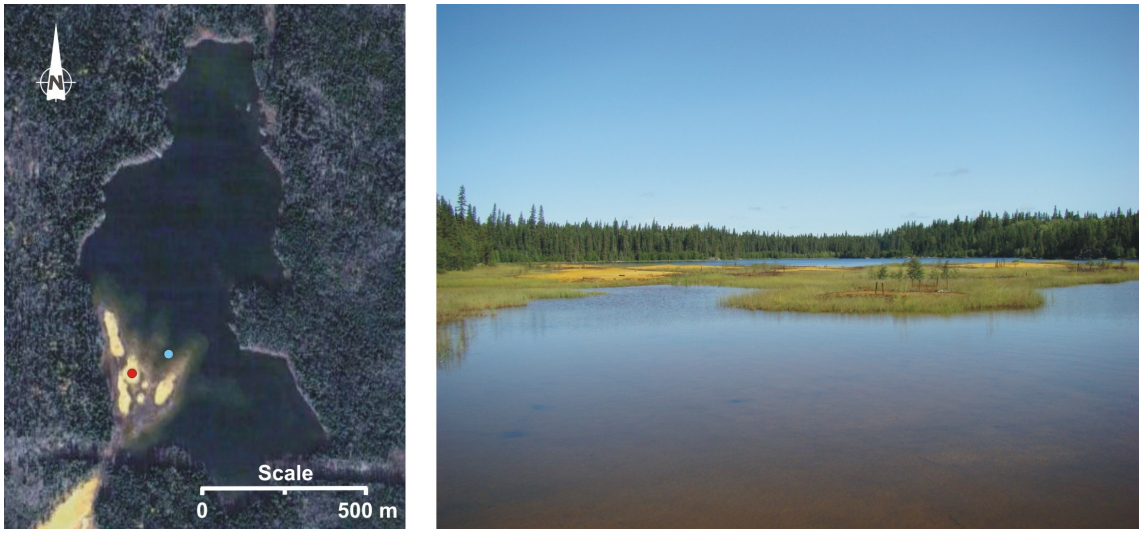

Figure 2. Image on left shows aerial view of Fox Lake and the tailings. Red circle represents the land-based sampling location and the blue circle represents the submerged sampling location. Photo on right shows a north view across the Fox Lake and the tailings.

Methods

Core samples were collected from two locations at the Fox Tailings in 2001; an exposed land-based location and a location submerged under a 1 m water cover (Figure 2). From each location, two cores were collected to a depth of 1 m for pore water squeezing and mineralogical/solid phase analyses. Core samples were subsequently collected in 2006 at each location to a depth of 1 m for microbiological enumerations.

In 2009, 1 m core samples were collected from each location for pore water squeezing. Also in 2009, 1.3 cm diameter piezometers were installed into the submerged tailings to depths of 0.12, 0.38, 0.63 and 0.88 m below the water/sediment interface for collection of groundwater samples.

Samples of the tailings solids were analyzed for total metal concentrations using HF/HNO_3 extraction followed by inductively coupled plasma – optical emission spectrometry (ICP–OES) analysis. Total sulfur was determined using a LECO induction furnace. Polished thin sections of the core materials were prepared without the use of water, thereby minimizing the dissolution of readily soluble minerals. The polished thin sections were examined by optical microscopy, using both transmitted and reflected light. Areas of the optical sections were examined further by scanning electron microscopy (SEM) and electron-microprobe analyses. The SEM study utilized a Phillips XL-30 instrument with a coupled energy-dispersion analyzer. The tailings material was also examined by X-ray diffractometry (XRD) using a Siemens rotating-anode instrument.

Pore water from the cores was extracted using a squeezing technique, as described by Patterson et al. (1978), and as later modified by Blowes et al. (1991) and Moncur et al. (2005). Water samples were collected in 60 mL syringes and passed through 0.45 µm cellulose-nitrate filters. Determinations of pore-water Eh and pH were made at least three times during the collection of each unfiltered sample to obtain representative results. The Eh was measured using an Orion platinum redox electrode (model 96-78BN), which was checked against Zobell's (Nordstrom, 1977) and Light's solution (Light, 1972). The pH was measured using an Orion Ross combination electrode (model 815600) calibrated with standard buffer solutions at pH 7, 4, and 1. Measurements of alkalinity were made on filtered samples using a Hach digital titrator and bromcresol green / methyl red indicator and with 0.16 *N* H_2SO_4. One aliquot of water was acidified with 12 *N* trace-metal grade HNO_3 to a pH of <1 for cation analysis, and another aliquot was left unacidified for anion analysis.

Pore water from the saturated zone was collected from the piezometers using a peristaltic pump and polyethylene tubing. All piezometers were bailed dry and allowed to recover prior to sampling. Measurements of Eh and pH were made in a sealed flow-through cell, maintained near groundwater temperature. The pH electrode was calibrated and the performance of the Eh electrode was checked before and after each sampling point. The temperature was measured at each sampling location. Water samples were filtered with 0.45 µm cellulose-nitrate filters and split into separate aliquots for alkalinity, H_2S, anion and cation analyses. The alkalinity was measured in the field using a Hach digital titrator. Dissolved H_2S was determined using the methylene blue procedure (SMEWW, 1992). Surface water samples were collected from Fox Lake annually between 2001 and 2009 following the same procedures as above.

All water samples were immediately refrigerated until analyses. Samples were shipped to the University of Waterloo and analyzed using ICP-OES for major cations, ICP-MS for trace metals and ion chromatography (IC) for anions. Values of $\delta^{34}S$ and $\delta^{18}O$ for dissolved SO_4 were measured from seven pore water samples and one surface water sample from Fox Lake. In addition, seven sulfide mineral samples were analyzed for $\delta^{34}S$ at the University of Calgary. All isotope ratios are reported in the delta notation ($\delta^{34}S$, $\delta^{18}O$) as parts per thousand (‰) relative to the Vienna Cañon Diablo Triolite (VCDT) standard.

Populations of neutrophilic sulfur-oxidizing bacteria (nSOB), sulfate-reducing bacteria (SRB) and iron-reducing bacteria (IRB) were enumerated using a five-tube most probable number (MPN) method. Detailed descriptions of these methods are provided by Lindsay et al. (2009a). Briefly, the nSOB growth medium contained 5.0 g L^{-1} $Na_2S_2O_3 \cdot 5H_2O$ as the electron donor and the pH was adjusted to 7.0. The nSOB medium was prepared in sterile deionized (DI) water, and 9 mL aliquots were dispensed into sterile culture tubes. The growth medium for SRB had a pH of 7.5, contained 4.5 g L^{-1} Na_2SO_4 as the electron

acceptor, and lactate and acetate as electron donors. The IRB growth medium contained 1.84 g L^{-1} Fe(III) EDTA as the electron acceptor, protease peptone as the electron donor, and the final pH was adjusted to 7.0. Media for SRB and IRB also was in DI water, and 9 mL aliquots were dispensed into 20 mL serum vials, which were sealed and capped, and sterilized. Growth media were inoculated with 1.0 g of sample collected from refrigerated 2006 core samples. Handling and inoculation of SRB and IRB media was performed in an anaerobic chamber. Enumeration of positive results was performed after four weeks.

Groundwater and surface water chemistry was interpreted with the assistance of the equilibrium chemical-speciation/mass-transfer model MINTEQA2 (Allison et al., 1990). The MINTEQA2 data base was modified to make it consistent with that of WATEQ4F (Ball and Nordstrom, 2001). MINTEQA2 was used to calculate the saturation indices for discrete minerals that may be controlling the concentrations of dissolved species in waters of Fox Lake and the Fox Tailings.

Results and Discussion

Fox Lake water level

Information regarding tailings deposition into Fox Lake is limited. Water levels from Fox Lake were not measured during or after tailings deposition; therefore, it is not known if there was a period during the past 60 years when the tailings may have been exposed to oxygen. Figure 3 shows a series of air photos of the Fox Tailings taken between 1952 and 2008. Due to the poor resolution and high reflectance of the 1952 image it is difficult to determine the extent of water cover over the tailings; however subsequent images of the tailings from 1968 to 2008 show that the majority of the tailings remained submerged. Minimal water level fluctuations of Fox Lake were observed during annual visits between 2000 and 2009. The water level in the land-based tailings was 0.5 below the ground surface in 2001 and 2009.

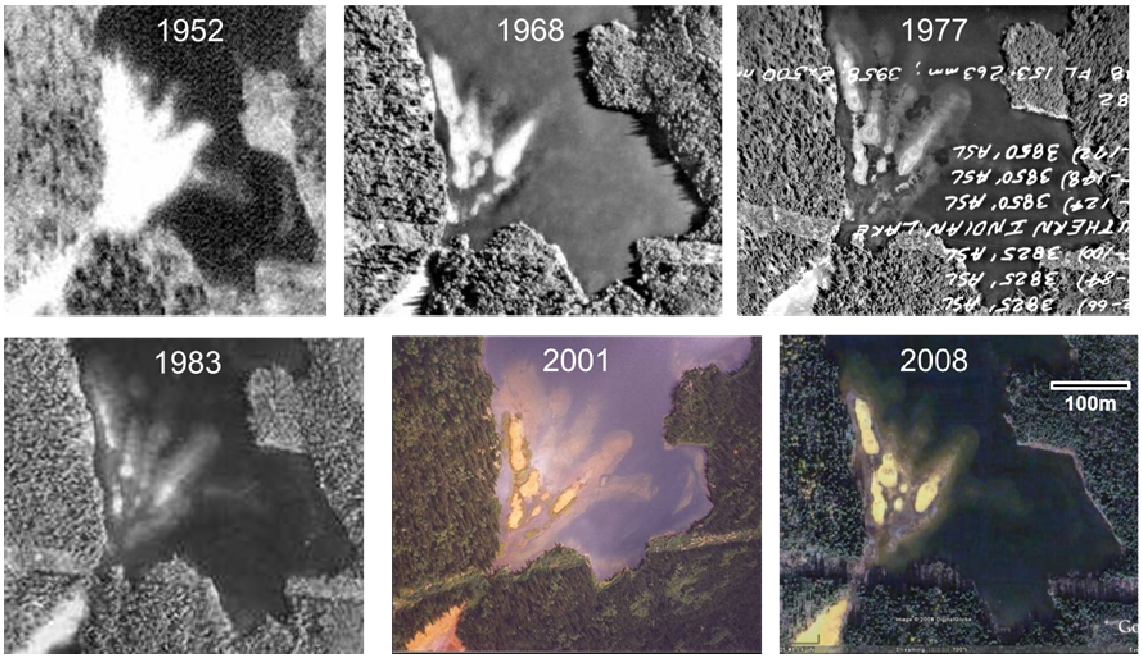

Figure 3. Aerial photos of Fox Lake and the submerged tailings between 1952 and 2008.

Mineralogy

Submerged Tailings

The upper 2 cm of the submerged tailings was strongly ochreous, and the interval from 2 to 6 cm was intensely ochreous whereas the remainder of the tailings to a depth of 1 m was blackish and megascopic

oxidation products were not observed. In the upper 2 cm of the tailings, reflected-light microscopic examination showed that major amounts of pyrite were present, and that none of the grains were altered. Pyrrhotite, typically as abundant as or slightly more so than pyrite (Moncur et al., 2005), occurred only sparingly as residual cores. More than 95 % of the pyrrhotite had been pseudomorphically replaced, typically as a rim of marcasite [FeS_2]. A few unaltered grains of chalcopyrite were present. Except for a single grain that was intergrown with chalcopyrite, sphalerite was absent.

At a depth of 6 cm the opaque minerals consisted of abundant, unaltered pyrite and pseudomorphs after pyrrhotite. A few grains of unaltered chalcopyrite, were present; sphalerite, however, was almost absent. A few grains of secondary covellite [CuS], each no more than 15 μm across, were observed within the pyrrhotite pseudomorphs. The pyrrohtite pseudomorphs, as in the preceding section, consisted predominantly of marcasite and voids. The sulfide assemblage at a depth of 18 cm consisted mainly of pyrite, which was unaltered, and of pyrrhotite that was variably altered. Some of the pyrrhotite was annular with marcasite rims and hollow cores, but the predominant alteration was narrow rims of marcasite, with the bulk of the pyrrhotite still preserved. Sphalerite occurrence was no longer rare with numerous grains observed in the section. At a depth of 20 cm major amounts of pyrite and pyrrhotite were present, and neither mineral was altered. Sphalerite was common, as were lesser amounts of chalcopyrite. Samples analyzed from depths of 34 and 39 cm were mineralogically similar to samples from 20 cm. Pyrite and pyrrhotite were abundant, as were chalcopyrite and sphalerite. Sulfide minerals exhibited no alteration in this zone.

Land-based tailings

The land-based tailings had a megascopically observable zone of ochreous oxidation that extended from the surface to a depth of 40 cm, followed by a transitional zone of weaker oxidation to unaltered tailings beginning at 60 cm. The uppermost portion of the ochreous zone, 0-6 cm, contained numerous grains of pyrite and chalcopyrite, but no pyrrhotite or sphalerite was observed. The proportion of chalcopyrite to pyrite was higher than observed in the unaltered tailings and some of the chalcopyrite grains had irregular margins that may be due to leaching. Pyrite lacked alteration rims, but in some microscopic fields of view a few grains were present, whereas in other fields of view, the mineral was absent. Therefore, most of the sulfide content of the sample was apparently destroyed. The zone from 33-36 cm was strongly ochreous, and the tailings contained more pyrite than did the preceding up-hole sample. However, the content was still about 25% of that observed in the unaltered samples. A few grains of chalcopyrite were present, but sphalerite and pyrrhotite was not observed.

An appreciable decline in oxidation was observed at a depth from 51-54 cm. The abundances of pyrite, and of pyrrhotite together with its associated secondary marcasite, were typical of those in unaltered tailings, as well as the presence of several grains of sphalerite marking its first appearance with depth. Although all of the pyrrhotite was altered, it varied from narrow to thick rims surrounding residual cores of unaltered pyrrhotite. Complete pseudomorphs after pyrrhotite were present, but they were much less common than particles that contained residual pyrrhotite. Samples collected from 62-65 cm and 72-75 cm were similar in that both contained abundant pyrite and pyrrhotite, with accessory amounts of sphalerite > chalcopyrite. The pyrrhotite was fresh and lacked alteration.

Porewater chemistry

The oxidation of sulfide minerals within the land-based tailings resulted in the release of elevated concentrations of dissolved SO_4 (up to 7500 mg/L), Fe (up to 3000 mg/L), trace metals and the generation of pH conditions between 1.9 and 4.6 (Figure 4). The highest concentrations of dissolved metals were observed near the tailings surface although elevated concentrations of dissolved Fe, SO_4 and other metals persisted with depth through the water table to a depth of 1 m. Measurable alkalinity was rarely detected in the pore water of the land-based tailings. Alkalinity values were 5 mg/L (as $CaCO_3$) at 0.75 m below the tailings surface and 3 mg/L (as $CaCO_3$) at 0.95 m below the surface. In contrast, pore water measured

from the submerged tailings contained circumneutral pH conditions, low concentrations of SO_4 and Fe and most dissolved metals were at or below analytical detection limits. Concentrations of dissolved ions, pH and Eh measured in 2001 and 2009 showed minimal variability (Figure 4). However, alkalinity concentrations measured in 2009 almost doubled those measured in 2001.

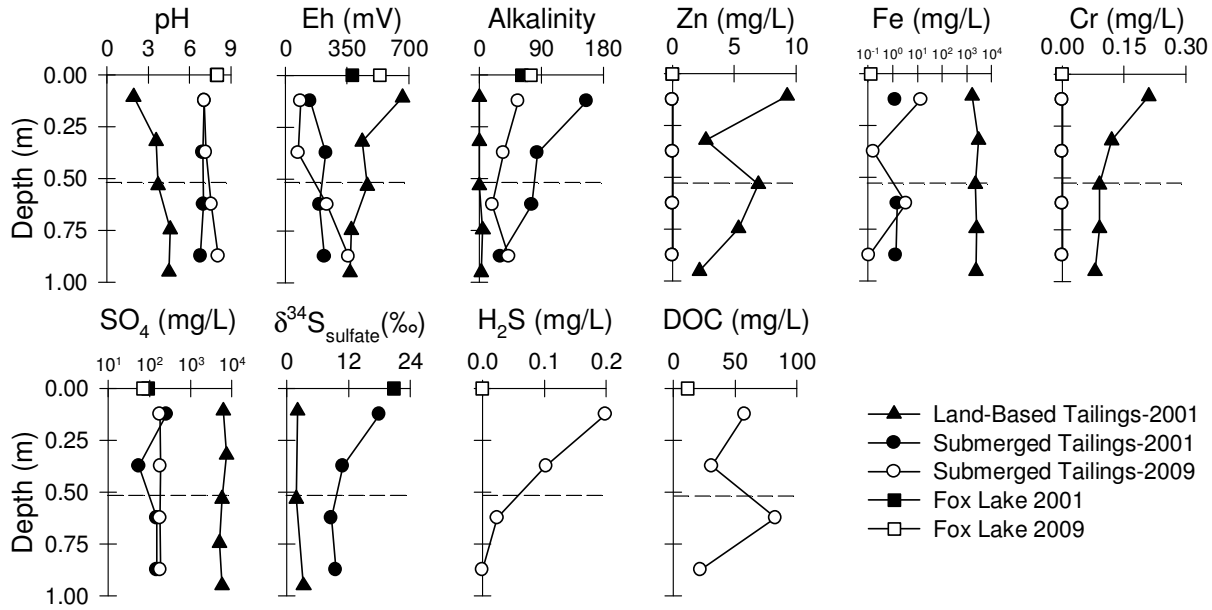

Figure 4. Profile through the land-based and submerged tailings showing pore water chemistry with depth. Dashed line represents location of the land-based water table. The surface-water/sediment interface of the submerged tailings is located at a depth of 0 m.

Sulfate reduction

For over five decades sulfur isotope ratio determinations on the SO_4 ion has been a valuable tool for determining sources of dissolved SO_4 in groundwater and surface water. Sulfur has 25 naturally occurring isotopes, only four of which are stable. Of those four, two (^{32}S, light and ^{34}S, heavy) make up the majority (99.22%) of sulfur on Earth. The vast majority (95.02%) of sulfur is found as ^{32}S with only 4.21% in ^{34}S (MacNamara and Thode, 1950). Positive values correlate to a greater amount of ^{34}S and more negative values correlate with greater ^{32}S in samples. Formation of sulfur minerals through non-biogenic processes does not strongly differentiate the light and heavy isotopes, although $\delta^{34}S$ values in minerals such as gypsum and barite are associated with a small (~1.65 ‰) fractionation (Thode and Monster 1965). Sulfur isotopes also do not exhibit significant fractionation between sulfide and sulfate during oxidation (Taylor et al. 1984; Edraki et al., 2005). Due to the conservative nature of $\delta^{34}S$ in non-biological processes, sulfur isotopes can serve as tracing element to identify their source. Biological processes, such as microbial sulfate reduction, can however lead to significant isotope fractionation of sulfur (Harrison and Thode, 1958). In this process the light isotope ^{32}S is preferentially metabolized and subsequently expelled as H_2S, leaving the remaining SO_4 progressively enriched as SO_4 concentrations decrease. Because of large apparent fractionations, ^{34}S is also an important tracer of biogeochemical processes.

Values of $\delta^{34}S$ and $\delta^{18}O$ for dissolved sulfate obtained from the land-based tailings pore waters, submerged tailings pore waters, and surface water from Fox Lake are presented in Figure 5. The $\delta^{34}S$ values measured form pore water in the land-based tailings showed little variation (1.9 to 3.2 ‰) and were similar to the $\delta^{34}S$ values of the primary sulfides (0.2 to 2.6 ‰).

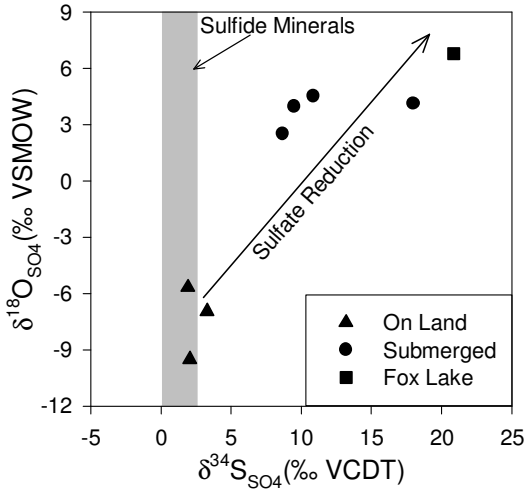

Figure 5. Plot of $\delta^{34}S$ versus $\delta^{18}O$ values of dissolved sulfate from on-land tailings, submerged tailings and surface water of Fox Lake. The shaded area represents the range of $\delta^{34}S$ values from seven sulfide minerals. SMOW - Vienna Standard Mean Ocean Water; VCDT – Vienna Canyon Diablo Trilite.

The $\delta^{34}S$ and $\delta^{18}O$ values of dissolved sulfate measured from the submerged tailings and Fox Lake showed significant fractionation indicating that microbially-mediated (dissimilatory) sulfate reduction had occurred (Figure 5). Microbially-catalyzed sulfate reduction, or dissimilatory sulfate reduction (DSR), is characterized by significant sulfur isotope fractionation with the remaining SO_4 becoming enriched in $\delta^{34}S$ with decreasing SO_4 concentrations (Harrison and Thode, 1958; Kaplan and Rittenberg, 1964; Fritz et al., 1989; Habicht and Canfield, 1997; Knöller et al, 2004). Sulfate reduction was also apparent from other geochemical parameters measured for the submerged tailings and for Fox Lake. As sulfate-reducing bacteria catalyze the oxidation of organic carbon, the reduction of SO_4 to H_2S (Berner, 1980) occurs through the reaction:

$$SO_4^{2-} + 2CH_2O \rightarrow H_2S + 2HCO_3^- \quad (1)$$

where CH_2O represents a generic organic compound. The organic carbon source in Fox Lake and the submerged tailings likely originated from overlying vegetation and DOC in the surface waters (Figure 4). The precipitation of sparingly-soluble metal-sulfides occurs when H_2S is produced in the presence of dissolved Fe^{2+} or other metals:

$$Me^{2+} + S^{2-} \rightarrow MeS \quad (2)$$

where Me^{2+} denotes a divalent metal such as Fe, Cd, Ni, Cu, Co and Zn; and MeS represents a metal sulfide precipitate. The sequence of reactions in equations (1) and (2) decreases the concentrations of dissolved SO_4, Fe, and other metals, and increases alkalinity and pH (Tuttle et al., 1969; Benner et al., 1999; Lindsay et al., 2009b). The reduction of SO_4 described in reaction (1) is consistent with the trends of increased pH, alkalinity, and H_2S, and with the decreased Eh observed in the submerged tailings pore water (Figure 4). Low populations of IRB and SRB were present within the ochreous zone of the land-based tailings; this zone was dominated by nSOB. Populations of nSOB declined with depth in the land-based tailings corresponding to an increase in SRB below the ochreous zone. This trend is indicative of oxygen consumption due to sulfide-mineral oxidation and DSR in the underlying anoxic zone. Within the submerged tailings, the largest populations of SRB and IRB occurred near the interface with the overlying water column. Populations of SRB and IRB generally decreased with depth, yet viable populations of these heterotrophic bacteria persisted throughout the submerged tailings.

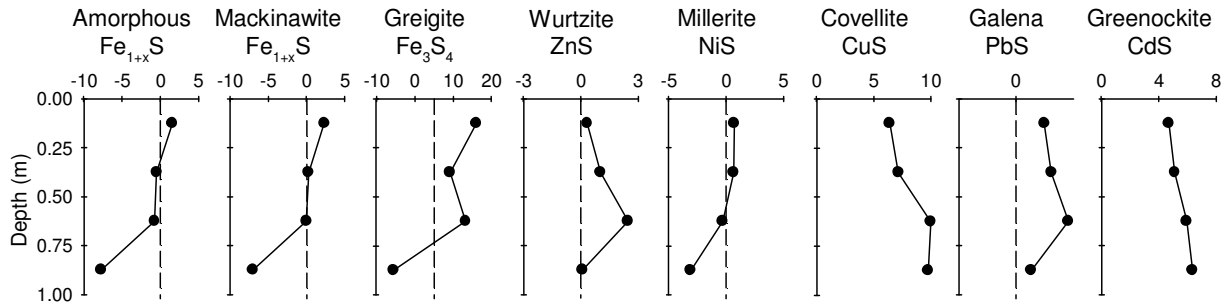

Figure 5. Saturation indices calculated using MINTEQA2, plotted versus depth in the submerged tailings. The surface-water/sediment interface is located at a depth of 0 m.

Saturation indices calculated using MINTEQA2 indicate that pore water from the submerged tailings approached saturation or became supersaturated with respect to secondary sulfide minerals (Figure 5). Speciation modeling is consistent with the presence of secondary covellite, and the presence of rims of secondary marcasite on unaltered primary pyrite at a depth of 6 cm in the submerged tailings. The rims occured on only a few grains and were extremely thin. The optical identification of the rims as marcasite was supported by EDS analysis. Other studies (e.g., Pedersen et al., 1993; Herbert et al., 2000; Paktunc and Davé, 2002) have also reported the presence of secondary sulfide minerals, which control metal and sulfate concentrations in sulfate-reducing zones at mining-impacted sites. The large shift in the $\delta^{34}S\text{-}SO_4$ values, increase of H_2S and populations of both SRB and IRB indicates that DSR was occurring in the submerged tailings pore water, limiting the loading of dissolved metals, sulfate and low pH water to Fox Lake.

Fox Lake water quality

Comparison of water quality parameters for the submerged tailings, land-based tailings and Fox Lake (Figure 4) shows the importance of limiting oxidation to minimize the production of low pH, high metal concentration waters. Despite the low pH, high SO_4 and metal concentrations present in the land-based tailings the water quality of Fox Lake remained circumneutral, likely due to the ameliorating influence of DSR (Table 2). Water quality data is sparse prior to 2001, but the limited data available seems to indicate a general improvement in water quality over the 25-year period.

Table 2. Water chemistry measured from Fox Lake surface water between 1984 and 2009.

Date	pH	Alkalinity mg/L $CaCO_3$	Fe mg/L	Zn mg/L	Cu mg/L	SO_4 mg/L
1984	7.3	-	-	0.26	0.56	-
1988	7.2	48	1	0.5	0.01	-
2001	7.97	62	0.085	<0.005	0.005	93
2002	8.44	57	<0.005	<0.005	<0.005	33
2003	7.79	68	0.38	<0.01	0.003	81
2004	7.34	88	0.192	<0.005	0.006	84
2005	7.53	86	1.03	0.005	<0.005	70
2006	9.56	70	-	-	-	-
2008	7.90	58	0.057	0.0021	0.0003	
2009	8.05	75	0.13	0.0020	<0.005	70

Conclusions

Sulfide-rich mine tailings were deposited into Fox Lake more than 60 years ago. The land-deposited tailings showed a well-defined, ochreous oxidation zone that extended from surface to about 40 cm depth. The interval from 40 to 60 cm is a transitional or intermediate zone of much weaker oxidation, and at depths >60 cm sulfide minerals in the tailings were not altered. In contrast to the thickness of the oxidation zone in the land-based tailings, the equivalent zone in the submerged tailings was thin, extending for only a few centimeters below the water-solids interface.

Pore water collected from the land-based tailings had low pH conditions, depleted alkalinity and elevated concentrations of dissolved sulfate and metals. Land-based tailings were dominated by populations of neutrophilic sulfur oxidizing bacteria, which catalyze sulfide-mineral oxidation in the presence of oxygen and water. Increased populations of sulfate-reducing bacteria below the ochreous zone were indicative of oxygen depletion resulting from sulfide-mineral oxidation in the overlying tailings. Conversely the natural colonization of vegetation over the subaqueous tailings resulted in the development of strong reducing conditions evident from circumneutral pH conditions, low concentrations of dissolved sulfate and metals, production of H_2S and strong sulfur fractionation indicating microbially-mediated (dissimilatory) sulfate reduction. Within the submerged tailings, secondary marcasite was observed in the relic ochreous zone occurring as coatings on primary minerals. This observation indicates that, following a period of oxidation, metals were subsequently sequestered from solution in this zone. This finding further emphasizes the influence of reducing conditions and microbial activity on metal mobility within mine tailings. Results from this study provide insight for the submergence of sulfide-rich tailings under a shallow water cover as a viable method for limiting sulfide-mineral oxidation over extended time periods.

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Acronyms

ICP–OES: Inductively Coupled Plasma–Optical Emission Spectrometry
ICP-MS: Inductively Coupled Plasma-Mass Spectrometry
IC: Ion Chromatography
SEM: Scanning Electron Microscopy
XRD: X-Ray Diffractometry
nSOB: Neutrophilic Sulfur-Oxidizing Bacteria
SRB: Sulfate Reducing Bacteria
DSR: Dissimilatory Sulfate Reduction
IRB: Iron Reducing Bacteria
MPN: Most Probable Number
VCDT: Vienna Cañon Diablo Triolite
SMOW: Vienna Standard Mean Ocean Water