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Geochemical and mineralogical aspects of sulfide mine tailings

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ABSTRACT

Tailings generated during processing of sulfide ores represent a substantial risk to water resources. The oxidation of sulfide minerals within tailings deposits can generate low-quality water containing elevated concentrations of SO_4 , Fe, and associated metal(loid)s. Acid generated during the oxidation of pyrite [FeS_2], pyrrhotite [$\text{Fe}_{(1-x)}\text{S}$] and other sulfide minerals is neutralized to varying degrees by the dissolution of carbonate, (oxy)hydroxide, and silicate minerals. The extent of acid neutralization and, therefore, pore-water pH is a principal control on the mobility of sulfide-oxidation products within tailings deposits. Metals including Fe(III), Cu, Zn, and Ni often occur at high concentrations and exhibit greater mobility at low pH characteristic of acid mine drainage (AMD). In contrast, (hydr)oxyanion-forming elements including As, Sb, Se, and Mo commonly exhibit greater mobility at circumneutral pH associated with neutral mine drainage (NMD). These differences in mobility largely result from the pH-dependence of mineral precipitation-dissolution and sorption-desorption reactions. Cemented layers of secondary (oxy)hydroxide and (hydroxy)sulfate minerals, referred to as hardpans, may promote attenuation of sulfide-mineral oxidation products within and below the oxidation zone. Hardpans may also limit oxygen ingress and pore-water migration within sulfide tailings deposits. Reduction-oxidation (redox) processes are another important control on metal(loid) mobility within sulfide tailings deposits. Reductive dissolution or transformation of secondary (oxy)hydroxide phases can enhance Fe, Mn, and As mobility within sulfide tailings. Production of H_2S *via* microbial sulfate reduction may promote attenuation of sulfide-oxidation products, including Fe, Zn, Ni, and Tl, *via* metal-sulfide precipitation. Understanding the dynamics of these interrelated geochemical and mineralogical processes is critical for anticipating and managing water quality associated with sulfide mine tailings.

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1. Introduction

Mining and processing of sulfide ores generates large volumes of waste materials that can have severe and widespread impacts on water resources (España et al., 2005; Concas et al., 2006; Moncur et al., 2006, 2014; Pérez-López et al., 2011). Sulfide ore deposits host globally significant amounts of Cu, Ni, Zn, Pb and other economically important metals. These metals commonly occur in chalcopyrite [CuFeS₂], pentlandite [(Fe,Ni)₉S₈], sphalerite [(Zn,Fe)S], and galena [PbS]; however, gangue minerals including pyrite and pyrrhotite often dominate sulfide assemblages. Sulfide ore deposits are also important sources of Au and Ag, which may occur as native elements or be associated with sulfides. Despite their economic importance, sulfide minerals are also major sources of potentially toxic accessory elements including As, Se, Cd, Sb, and Hg. These elements may occur as discrete sulfides or as trace impurities in other ore and gangue sulfide minerals (Plumlee, 1999). For example, common sources of As in sulfide ore deposits and associated mine wastes include arsenopyrite [FeAsS] and arsenian pyrite [Fe(As_xS_(1-x))₂]. The mineralogical and geochemical composition of sulfide mine wastes largely controls their potential for negative environmental impacts.

Mill tailings are a principal solid waste generated at sulfide mining operations. Sulfide ore minerals are generally concentrated by milling and froth flotation, which produces tailings containing gangue minerals and residual sulfides. Milling involves crushing and grinding to reduce particle size and liberate ore minerals from the rock matrix. The resulting clay- to silt-sized particles are combined with water to form slurry and then treated with surfactants to render sulfide ore minerals hydrophobic. Anionic surfactants commonly used for sulfide flotation include xanthates and dithiophosphates. The fine-grained slurry is then introduced to aerated flotation cells where a frothing agent is added to promote bubble formation. The hydrophobic sulfide minerals attach by surface tension to the bubble interface and are transported vertically to

the surface of the flotation cell. The sulfide-bearing froth is collected by decantation and residual slurry may undergo additional concentration. The selectivity of froth flotation for specific sulfide minerals is dependent upon surfactant, slurry pH, and surface interactions with dissolved ions. Fuerstenau et al. (2007) present a comprehensive review of sulfide mineral flotation. Gravity circuits may also be employed to recover native Au and Ag or to separate other high specific gravity mineral phases. After ore minerals have been extracted and concentrated, the resulting tailings are commonly dewatered and deposited in sub-aerial tailings impoundments or stockpiles (Blowes et al., 2003).

The extent of environmental impacts associated with sulfide tailings deposits depends upon their mineralogical and geochemical composition, and upon *in-situ* chemical, biological, and physical processes. Silicates, carbonates and sulfides generally dominate the mineralogical assemblage of fresh tailings. The sulfide mineral component includes both gangue minerals and residual ore minerals not extracted during concentration due to ineffective separation from the rock matrix. Sulfide minerals are thermodynamically unstable in the presence of oxygen and water. The resulting oxidative weathering of sulfides can generate H^+ and release sulfate and metal(loid)s to tailings pore waters. Rates of sulfide-mineral oxidation are controlled by several factors including oxygen availability, pore-water pH, and the activity of Fe- and S-oxidizing bacteria. Subsequent precipitation-dissolution, reduction-oxidation (redox), and sorption-desorption reactions control pore-water pH and the mobility of these weathering products.

The pH of tailings pore water and drainage is a principal control on dissolved concentrations of metal(loid)s released during sulfide mineral oxidation (Heikkinen et al., 2009; Nordstrom, 2011a, 2011b; Smuda et al., 2014). Acid mine drainage (AMD) develops in tailings deposits where the neutralization capacity of carbonate minerals is depleted due to ongoing

sulfide-mineral oxidation. Several metals including Fe, Al, Mn, Zn, Ni, Cu, and Pb may occur at high dissolved concentrations under AMD conditions. In contrast, neutral mine drainage (NMD) conditions generally persist in tailings deposits where carbonate dissolution effectively neutralizes acid generated by ongoing sulfide-mineral oxidation. These tailings are generally characterized by elevated concentrations of weakly hydrolyzing metals including Fe(II), Zn and Cd, and (hydr)oxyanion-forming elements including As, Se, and Sb.

The transport and attenuation of sulfide-mineral oxidation products are influenced by precipitation-dissolution, sorption-desorption, and redox reactions. High dissolved concentrations of Fe and SO_4 generated *via* sulfide oxidation can promote formation of hardpan layers comprised of Fe (oxy)hydroxides or (hydroxy)sulfates. Moreover, gypsum [$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$] precipitation is often a principal control on dissolved SO_4^{2-} concentrations in carbonate-rich tailings deposits. Redox reactions can strongly influence the mobility of elements including S, Fe, As, and Se, which exhibit multiple oxidation states. Iron reduction can promote dissolution or transformation of Fe(III) (oxy)hydroxides and, therefore, has potential to impact metal(loid) mobility. Production of H_2S *via* sulfate reduction can promote precipitation of sparingly soluble metal-sulfide phases, whereas reduction of As(V) to As(III) typically enhances As mobility. Finally, pH-dependent sorption onto tailings solids can strongly influence the mobility of metals and trace elements released *via* sulfide-mineral oxidation. Under moderately acidic to circumneutral pH conditions, the mobility of several dissolved metal(loid) oxyanions including H_2AsO_4^- , SeO_4^{2-} and $\text{Sb}(\text{OH})_6^-$ is limited by sorption onto positively charged mineral surfaces.

An integrated understanding of these complex interactions among chemical, biological, and physical processes is critical for anticipating and mitigating potential environmental impacts associated with sulfide tailings. Several comprehensive reviews of geochemical (Blowes et al.,

2003; Blowes et al., 2014), mineralogical (Alpers et al., 1994a; Jambor, 1994, 2003; Jambor and Blowes, 1998), microbiological (Gould et al., 1994; Nordstrom and Southam, 1997; Gould and Kapoor, 2003; Johnson and Hallberg, 2003; Nordstrom, 2003) and hydrogeological (Blowes et al., 2003; Robertson, 1994) aspects of sulfide mine tailings and resulting mine drainage have been published over the past two decades. Detailed reviews on aspects of tailings dams (Kossoff et al., 2014) and methods for geochemical and mineralogical characterization of mine wastes (Raudsepp and Pani, 2003; Weisener, 2003; Jamieson et al., this issue) have also been published during this time. Price (2009) provides a comprehensive description of methods for predicting drainage chemistry from sulfide mine tailings and other sulfide-bearing geologic materials.

Rather than providing an incremental update to the information provided in these publications, this review combines information derived from three detailed case studies with current literature to illustrate the processes and conditions that control sulfide-mineral oxidation and the subsequent mobility of associated reaction products within sulfide mine tailings. Case studies include the Greens Creek Mine (Alaska, USA), Nickel Rim Mine (Ontario, Canada) and Sherritt-Gordon (Sherridon) Mine (Manitoba, Canada) (Fig. 1). The Greens Creek Mine is a NMD site and the Sherridon Mine is an AMD site. Although AMD conditions exist at the Nickel Rim Mine, carbonate mineral dissolution sustains zones of circumneutral pH within the tailings deposit. These three case studies provide valuable insights into a range of geochemical and mineralogical aspects of sulfide mine tailings.

2. Site Descriptions

2.1. Greens Creek mine

The Greens Creek mine is located approximately 30 km southwest of Juneau, Alaska, USA (Fig. 1). Mean annual air temperature and precipitation were 6.0°C and 1380 mm a⁻¹,

respectively, from 1997 to 2007. This late Triassic sulfosalt-bearing polymetallic stratiform massive sulfide deposit contains on average 13.9 wt. % Zn, 5.1 wt. % Pb, 599 g t⁻¹ Ag, and 4.8 g t⁻¹ Au. This deposit exhibits syngenetic, diagenetic and epigenetic features characteristic of volcanogenic massive sulfide (VMS), sedimentary exhalative (SEDEX), and Mississippi Valley-type (MVT) deposits (Taylor and Johnson, 2010). Discontinuous mineralization occurred at the contact between siliceous metavolcanic rocks and calcareous metasedimentary rocks (Taylor et al., 2010). Primary ore minerals include sphalerite, galena, tetrahedrite [(Cu,Fe)₁₂Sb₄S₁₃], pyrrargyrite [Ag₃SbS₃], and electrum [(Au,Ag)] (Lindsay et al., 2009a). The hanging wall consists of metasedimentary rocks ranging from dolomite to carbonate-poor shale with moderate organic carbon content (Johnson et al., 2010). The footwall is dominated by mafic to ultramafic volcanic rocks, with siliceous phyllite, sericite phyllite and chlorite phyllite occurring with increasing distance from the zone of mineralization (Taylor et al., 2010).



Fig. 1. Map showing locations of the Greens Creek, Nickel Rim and Sherridon Mines.

Development of the Greens Creek Mine began in 1986 and full-scale ore processing commenced in 1989 (Condon and Lear, 2006). Ore is ground to less than 50 μm in a semi-autonomous grinding and ball mill circuit, and subsequently passed through a series of gravity, alkaline flotation, and regrind circuits. This process is used to produce Zn, Pb, and bulk

concentrates, as well as a gravity Au concentrate. Tailings are thickened to between 60 and 70 wt. % solids and subsequently filter pressed to 11–12 wt. % moisture. Roughly one half of the tailings are transported by truck to a storage facility where they are dumped, spread in 1 m lifts, and roller compacted in a sub-aerial dry stack tailings storage facility.

Table 1. Summary of mine operations and tailings mineralogy^a for case study sites.

	Mine		
	Greens Creek	Nickel Rim	Sherridon
Location	Admiralty Island Alaska, USA	Sudbury Ontario, Canada	Sherridon Manitoba, Canada
Ore type	Zn-Ag-Pb-Au	Ni-Cu	Zn-Cu-Au-Ag
Active mining	1989–1993; 1996–	1953–1958	1930–1932; 1937–1951
Milling process	Flotation & Gravity	Flotation	Flotation
Tailings deposition	Dry Stack	Hydraulic	Hydraulic
Primary Mineralogy			
Carbonates	25–37 wt. %	0.2 wt. %	>1 wt. %
Silicates	15–27 wt. %	90–95 wt. %	40–85 wt. %
Sulfides	30–45 wt. %	5–10 wt. %	8–60 wt. %
Principal sulfides	py, sp, gn	Po	po, py
Arsenopyrite [FeAsS]	trace	-	trace
Chalcopyrite [CuFeS ₂]	trace	<0.5 wt. %	>1 wt. %
Galena [PbS]	<1.5 wt. %	-	trace
Marcasite [FeS ₂]	-	<0.5 wt. %	trace
Pentlandite [(Fe,Ni) ₉ S ₈]	-	<0.5 wt. %	-
Pyrite [FeS ₂]	20–40 wt. %	0.6 wt. %	5–28 wt. %
Pyrrhotite [Fe _(1-x) S]	-	9 wt. %	3–40 wt. %
Sphalerite [(Zn,Fe)S]	<4 wt. %	-	<4 wt. %
Tetrahedrite [(Cu,Fe) ₁₂ Sb ₄ S ₁₃]	trace	-	-
Principal carbonates	dol	Cal	cal
Calcite [CaCO ₃]	1.5–4 wt. %	≤0.2 wt. %	>1 wt. %
Dolomite [CaMg(CO ₃) ₂]	23–33 wt. %	-	-
Siderite [FeCO ₃]	-	-	trace

^acal: calcite; dol: dolomite; po: pyrrhotite; py: pyrite; sp: sphalerite

The fine-grained tailings contain up to 45 wt. % sulfides and 37 wt. % carbonates (Table 1; Lindsay et al., 2009a). The sulfide-mineral assemblage is dominated by pyrite and contains moderate amounts of sphalerite and galena. Arsenopyrite, chalcopyrite, and tetrahedrite are present in trace amounts. The non-sulfide gangue mineral assemblage is composed of dolomite [CaMg(CO₃)₂], quartz [SiO₂], barite [BaSO₄], calcite [CaCO₃] and several minor phases. In addition to major elements found in the tailings mineral assemblage, trace elements including Cd, Cr, Mn, Mo, Ni, Se and Tl are present (Lindsay et al., 2009a).

Tailings porosity ranges from approximately 30–40 vol. %. The water table is commonly positioned more than 10 m below the crest of the tailings deposit; however, tension-saturated conditions can extend upward to within 2 m of the tailings surface. The saturated hydraulic conductivity is approximately 10⁻⁶ m s⁻¹ and in the vadose zone declines concomitantly with water saturation to less than 10⁻⁷ m s⁻¹ (Lindsay et al., 2011a). Tailings pore-water is characterized by circumneutral pH, high SO₄ concentrations, with elevated concentrations of Zn, Mn, As, Sb, and other metal(loid)s (Table 2). High concentrations of thiosulfate (S₂O₃), which are attributed to the decomposition of Na-isopropyl xanthate (Lindsay et al., 2009a), persisted for 2–3 years following tailings deposition.

2.2. Nickel Rim mine

The former Nickel Rim mine is located 35 km northeast of Sudbury, Ontario, Canada (Fig. 1). This area is situated in a boreal Precambrian shield region with a mean annual temperature of 3.5°C and annual precipitation of 870 mm a⁻¹. Sulfide minerals were hosted in quartz diorite lenses as a series of irregular, disconnected ore bodies that were massive, disseminated, or brecciated. The ore lenses were confined within norite in the hanging wall and granite in the footwall (Johnson et al., 2000). Sulfide minerals in the orebodies consisted mainly of pyrrhotite,

with minor amounts of pyrite, pentlandite, chalcopyrite and marcasite [FeS₂] (Table 1). The ore grade varied between lenses, with averages of 1.2 wt. % Ni and 0.38 wt. % Cu (Thomson, 1961; Mamen, 1955).

Table 2. Range of selected parameter values for tailings pore-water chemistry at case study sites.

Parameter	Units	Mine		
		Greens Creek	Nickel Rim	Sherridon ^a
pH		6.6 - 8.8	2.0-8.0	0.6 - 5.8
Alkalinity	mg L ⁻¹ (as CaCO ₃)	0 - 800	< 20	0 - 127
SO ₄	mg L ⁻¹	200 - 18,000	100 - 24,000	6,100 - 280,000
S ₂ O ₃	mg L ⁻¹	<1 - 3,500	n.d.	n.d.
Ca	mg L ⁻¹	230 - 1,500	10 - 650	240 - 650
Mg	mg L ⁻¹	<1 - 4,700	10 - 1,500	12 - 1,680
Fe _T	mg L ⁻¹	<0.5 - 27	100 - 9,800	2,050 - 129,000
Zn	mg L ⁻¹	<0.005 - 231	0.1 - 10	1.4 - 54,900
Al	mg L ⁻¹	<0.05 - 0.74	<0.05 - 1,100	<0.05 - 7,200
Cd	mg L ⁻¹	<0.005 - 0.32	<0.01 - 1	0.13 - 97
Cu	mg L ⁻¹	<0.005 - 0.63	<0.01 - 13	<0.005 - 1620
Pb	mg L ⁻¹	<0.01 - 0.99	<0.02 - 0.5	<0.020 - 5.2
Mn	mg L ⁻¹	<0.05 - 58	1 - 55	1.8 - 230
Ni	mg L ⁻¹	<0.005 - 2.4	1 - 700	<0.010 - 15.3
Sb	µg L ⁻¹	<1 - 360	n.d.	n.d.
As	µg L ⁻¹	<10 - 80	n.d.	<100 - 41,000
Mo	µg L ⁻¹	<5 - 1,900	< 0.005	<5 - 1,100
Se	µg L ⁻¹	<5 - 510	n.d.	<5 - 1060
Ag	µg L ⁻¹	<1 - 290	n.d.	<5 - 3,700
Tl	µg L ⁻¹	<0.5 - 5,900	n.d.	<50 - 1,700

^aCamp tailings deposit; n.d.: not determined.

Development of the Nickel Rim mine commenced in 1929, while underground production was initiated in 1943. On-site milling and tailings disposal began in 1953 and ended in 1958. Ore was crushed on site to less than 7.62 cm diameter. A fine-grained (<1.27 cm) magnetic product was produced and shipped offsite for smelting, whereas the coarse material (1.27 to 7.72 cm)

was further crushed then ground in a rod mill (Johnson, 1993). Froth flotation was used to recover Ni and Cu from the crushed and ground ore. Rejected tailings, which contained 0.16 wt. % Ni and 0.054 wt % Cu (Mamen, 1955), were disposed as slurry into several valleys and a lake. Johnson et al. (2000) characterized the pore-water geochemistry and mineralogy of the largest tailings impoundment on the property, covering an area of 9.4 ha ranging in thickness from less than 1 m to 10.5 m. Underlying the tailings impoundment is an aquifer composed of silty, fine sand with local gravel and boulder-sized material, which was studied in detail by Bain et al. (2000).

Total sulfur in the unoxidized tailings ranged between 0.5 and 5 wt. % (average 4.5 wt. %), with pyrrhotite as the principal sulfide (> 98%) and minor amounts of chalcopyrite, pentlandite [(Fe,Ni)₉S₈], pyrite, and marcasite (Table 1; Jambor and Owens, 1993). Carbonate content of the tailings ranged from 0.1 to 3 wt.% as CaCO₃ (Johnson, 1993). The primary silicate minerals in the tailings were calcic plagioclase and amphibole with considerable amounts of clinopyroxene, chlorite, biotite, talc, quartz, and magnetite. Sulfide oxidation reactions within the tailings, mainly of pyrrhotite, generated low-pH waters containing up to 9,800 mg L⁻¹ Fe, 24,000 mg L⁻¹ SO₄, 700 mg L⁻¹ Ni, and other metal(loid)s (Table 2; Johnson et al., 2000).

2.3. Sherridon mine

The former Sherritt-Gordon mine is located in a continental boreal region approximately 700 km northwest of Winnipeg, Manitoba, Canada (Fig. 1). The mean annual precipitation of the area (1927–2012) is 463 mm and evapotranspiration is 350 mm (Environment Canada, 2012). The average monthly temperatures range from –21°C in January to 18°C in July, with a mean annual temperature of 0.5°C.

Two Precambrian (Aphebian period) VMS lenses and their associated, remobilized offshoots yielded ore containing 2.5 wt. % Cu, 3 wt. % Zn, 0.6 g t⁻¹ Au and 20–30 g t⁻¹ Ag. The mined lenses, each measuring roughly 5 m thick, were enclosed within quartz-rich gneiss except for local minor contact with pegmatite, amphibolite and amphibole-bearing gneiss. According to Goetze and Froese (1982), the ore was mineralogically simple consisting mainly of pyrite, pyrrhotite, sphalerite, chalcopyrite, rare magnetite [Fe²⁺Fe³⁺₂O₄] and exsolution laths of cubanite [CuFe₂S₃] in chalcopyrite. Rare arsenopyrite was reported by Farley (1949) who also described the presence of irregular occurrences of galena in local shear zones along hanging-wall contact. The galena occurred in veinlets and disseminations in the gneissic host rocks and contained particles of native Au. A total of 7.7 Mt of pyritic ores were milled between 1931 and 1951, producing 166,093 t of Cu, 135,108 t of 50 % Zn concentrate, and minor amounts of Ag (91,320 kg) and Au (2,867 kg) (Mineral Resources Branch, 1978).

Sulfide-rich tailings from the mining operations were discharged between 1931 and 1951. Mining was suspended from 1932 until 1937, and sphalerite was not recovered during concentration until 1942. Approximately 7.4 Mt of tailings were deposited into three separate impoundments covering a combined area of 47 ha. The Camp tailings were 7 ha in area and deposited between 1931 and 1932, whereas the Woods tailings were 40 ha in area and were deposited between 1937 and 1951. A small volume of tailings, less than 1 ha, were deposited directly into Fox Lake near the end of mining in 1951.

Tailings were fine-grained with D10 values ranging from 0.04 to 0.1 mm; however, diameters of up to 0.5 mm were common (Moncur et al., 2005). The tailings contain up to 60 wt. % as sulfide, mainly as pyrrhotite and pyrite, with pyrrhotite equaling or exceeding pyrite in all observed samples, except in the oxidized zones. Other primary sulfide minerals in the

tailings include sphalerite, chalcopyrite, marcasite, and trace amounts of arsenopyrite and galena (Moncur et al., 2009). The non-sulfide gangue assemblage of the tailings consists of quartz, K-feldspar, albite, and biotite, with chlorite and amphibole making up about 1 to 2 wt. %. Trace amounts of talc [$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$], ilmenite [FeTiO_3], magnesite [MgCO_3], sillimanite [Al_2SiO_5], rutile [TiO_2], titanite [CaTiSiO_5], gahnite [ZnAl_2O_4], and garnet [$\text{Fe}^{2+}_3\text{Al}_2(\text{SiO}_4)_3$], cordierite [$\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$], epidote [$\text{Ca}_2\text{Al}_2(\text{Fe}^{3+},\text{Al})\text{Si}_3\text{O}_{12}(\text{OH})$], siderite [FeCO_3], clinopyroxene [$(\text{Ca},\text{Na})(\text{Mg},\text{Fe},\text{Al})(\text{Si},\text{Al})_2\text{O}_6$], and hematite [Fe_2O_3] are also present (Moncur et al., 2005).

The water table was near surface adjacent to surface water; however, unsaturated zones over 4 m thick were observed in elevated areas of the Camp tailings (Moncur et al., 2005). Carbonate minerals comprise up to 0.05 wt.% of tailings in the vadose zone and up to 1 wt.% in deeper tailings below the water table. Over 70 years of sulfide oxidation in the upper 50 cm of the Camp tailings has generated pore water in the unsaturated zone with a pH less than 1 and high concentrations of dissolved sulfide oxidation products, including up to $129,000 \text{ mg L}^{-1}$ Fe, $280,000 \text{ mg L}^{-1}$ SO_4 , and $55,000 \text{ mg L}^{-1}$ Zn (Moncur et al., 2005). Below the water table concentrations remain elevated throughout the tailings, with up to $91,600 \text{ mg L}^{-1}$ and $60,600 \text{ mg L}^{-1}$ SO_4 and Fe, respectively.

3. Sulfide-mineral oxidation

Sulfide mineralization is common to ore deposits mined by the metals, minerals, and energy sectors. As a result, sulfide-mineral oxidation within mining wastes is one of the most significant environmental challenges faced by the mining industry worldwide (Blowes et al., 2014). This issue is largely attributed to storage of mining and mineral processing residues in sub-aerial deposits, where sulfide minerals are thermodynamically unstable.

3.1. Pyrite and pyrrhotite

Pyrite is the most common sulfide in the Earth's crust (Rimstidt and Vaughan, 2003; Murphy and Strongin, 2009) and is the principal sulfide mineral at the Greens Creek and Sherridon mines, with minor amounts at Nickel Rim. The oxidation of pyrite occurs when the mineral surface is exposed to molecular oxygen (O₂) and water (H₂O):



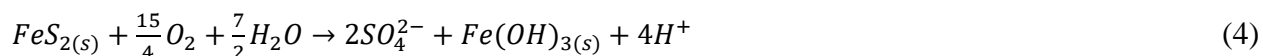
This reaction releases one mole of Fe(II), two moles of SO₄, and generates two moles of H⁺ per mole of pyrite oxidized (Nordstrom, 1982). Trace elements that occur as impurities in pyrite also may be liberated *via* pyrite oxidation (eq. 1). For example, pyrite is a common carrier of As (Savage et al., 2000; Nordstrom, 2002; Paktunc et al., 2006; Paktunc, 2008) and can also contain other trace elements such as Pb, Sb, Bi, Cu, Co, Ni, Zn, Au, Ag, Se and Te (Deditius et al., 2011). Microprobe analysis of pyrite from the Sherridon mine detected Co, Ni, Zn, Cd and As incorporated within the crystal structure (Moncur et al., 2005). Pyrite from the Nickel Rim mine contained 2–3 wt. % Ni (Jambor and Owens, 1993). In the presence of excess O₂, Fe(II) will subsequently oxidize to Fe(III) and consume one mole of H⁺:



Hydrolysis of Fe(III), which typically occurs at pH values greater than 5, promotes precipitation of Fe(III) hydroxides (where Fe(OH)₃ is a replacement for ferrihydrite [5Fe₂O₃·9H₂O]) and generates additional H⁺:

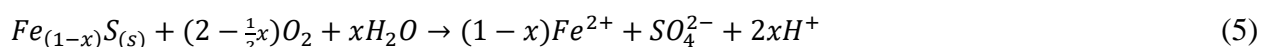


Although Fe(II) oxidation (eq. 2) consumes one mole of H⁺, subsequent Fe(III) hydrolysis (eq. 3) produces three moles of H⁺. Combining these reactions (i.e., eqs. 1–3) gives the overall reaction:

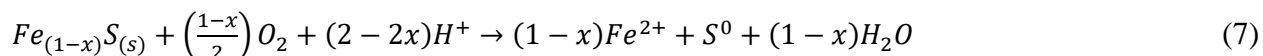
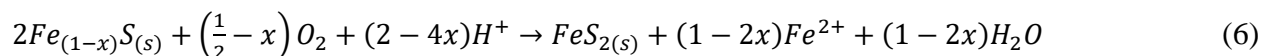


In this overall reaction, each mole of pyrite releases two moles of SO_4 , four moles of H^+ , and an Fe(III)-(oxy)hydroxide precipitate. It should be noted that the above reactions for pyrite oxidation are simplified equations and do not fully describe the complex reactions required to reach the final reaction products (Garrels and Thompson, 1960; Nordstrom and Southam, 1997).

Pyrrhotite is a major sulfide mineral in tailings deposits at the Nickel Rim and Sherridon mines, but was not observed at Greens Creek. The crystal structure of pyrrhotite is disordered with vacancies related to the Fe(II) deficiency, which can be charge-compensated by Fe(III) (Jambor, 2003; Blowes et al., 2014). Similar to pyrite, pyrrhotite commonly hosts trace elements including Ni and Co (Gunsinger et al., 2006a). Pyrrhotite in tailings from the Sherridon and Nickel Rim mines contained Ni impurities. The oxidation of pyrrhotite by O_2 is described by Nicholson and Scharer (1994) as:

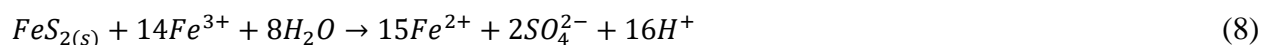


The amounts of Fe(II) and H^+ released during pyrrhotite oxidation (eq. 5) are dependent upon Fe content. The oxidation rate of pyrrhotite by O_2 is 20 to 100 times faster compared to pyrite oxidation by O_2 (Janzen et al., 2000); this difference may be related to the deficiency of Fe in the pyrrhotite structure (Blowes et al., 2014). Oxidation of pyrrhotite at the Sherridon and Nickel Rim mines resulted in secondary replacement rims of marcasite (Moncur et al., 2005) and elemental S (Johnson et al., 2000) at the mineral surface. Secondary Fe(III) (oxy)hydroxides and Fe(III) sulfates were commonly observed in alteration rims from the oxidized Sherridon tailings (Fig. 2). The partial oxidation of pyrrhotite proceeds as (Nicholson and Scharer, 1994; Gunsinger et al., 2006a):

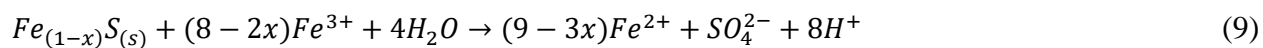


The formation of secondary alteration rims of marcasite (eq. 6) and elemental S (eq. 7) limits the proportion of sulfide transformed to SO_4 (Blowes et al., 2014) and slows oxidation rates (Moncur et al., 2009). Similar to pyrite, the oxidation of Fe(II) to Fe(III) (eq. 2) and subsequent precipitation of Fe(III) (oxy)hydroxide (eq. 3) generates an additional three moles of H^+ per mole of pyrrhotite (Nicholson and Scharer, 1994; Janzen et al., 2000; Thomas et al., 1998).

At circumneutral pH characteristic of tailings pore water at the Greens Creek mine, atmospheric O_2 is the principal electron acceptor during pyrite oxidation. Under acidic conditions ($pH < 3$), as observed at Nickel Rim and Sherridon, Fe(III) can remain in solution and become the dominant oxidant (Singer and Stumm, 1970):



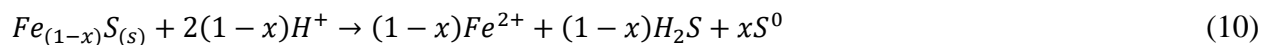
In this case, the oxidation of pyrite by Fe(III) results in Fe(II) becoming the dominant form of Fe in solution. In addition to Fe, 16 moles of H^+ are generated during this reaction (eq. 8). Similar to pyrite, pyrrhotite can undergo oxidation by dissolved Fe(III) (Janzen et al., 2000):



The presence of Fe(III) in pyrrhotite may increase the rate of Fe(II) oxidation, thereby accelerating the overall oxidation of pyrrhotite (Moncur et al., 2009). Nordstrom (1982) observed that the oxidation of sulfide minerals by aqueous Fe(III) is more rapid than atmospheric O_2 oxidation.

At the Sherridon mine, pore water from below the water table in the Camp tailings deposit exhibited pH ranging from 3.4 to 5.8 (average = 4.8) and dissolved concentrations of H_2S from

0.03 to 0.10 mg L⁻¹ (average = 0.06 mg L⁻¹; Moncur et al., 2005). Non-oxidative dissolution of pyrrhotite under acidic conditions generates Fe(II), H₂S and elemental S (Chiriță and Rimstidt, 2014):



The highest concentrations of dissolved H₂S in pore water from the Camp tailings were correlated with the lowest pH, suggesting that the production of H₂S is a result of pyrrhotite dissolution by acid waters.

3.2. Other iron-bearing sulfides

The primary concern for acid generation and the release of SO₄, Fe, and dissolved metal(loid)s are generally the oxidation of pyrite and pyrrhotite; however, other Fe-bearing sulfide minerals can also contribute to the generation of low-quality pore water and drainage. For example, at least two of sphalerite, chalcopyrite, and arsenopyrite were present in tailings deposited at the Greens Creek, Sherridon and Nickel Rim mines (Table 1).

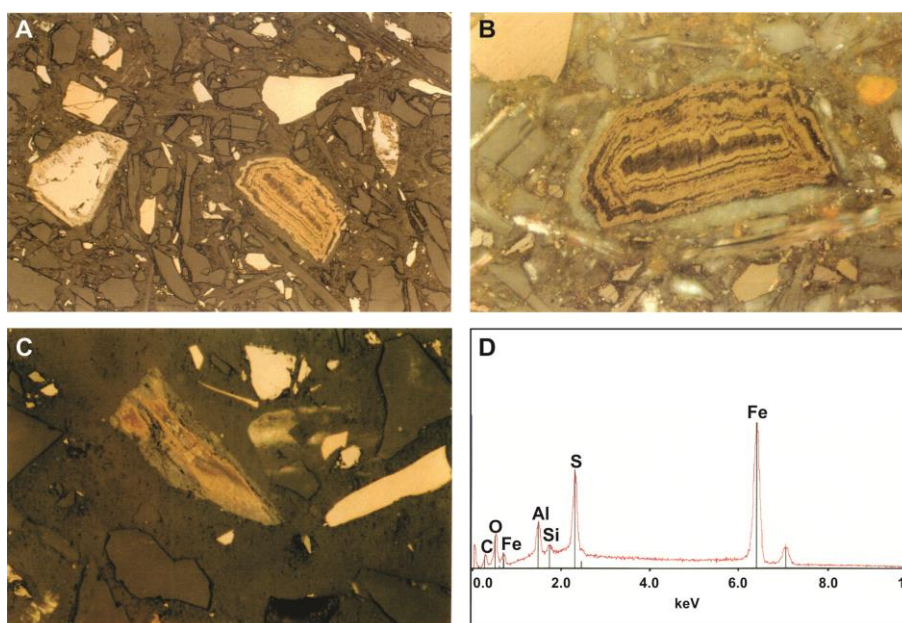
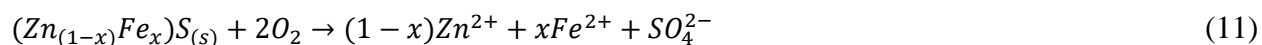
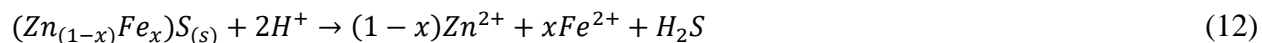


Fig. 2. Images of the Sherridon tailings; (A) Plain reflected light shows fresh pyrrhotite (white) and pyrite (slightly yellowish), and various stages of pyrrhotite replacement including complete pseudomorphism by marcasite where the dark zones are voids (width of field 0.625 mm). (B) This zoned pseudomorph, shown with nearly crossed polarizers, has a whitish rim consisting largely of jarosite accompanied by sparse, dispersed crystals of low-Fe alunite (width of field 0.03 mm). The black matrix within the grain interior is the mounting medium, originally interpreted to have been melanterite. (C) Plain reflected light showing whitish grains of pyrite (width of field 0.3 mm). Near the centre is a pseudomorph after pyrrhotite, the central part of which is naturally tarnished marcasite. The grey rim is Fe(III) (oxy)hydroxide, containing percent-level amounts of Al and S as indicated in the corresponding energy dispersive X-ray spectroscopy (EDS) spectrum (D).

Partial substitution of Fe for Zn is common in sphalerite (Pring et al., 2008), and other elements including Mn, Cd, and Hg may occur as impurities (de Giudici et al., 2002). Electron-microprobe analyses of sphalerite from the Sherridon tailings revealed up to 8 wt. % Fe, and ≤ 0.5 wt. % Cd, Mn and As. The oxidation of sphalerite by O_2 is represented by:

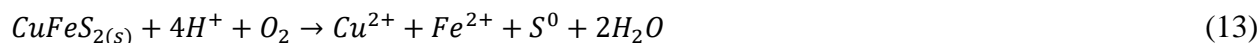


During oxidation, the initial dissolution rate for Fe-bearing sphalerite is rapid, but declines with time (Buckley et al., 1989; Weisener et al., 2003; Stanton et al., 2008). Furthermore, both the oxidation and dissolution rates tend to increase with Fe content (Perez and Dutrizac, 1991; Weisener, 2002). Similar to pyrrhotite, sphalerite is acid soluble and can dissolve to produce H_2S under acidic pH conditions (Nordstrom and Alpers, 1999):



Sphalerite is therefore commonly depleted under acidic conditions within weathered tailings deposits. In addition to S species, these reactions (i.e., eqs. 11, 12) release Zn, Fe, and associated metal(loid)s to tailings pore waters.

Chalcopyrite was present in tailings at the Greens Creek, Nickel Rim and Sherridon mines. The chalcopyrite oxidation rate increases in Fe(II)-sulfate solutions due to O₂ consumption and enhanced H⁺ transfer at the mineral surface (Hiro Yoshi et al., 1997):

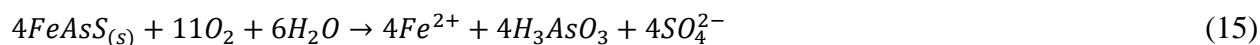


The dissolution of chalcopyrite results in the release of Fe(II) and Cu, and consumes four moles of H⁺. However, the subsequent oxidation of Fe(II) (eqs. 2, 3) and S⁰ generates H⁺:



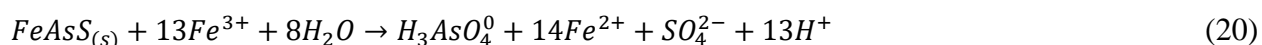
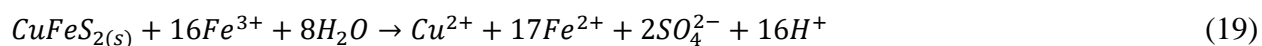
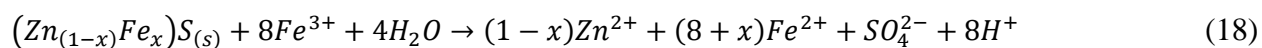
The dissolution rate of chalcopyrite can be controlled by a number of factors. Galvanic interactions, where charge transfer occurs between two contacting sulfide minerals in an electrolyte solution, may enhance chalcopyrite dissolution kinetics (Holmes and Crundwell, 1995). For example, close association with pyrite and molybdenite can increase chalcopyrite dissolution rates (Dutrizac and MacDonald, 1973; Blowes et al., 2003; Liu et al., 2008).

Arsenopyrite was observed in trace amounts in the Greens Creek and Sherridon tailings. The oxidation of arsenopyrite by atmospheric O₂ results in (Walker et al., 2005):



These reactions (eqs. 15–17) release of Fe(II), SO₄, As, and H⁺. In mine tailings, arsenopyrite grains are commonly surrounded by rims of secondary minerals, limiting O₂ diffusion to the mineral surface and, therefore, controlling oxidation rates and As release (Paktunc et al., 2004).

The generation of Fe(III) in acidic solutions by the oxidation of pyrite and pyrrhotite can enhance the oxidation of sphalerite, chalcopyrite and arsenopyrite. The oxidative dissolution of these minerals by Fe(III) is shown by (Rimstidt et al., 1994):



The oxidation of these minerals releases dissolved Fe(II), Zn, Cu, As, and H⁺. The mobility of the released elements depends upon pH and secondary reactions within tailings deposits.

Tetrahedrite and pentlandite observed at the Greens Creek and Nickle Rim tailings, respectively (Table 1), are also Fe-bearing and potentially contribute to acid generation promoting metal(loid) mobility. In addition to Fe-bearing sulfide minerals, under low pH conditions, the dissolution of biotite [K(Fe)₃AlSi₃O₁₀(OH)₂], and magnetite can provide additional acid generation through Fe(II) release and subsequent oxidation to Fe(III) (eq. 2) and hydrolysis (eq. 3).

3.3. Microbial processes

The biogeochemical cycling of S and Fe strongly influences sulfide-mineral oxidation and, therefore, acid generation and metal release in tailings deposits. Consequently, microorganisms that gain energy by oxidizing reduced forms of S and Fe are common in these deposits (Schippers et al., 2010 and references therein). Archaea and bacteria capable of oxidizing S or Fe have been detected in tailings and other sulfide-bearing mine wastes. However, these bacteria generally exhibit optimum growth between 20 and 45°C (i.e., mesophiles) and are generally

more common than S- and Fe-oxidizing archaea, which typically grow at higher temperatures (i.e., thermophiles).

Sulfur-oxidizing bacteria commonly found in sulfide tailings deposits include neutrophiles (e.g., *Thiobacillus thioparus*) and acidophiles (e.g., *Acidothiobacillus thiooxidans*) that grow optimally under NMD and AMD conditions, respectively (Blowes et al., 1996, 1998; Benner et al., 2000; Diaby et al., 2007; Schippers et al., 2010; Lindsay et al., 2011c). These bacteria are unable to oxidize sulfide minerals directly and, therefore, gain energy by oxidizing S^{2-} , S^0 , $S_2O_3^{2-}$ and other intermediate S species (Gould and Kapoor, 2003). Complete oxidation generates H^+ and SO_4 (e.g., eq. 14), thereby limiting accumulation of intermediate S species produced *via* sulfide-mineral oxidation (eqs. 7, 13). This process is thought to enhance oxidation rates by limiting formation of secondary S-bearing precipitates (e.g., elemental S) and, therefore, preventing passivation of sulfide-mineral surfaces (Dopson and Lindstrom, 1999). The generation of H^+ can also promote non-oxidative dissolution of acid-soluble sulfide minerals, including pyrrhotite (eq. 10) and sphalerite (eq. 12). Consequently, S-oxidizing bacteria play an important role in the development of AMD conditions within sulfide tailings deposits.

Sulfide tailings deposits characterized by AMD conditions commonly exhibit elevated populations of acidophilic Fe-oxidizing bacteria (Johnson and Hallberg, 2003). This observation reflects the central role that *Acidithiobacillus (At.) ferrooxidans* and other Fe-oxidizers play in sulfide-mineral oxidation and, therefore, AMD generation. These bacteria gain energy *via* Fe(II) oxidation to Fe(III) (eq. 2), which is soluble under acidic pH conditions. Iron-oxidizing bacteria can mediate this process while attached to sulfide-mineral surfaces (direct mechanism) or in the bulk solution (non-contact leaching) (Hallberg and Johnson, 2001; Blowes et al., 2014). However, Fe(III) produced by Fe oxidizers is subsequently reduced to Fe(II) *via* sulfide-mineral

oxidation. Oxidation rates for pyrite (eq. 8), pyrrhotite (eq. 9) and other Fe-bearing sulfide minerals (eq. 18–20) ultimately become limited by the rate of Fe(II) oxidation (Singer and Stumm, 1970). Microbial rates of Fe(II) oxidation at acidic pH are up to 10^5 times higher than abiotic rates (Nordstrom and Southam, 1997; Nordstrom, 2003). As a result, acidophilic Fe-oxidizing bacteria can considerably increase rates of sulfide-mineral oxidation and AMD generation.

Although Fe(III) exhibits limited solubility at circumneutral pH, acidophilic Fe-oxidizing bacteria have also been reported in sulfide mine wastes characterized by NMD conditions (Southam and Beveridge, 1993; Blowes et al., 1996; Blowes et al., 1998; Lindsay et al., 2009). Under bulk circumneutral pH conditions, *At. ferrooxidans* can overcome pH limitations on growth by forming acidic microenvironments at sulfide-mineral surfaces (Southam and Beveridge, 1992; Mielke et al., 2003; Pace et al., 2005; Dockrey et al., 2014). The formation of secondary Fe(III) (oxy)hydroxide and Fe(III) (oxy)hydroxysulfate phases has been attributed to *At. ferrooxidans* (Mielke et al., 2003; Pace et al., 2005; Dockrey et al., 2014). These secondary phases are thought to limit diffusive transport of oxidation products from sulfide-mineral surfaces and, therefore, increase Fe(III) solubility within close proximity of these surfaces (Mielke et al., 2003; Dockrey et al., 2014). This process is thought to allow *At. ferrooxidans* to gain energy through Fe oxidation under bulk NMD conditions. As a result, acidophilic Fe-oxidizing bacteria may contribute to sulfide-mineral oxidation in NMD and AMD settings.

Most-probable number (MPN) enumerations revealed that neutrophilic S-oxidizing bacteria were more abundant within Greens Creek tailings than acidophilic S- and Fe-oxidizing bacteria (Lindsay et al., 2009a). Subsequent molecular characterization of these microbial communities confirmed the presence of neutrophilic S-oxidizing bacteria within these tailings (Lindsay et al.,

2011c). These bacteria were genetically similar to *Thiobacillus* spp. that can oxidize S^{2-} and $S_2O_3^{2-}$ to SO_4 using O_2 (i.e., *Thiobacillus thiophilus*) or NO_3 (i.e., *Thiobacillus denitrificans*) as electron acceptors. Therefore, the microbial community within the Greens Creek tailings deposit has potential to promote sulfide-mineral oxidation both in the presence and absence of O_2 . However, low dissolved concentrations of NO_3 within tailings pore water at the Greens Creek limit the importance of this mechanism of sulfide-mineral oxidation.

3.4. Resistance and alteration

Tailings impoundments usually contain a diversity of sulfide minerals, each with a specific susceptibility to oxidation. Jambor (1994) observed a relative sequence for sulfide-mineral oxidation proceeding from the most reactive to most resistant phases. The relative resistance of sulfide minerals to oxidation assumes that grain sizes and textures are similar within a specific tailings deposit. The sequence of sulfide mineral oxidation (Table 3) is based upon optical examination of thin sections prepared for samples from several sulfide tailings impoundments including the Sherridon, Nickel Rim, and Greens Creek mines. The order applies to primary sulfide minerals, with the exception of magnetite, a primary Fe-oxide that is commonly associated with sulfide tailings.

Magnetite has a high resistance to oxidation, which makes it a suitable proxy for identifying zones of extensive oxidation. For example, sulfide minerals within the Camp tailings deposit at the Sherridon mine have undergone more than 70 years of intense weathering. Complete obliteration of sulfide was observed near the tailings surface; however, magnetite persisted in this zone and exhibited a pitted texture from apparent oxidation (Moncur et al., 2009a). Magnetite observed below this zone exhibited limited weathering. Sulfide grains were

completely consumed within the oxidation zone in the Nickel Rim tailings, except for trace amounts of chalcopyrite (Johnson et al., 2000). Magnetite grains in the active oxidation zone was partially replaced by Fe(III) (oxy)hydroxide rims, indicating that the shallow tailings were approaching late-stage oxidation.

Table 3. Relative resistance of sulfide minerals and magnetite in oxidized tailings (revised after Moncur et al., 2009).

Mineral	Formula	Resistance	
Pyrrhotite	$\text{Fe}_{(1-x)}\text{S}$	low	
Galena	PbS	↓	
Sphalerite	$(\text{Zn}_{(1-x)}, \text{Fe}_x)\text{S}$		
Bornite	Cu_5FeS_4		
Pentlandite	$(\text{Fe}, \text{Ni})_9\text{S}_8$		
Arsenopyrite	FeAsS		
Marcasite	FeS_2		
Pyrite	FeS_2		
Chalcopyrite	CuFeS_2		
Magnetite	$\text{Fe}^{2+}\text{Fe}^{3+}_2\text{O}_4$		
Molybdenite	MoS_2		high

To illustrate the relative resistance in a practical context, Blowes and Jambor (1990) developed the sulfide alteration index (SAI). The SAI is a numerical scale to show the relative degree of sulfide alteration of sulfide mineral grains through a depth profile of a tailings pile. The scale is based on optical microscopy where a sample-to-sample comparison is made on the extent of alteration and assigned a value (Table 4). The concept of the SAI has been applied to a number of different sites with varying mineralogy (e.g., Shaw et al., 1998; McGregor et al., 1998; Moncur et al., 2005; Gunsinger et al., 2006a; Moncur et al., this issue). Pyrrhotite exhibits greater susceptibility to alteration than other sulfide minerals; therefore, the SAI scale is related to the extent of pyrrhotite alteration (Blowes et al., 2014). When pyrrhotite is observed without

any alteration, a SAI of 0 is applied. A SAI of 10 is assigned when all sulfide minerals have been consumed except for traces of chalcopyrite.

Table 4. Sulfide alteration index (SAI) of the Sherridon tailings (revised after Moncur et al., 2005).

Index	Mineral Alteration
10	Almost complete oxidation of sulfides; traces of chalcopyrite \pm pyrite
9	Only sparse pyrite and chalcopyrite; no pyrrhotite or sphalerite
8	Pyrite and chalcopyrite common, but chalcopyrite proportion higher than normal possibly because of pyrite dissolution; no pyrrhotite or sphalerite
7	Pyrite and chalcopyrite proportions normal; pyrrhotite absent but sparse sphalerite present
6	Pyrrhotite absent but sphalerite common
5	Pyrrhotite represented by marcasite pseudomorphs
4	First appearance of pyrrhotite, but only as remnant cores
3	Cores of pyrrhotite abundant
2	Well-developed cores of pyrrhotite, with narrower alteration rims; replacement by marcasite decreasing, and pseudomorphs are absent
1	Alteration restricted to narrow rims on pyrrhotite

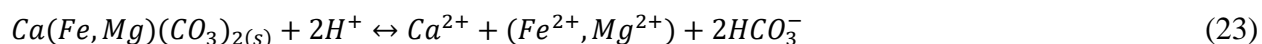
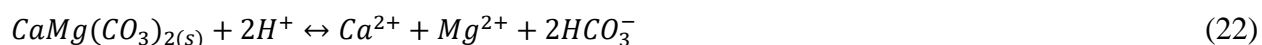
4. Acid neutralization

The dissolution of acid-neutralizing minerals is a principal control on pore-water and drainage pH, the mobility of metal(loid)s, and rates of sulfide-mineral oxidation (Holmström et al., 1999a). Acid generated *via* sulfide-mineral oxidation is neutralized by the dissolution of carbonate, (oxy)hydroxide, and silicate minerals within sulfide tailings deposits. Morin et al. (1988) proposed a conceptual model for acid neutralization whereby step increases in pore-water pH with depth resulted from successive dissolution of calcite, siderite [FeCO₃], Al (oxy)hydroxides, Fe(III) (oxy)hydroxides, and silicates. The inclusion of dolomite and ankerite [Ca(Fe,Mg)(CO₃)₂] facilitated application of this model to additional sulfide tailings deposits (Blowes and Jambor, 1990; Blowes et al., 1991, 1998; Johnson et al., 2000). Laboratory column experiments and reactive transport modeling by Jurjovec et al. (2002; 2004) further constrained

the spatial and temporal dynamics of acid-neutralizing reactions. In particular, these experimental studies highlighted the roles of secondary carbonate and (oxy)hydroxide in the acid neutralization sequence within sulfide tailings. Subsequent field studies have reinforced this conceptual model of successive acid neutralization reactions and corresponding increasing pH plateaus within sub-aerial sulfide tailings deposits (Moncur et al., 2005; Gunsinger et al., 2006b).

4.1. Carbonate dissolution

Equilibrium dissolution of calcite, dolomite, and ankerite can maintain circumneutral pH conditions in tailings pore water and drainage. Calcite dissolution commonly produces pore-water pH values ranging from 6.5 to 7.5 (Blowes and Ptacek, 1994; Blowes et al., 2003); however, pH values approaching 8.0 have been reported for tailings where dolomite and ankerite are the principal carbonates (Blowes et al., 1998; Lindsay et al., 2009a). In general, carbonate mineral dissolution consumes H^+ , releases divalent cations (e.g., Ca, Mg, Fe) and generates aqueous carbonate species:



The relative contribution of these carbonate minerals to acid neutralization ultimately depends upon their abundance and reactivity. Laboratory studies of carbonate dissolution in sulfide waste rock have demonstrated that grain size and, therefore, surface area are important controls on acid neutralization (Strömberg and Banwart, 1999). Moreover, Jurjovec et al. (2002) found that carbonate dissolution can be kinetically constrained by transport limitations and mineral surface passivation, which can result from the precipitation of secondary phases, for example gypsum or

Fe(III) (oxy)hydroxides, at carbonate mineral grain margins (Booth et al., 1997; Al et al., 2000). These kinetic limitations have the potential to decrease carbonate dissolution rates and, therefore, inhibit acid neutralization.

Dolomite dissolution is the predominant acid-neutralizing reaction in the Greens Creek tailings deposit (Fig. 4). This carbonate mineral comprises up to 33 wt. % of the tailings mineral assemblage and is the second most abundant component after pyrite (Table 1). Lindsay et al. (2009a) observed pore water pH ranging from 6.7 to 8.0 approximately five years after tailings deposition (Fig. 4). The lowest pH values were observed within a shallow zone of sulfide-mineral oxidation that extends approximately 0.25 m below the tailings surface. Although these tailings also contain 3.4 ± 0.8 wt. % calcite, large increases in pore-water Mg concentrations immediately below the oxidation zone are indicative of dolomite dissolution (Lindsay et al., 2009a). Circumneutral pH conditions are likely to persist within the Greens Creek tailings due to ongoing carbonate-mineral dissolution.

Acid generated *via* pyrrhotite oxidation completely depleted carbonate minerals within the sulfide-mineral oxidation zone at both the Nickel Rim and Sherridon mines. However, pore-water pH values between 6.5 and 7.0 were observed at greater depth in the Nickel Rim tailings deposit. Johnson et al. (2000) attributed this circumneutral pH plateau to the dissolution of calcite, which comprised ≤ 0.2 wt. % of the tailings mineral assemblage. Pore-water pH values decreased to approximately 5.5 immediately overlying the zone of calcite dissolution (Johnson et al., 2000). Similarly, the Camp tailings deposit at the Sherridon mine exhibited a buffering plateau at pH 5.5 positioned below the water table (Moncur et al., 2005). These pH 5.5 plateaus are attributed to acid neutralization coupled with siderite dissolution in the absence of calcite.

Dissolution of primary carbonates can promote precipitation of secondary siderite in the presence of Fe(II) released derived from sulfide-mineral oxidation (Al et al., 2000; Jurjovec et al., 2002). Subsequent depletion of calcite, dolomite, and/or ankerite due to sustained oxidation is generally followed by an abrupt decline in pore-water pH (Jurjovec et al., 2002). This decline can be moderated *via* dissolution of secondary siderite stored during the dissolution of primary carbonates. This reaction proceeds at $\text{pH} < 6$ and consumes two moles of H^+ per mole of siderite, while liberating one mole of Fe(II) and two moles of carbonic acid (H_2CO_3):



However, subsequent Fe(II) oxidation and Fe(III) hydrolysis (eqs. 2, 3) produces two moles of H^+ per mole of siderite. These reactions may occur upon discharge of tailings pore water to oxic environments including seeps and surface waters. Despite temporarily limiting decreases in pore-water pH, siderite dissolution ultimately provides no net increase in acid neutralization capacity.

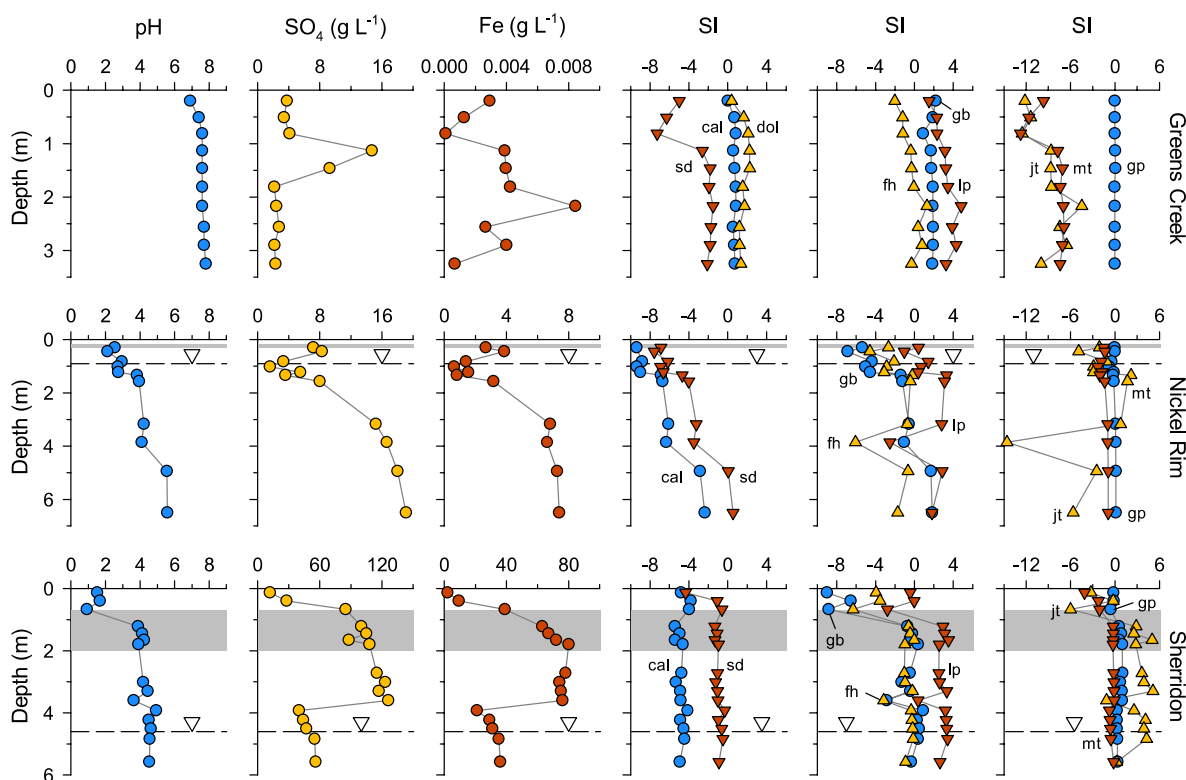


Fig. 3. Depth profiles of pore-water chemistry (pH, SO₄, Fe) and modeled saturation indices (SI; cal: calcite; dol: dolomite; sd: siderite; gb: gibbsite; fh: ferrihydrite; lp: lepidocrocite; gp: gypsum; jt: jarosite; and mt: melanterite) for Greens Creek (GC; TC2-2009), Nickel Rim (NR; NR1-1992; after Johnson et al., 2000), and Sherridon (SG; S3-2001; after Moncur et al., 2005). Shaded regions represent vertical extent of hardpan. Dashed line with gradient symbol denotes water table elevation. The water table in the Greens Creek tailings was positioned more than 10 m below the tailings surface.

4.2. (Oxy)hydroxide dissolution

In contrast to equilibrium with respect to carbonate minerals, equilibrium with respect to Al and Fe (oxy)hydroxides produces pH plateaus at approximately 4 and 3, respectively. These phases accumulate within tailings as a result of sulfide-mineral oxidation, aluminosilicate dissolution, and subsequent carbonate dissolution (Blowes et al., 1991; Jurjovec et al., 2002; Gunsinger et al., 2006b). Extensive sulfide oxidation can generate highly acidic pore waters characterized by high dissolved Fe concentrations (Moncur et al., 2005). Consequent dissolution of aluminosilicate minerals within the sulfide oxidation zone also contributes Al to solution (Blowes et al., 1991; Jurjovec et al., 2002). Iron(III) and Al (oxy)hydroxide phases precipitate below the oxidation zone as acidic pore water migrates downward and is neutralized *via* carbonate mineral dissolution (Moncur et al., 2005). These (oxy)hydroxides subsequently contribute to acid neutralization following depletion of carbonate minerals due to sustained sulfide-mineral oxidation. Under acidic conditions, equilibrium dissolution of these phases consumes H⁺ and liberates either Fe(III) or Al:



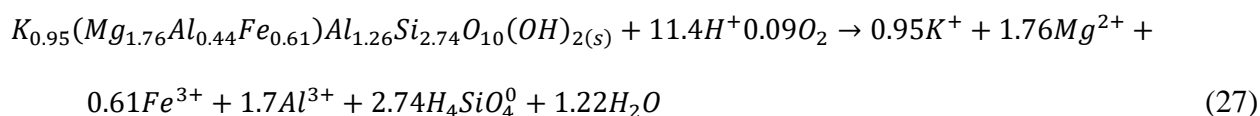
Pore water within zones of (oxy)hydroxide dissolution is therefore characterized by pH ranging from approximately 2.5 to 4 and high dissolved Fe(III) and Al concentrations.

Tailings deposits at the Nickel Rim and Sherridon mines exhibit pH plateaus characteristic of (oxy)hydroxide dissolution. Pore water within the oxidation zone of the Nickel Rim tailings deposit exhibited acidic pH values between 2 and 3 (Fig. 3), and was undersaturated with respect to Fe(III) (oxy)hydroxides (Johnson et al., 2000). An underlying zone of Al(OH)₃ dissolution was apparent from a pore-water pH 4 plateau corresponding to pore water at or near saturation with respect to Al(OH)₃ (Johnson et al., 2000). In contrast to the Nickel Rim mine, a pH plateau characteristic of Fe(III) (oxy)hydroxide dissolution was not observed in the Camp deposit at the Sherridon mine. The absence of this plateau may result from the preferential formation of secondary Fe (hydroxy)sulfates; however, Fe(III) (oxy)hydroxides including ferrihydrite and lepidocrocite were observed in the Sherridon tailings (Moncur et al., 2005). A pore-water pH plateau at approximately 4.3 was attributed to Al(OH)₃ dissolution below the oxidation zone (Moncur et al., 2005). Geochemical modeling indicated that pore water was at or near saturation with respect to gibbsite [Al(OH)₃] (Fig. 3). Similar results have been reported for other sulfide tailings deposits (Blowes et al., 1991; Gunsinger et al., 2006b).

4.3. Silicate dissolution

Silicate dissolution has potential to contribute to acid neutralization in sulfide tailings deposits (Jambor et al., 2002, 2007; Plante et al., 2012). However, the extent of pH buffering depends upon the relative rates of acid production – *via* sulfide-mineral oxidation – and silicate dissolution (Lapakko and Antonson, 2013). In sulfide-rich tailings, silicate dissolution becomes the principal acid-neutralizing reaction following depletion of carbonate and (oxy)hydroxide phases. Although silicate dissolution rates increase under highly acidic conditions, corresponding

pH buffering is generally minimal due to the relatively high rates of acid production (Jambor et al., 2002; Jurjovec et al., 2002; Salmon and Malmström, 2006). Although a pH plateau associated with Fe(III) (oxy)hydroxide dissolution was not observed for the Camp tailings deposit at the Sherridon mine, a pore-water pH plateau at 1.4 was attributed to silicate dissolution within the sulfide-mineral oxidation zone. Silicate dissolution within this zone, which extended roughly 0.9 m below the tailings surface, resulted in the depletion of biotite (Fig. 4), chlorite, and smectite (Moncur et al., 2005). Assuming biotite stoichiometry reported by Moncur et al. (2005), congruent dissolution of biotite at pH less than 3 consumes acid and releases K, Mg, Fe, Al and H_4SiO_4 to tailings pore water according to the following reaction:



High concentrations of both Al and K in tailings pore water at the Sherridon mine are, therefore, indicative of silicate dissolution. Ongoing pyrrhotite oxidation and the limited acid neutralization capacity of remaining silicates resulted in pore-water pH declining to < 1 at some locations within the oxidation zone (Moncur et al., 2005).

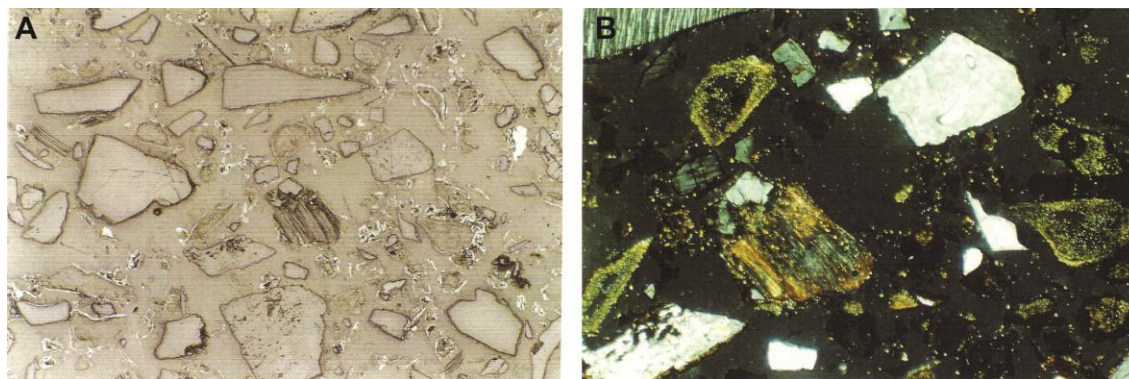


Fig. 4. Photomicrographs of the Sherridon tailings: (A) in plain reflected light showing at the center a pseudomorph after biotite with adjacent low-reflectance pseudomorphs after pyrrhotite (width of field 2.6 mm); and (B) in transmitted light with polarizers crossed showing

replacement of biotite by silica (bluish grey), with the pseudomorphs after pyrrhotite consisting of extremely fine-grained jarosite surrounding (black) voids (width of field 1.25 mm).

Silicate dissolution has potential to buffer pH in low-sulfide tailings, such as those generated from Cu and Ni ores hosted in mafic rocks of the Duluth complex in northeastern Minnesota, USA (Lapakko et al., 2013). Tailings generated from this deposit contain 0.2 wt. % S comprised of pyrrhotite (0.13 wt. % S), chalcopyrite (0.05 wt. % S), and pentlandite (0.02 wt. % S). The tailings also contain calcic plagioclase (~60 wt. %), olivine (~10 wt. %) and augite (~10 wt. %), as well as trace amounts of carbonates. Drainage generated from laboratory weathering of these tailings exhibited circumneutral pH values, which were consistently above 6.4 over the 10-year duration of the experiment (Lapakko et al., 2013). The pH buffering observed in these experiments was largely attributed to the plagioclase dissolution in these low-sulfide tailings. These results are consistent with the findings of Jambor et al. (2007), who reported that calcic plagioclase was a major contributor to the neutralization potential of non-ultramafic rocks.

5. Transport and attenuation

The occurrence of metal(loid)s is constrained by the mineralogical and geochemical composition of tailings solids. However, their mobility in tailings pore-water and drainage is controlled by pH-dependent secondary precipitation-dissolution and sorption-desorption reactions, as well as biogeochemical redox processes (Nordstrom, 2011a). Metals including Fe(III), Al, Zn, and Cu often exhibit high dissolved concentrations and greater mobility in acidic versus circumneutral pH pore waters. In contrast, (hydr)oxyanion-forming elements (e.g., As, Se, Mo, Sb) are often mobile in circumneutral to alkaline pore waters. Elevated concentrations of weakly-hydrolyzing metals including Fe(II), Mn(II), and Zn are common in circumneutral pH pore water. Extremely acidic pore water and drainage may also contain high dissolved

concentrations of (hydr)oxyanion-forming elements (Nordstrom et al., 2000; Moncur et al., 2005; Majzlan et al., 2014; Table 2). However, the transport and attenuation of redox-sensitive elements (e.g., Fe, Mn, As, Se, Sb) is not only dependent upon pH, but also biogeochemical redox processes that determine oxidation states and influence aqueous speciation. Therefore, AMD commonly exhibits high dissolved concentrations of Fe, Al, Cu, Ni, Zn, and Mn (Johnson et al., 2000; España et al., 2005; Moncur et al., 2005; Gunsinger et al., 2006b), whereas elevated concentrations of Ni, Zn, Mn, As, Mo, and Sb may occur in NMD (Dold, 2006; Heikkinen et al., 2009; Lindsay et al., 2009a; Majzlan et al., 2011; Lalinská-Voleková et al., 2012).

5.1. Secondary minerals

The formation of secondary minerals within tailings deposits is a principal control on the transport of sulfide-mineral oxidation products (Blowes et al., 1991; McGregor and Blowes, 2002; Quispe et al., 2013a). Precipitation of Fe(III) (oxy)hydroxides and Fe(III) hydroxysulfates generally occurs within the oxidation zone, whereas hydrated Fe(II) sulfates may precipitate in water-unsaturated tailings below the oxidation zone. Gypsum precipitation may occur within both of these zones. Extensive secondary mineral formation can lead to formation of cemented layers of secondary and primary minerals commonly referred to as hardpan. These layers may limit pore-water migration and oxygen ingress, and, therefore, inhibit sulfide-mineral oxidation within underlying tailings (Blowes et al., 1991; Graupner et al., 2007; Kohfahl et al., 2010; Quispe et al., 2013b). Hardpans are also temporary sinks for other metal(loid)s released during weathering of sulfide tailings (Blowes et al., 1991; McGregor and Blowes, 2002; Moncur et al., 2005; Alakangas and Öhlander, 2006; Gunsinger et al., 2006a, 2006b; Graupner et al., 2007; DeSisto et al., 2011).



Fig. 5. Vertical cross-section of oxidized Camp tailings from the Sherridon Mine. Oxidized zone with discontinuous Fe(III) hardpan (reddish-brown) overlying continuous Fe(II) hardpan (white and gray-blue). Shovel is approximately 0.7 m long.

The mineralogical composition of hardpan layers is influenced by sulfide-mineral oxidation and acid-neutralization reactions. Moncur et al. (2005) observed two distinct zones of secondary-mineral precipitation within the Camp tailings at the Sherridon Mine (Fig. 5). The upper zone was a horizontally discontinuous Fe(III)-rich hardpan layer measuring less than 0.1 m in thickness and located within the oxidation zone. This hardpan was characterized by the presence of ferrihydrite, goethite [α -FeOOH], lepidocrocite [γ -FeOOH], and jarosite [$\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$], and the general absence of secondary Fe(II) phases. The lower zone was a continuous Fe(II)-rich hardpan measuring approximately 1 m thick that was observed below the active oxidation zone. The dominant Fe(II) phases included melanterite [$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$] and rozenite [$\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$]; minor amounts of Fe(III) precipitates including jarosite, goethite, lepidocrocite, and ferrihydrite were also observed. Gypsum was an important component of both the Fe(III) and Fe(II) hardpan layers in the Camp tailings deposit at the Sherridon Mine (Moncur et al., 2005).

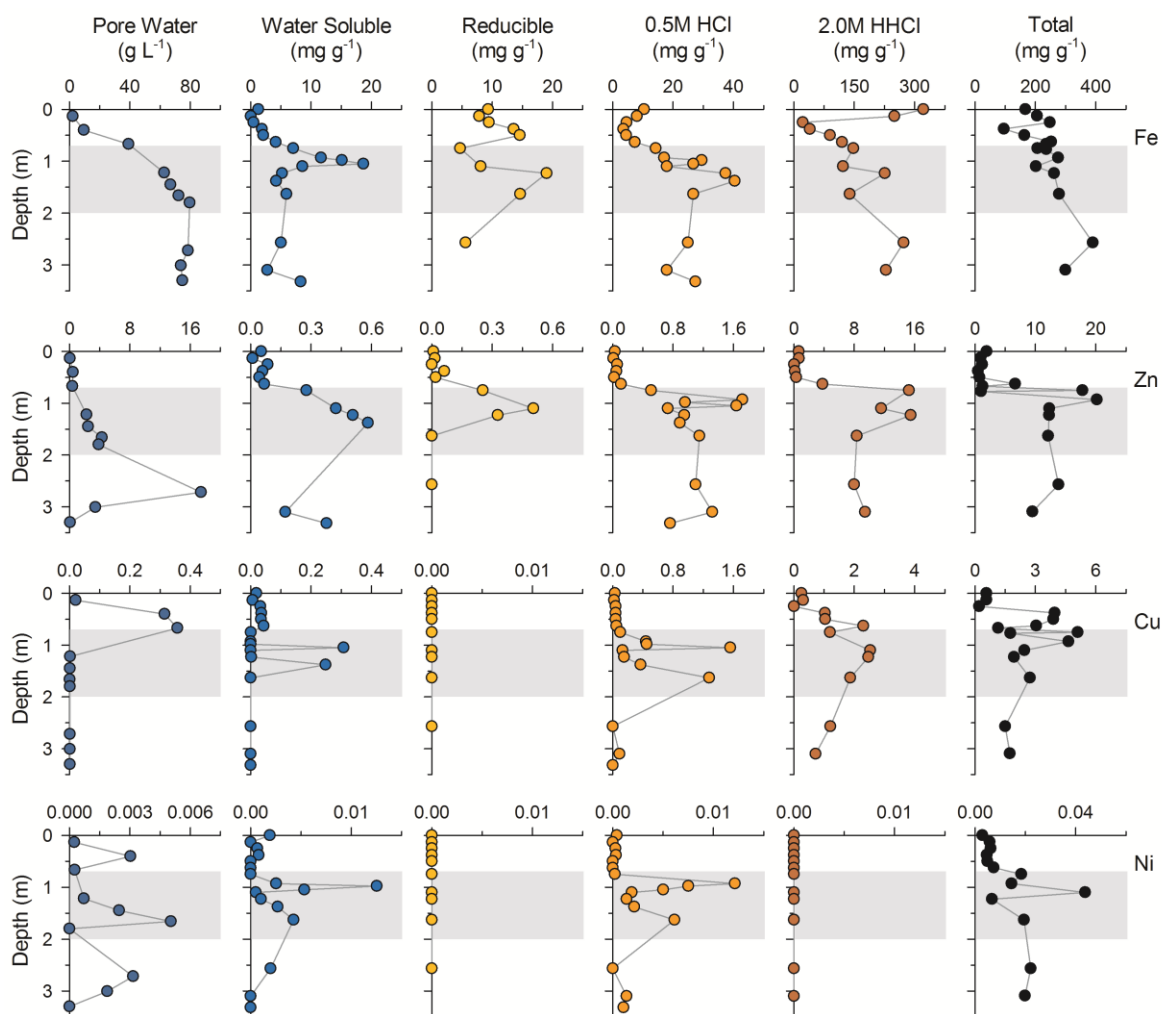


Fig. 6. Depth profiles of pore-water chemistry and selective extraction data for Fe (total), Zn, Cu, and Ni from Camp tailings core samples obtained in 2001. Extractions targeted: (i) water soluble phases (DI water); (ii) amorphous (oxy)hydroxides (ascorbate); (iii) poorly crystalline (oxy)hydroxides, carbonates and adsorbed metals (0.5M HCl); (iv) amorphous + crystalline (oxy)hydroxides and adsorbed metals (2.0M hydroxylamine hydrochloride (HHCl)); and (v) total elemental contents (after Gunsinger et al. 2006b). The shaded region represents the vertical extent of the continuous Fe(II) hardpan.

A horizontally continuous Fe(III) hardpan layer was observed within the Nickel Rim tailings deposit. This hardpan formed within the oxidation zone and was comprised of jarosite, goethite, and gypsum. Although a distinct Fe-bearing hardpan layer was not observed within the Greens

Creek tailings deposit, gypsum precipitation was inferred based upon solid-phase extractions and geochemical modeling. Pore-water within these tailings was consistently at saturation with respect to gypsum and an accumulation of water-soluble SO_4 was observed immediately below the sulfide-mineral oxidation zone (Lindsay et al., 2009a; Lindsay et al., 2011a). Geochemical modeling also suggested that secondary Fe(III) (oxy)hydroxides (e.g., ferrihydrite, lepidocrocite, goethite) precipitate within and below the oxidation zone in the Greens Creek tailings deposit. These modeling results were in general agreement with selective extraction data (Lindsay et al., 2011a).

5.1.1. *Iron(III) (oxy)hydroxides*

The formation of Fe(III) (oxy)hydroxides strongly influences the transport of sulfide-mineral oxidation products within tailings deposits. These secondary precipitates are important sinks for metal(loid)s including Cu, Ni, Zn, As, and Sb (Foster et al., 1998; Alakangas and Öhlander, 2006; Gunsinger et al., 2006b; Parviainen, 2009; Essilfie-Dughan et al., 2012; Lalinská-Voleková et al., 2012). Selective solid-phase extractions performed on Camp tailings highlight contribution of Fe(III) (oxy)hydroxides to metal attenuation (Fig. 6). Results indicate that these phases are present both within and directly above the thick continuous hardpan layer that is positioned below the oxidation zone. Co-precipitation with amorphous to crystalline Fe(III) (oxy)hydroxides likely contributed to Zn and Cu attenuation at these depths. Reducible Fe comprised 54 wt. % of minerals within the tailings hardpan at the Nickel Rim mine. This layer exhibited relative enrichment in total extractable Cu (50 %), Ni (37 %), and Zn (44 %) compared to non-cemented tailings (McGregor and Blowes, 2002).

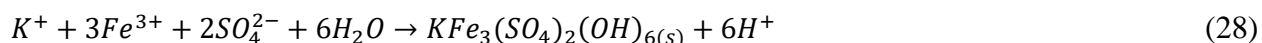
Selective extractions on tailings from the Greens Creek mine revealed that the majority of Fe(III) occurred as amorphous or poorly-crystalline (oxy)hydroxides (Lindsay et al., 2009a). The

amorphous fraction, which was extracted using a weak reductant, was also an important sink for Zn, Ni, As, and Sb. This observation demonstrates that co-precipitation with secondary Fe(III) (oxy)hydroxides is an important control on the transport of these elements. Solid-phase As contents within secondary Fe(III) (oxy)hydroxides can range from less than 2 wt. % to greater than 20 wt. % in weathered sulfide tailings (Walker et al., 2005; Corriveau et al., 2011; Lalinská-Voleková et al., 2012; Parviainen et al., 2012). Additionally, Lalinská-Voleková et al. (2012) observed an average Sb content of 5.7 wt. % for amorphous Fe(III) (oxy)hydroxide coatings on arsenopyrite grains within weathered sulfide tailings. The transformation of poorly crystalline Fe(III) (oxy)hydroxides to goethite or hematite can affect the long-term stability of adsorbed metal(loid)s. Ferrihydrite transformation due to oxidative (Ford et al., 1998) and reductive (Pedersen et al., 2006) transformation has been shown to promote structural incorporation of Mn, Ni, and As(V) into reaction products. Although this process has also been shown to promote net desorption of metals including Pb and Cd, incorporation of metal(loid)s during transformation has potential to enhance their long-term stability within tailings deposits (Ford et al., 1998; Pederson et al., 2006).

Sorption onto Fe(III) (oxy)hydroxides can be an important control on the transport and attenuation of (hydr)oxyanion forming elements including As and Sb (Dixit and Hering, 2003; Leuz et al., 2006). These elements tend to occur as negatively charged species under acidic conditions, where Fe(III) (oxy)hydroxide surfaces exhibit net positive charge (Parks, 1965). As a result, the formation of inner sphere complexes with these surfaces can be an important control on the mobility of As, Sb, and other (hydr)oxyanion-forming metal(loid)s within tailings deposits (Foster et al., 1998; Lindsay et al., 2009a).

5.1.2. Iron(III) hydroxysulfates

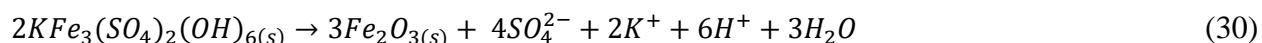
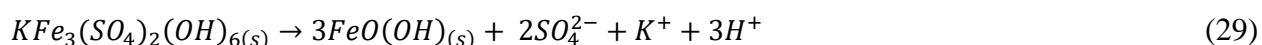
Jarosite precipitation is another important control on dissolved metal(loid) concentrations within sulfide tailings (Blowes et al., 1991; Savage et al., 2000; Gunsinger et al., 2006a; Dold and Fontboté, 2001; Hudson-Edwards and Wright, 2011). Jarosite commonly forms under oxic, low-pH conditions where Fe(III) and SO₄ derived from sulfide oxidation combine with K⁺ from silicate dissolution:



Substitution of Na⁺ or H₃O⁺ for K⁺ in this reaction produces natrojarosite [NaFe₃(SO₄)₂(OH)₆] or hydronium jarosite [H₃OFe₃(SO₄)₂(OH)₆], respectively. The accumulation of jarosite within the oxidation zone and hardpan layers of sulfide-rich tailings has been widely reported (Blowes et al., 1991; McGregor et al., 1998; Johnson et al., 2000; Dold and Fontboté, 2001, 2002; Moncur et al., 2005; Gunsinger et al., 2006a; Hayes et al., 2014). Moncur et al. (2005) found that jarosite was a principal weathering product of sulfide oxidation within Camp tailings at the Sherridon mine. This secondary Fe(III) hydroxysulfate phase was detected throughout the oxidation zone and occurred as a minor phase within the Fe(II) hardpan layer (Moncur et al., 2005). Jarosite precipitated within the hardpan layer of the Camp tailings deposit contained appreciable amounts of Al, which is consistent with Al substitution for Fe in the jarosite-alunite solid-solution series.

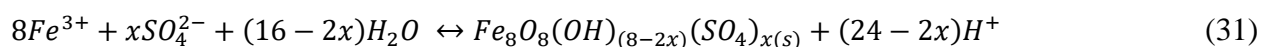
Mineralogical examination of Nickel Rim tailings indicated that abundant jarosite occurred near the lower extent of the oxidation zone (Jambor and Owens, 1993; McGregor et al., 1998; Johnson et al., 2000). Jarosite precipitation is an important mechanism of Fe and SO₄ attenuation within tailings at the Nickel Rim and Sherridon mines. However this secondary Fe(III) hydroxysulfate may also contribute to the attenuation of Cu, Ni, Zn, As, and other elements (Dutrillac and Dinardo, 1983; Dutrillac and Chen, 1984; Savage et al., 2000; Dold and Fontboté,

2001; Hudson-Edwards and Wright, 2011). Attenuation of Cu, Ni and Zn is achieved by substitution at K or Fe sites of jarosite surfaces (Hudson-Edwards and Wright, 2011; Dutrizac and Chen, 1984). Substitution of As(V) tetrahedra for SO₄ in jarosite can also be an important mechanism of As attenuation within oxidized tailings (Foster et al., 1998; Savage et al., 2000; Walker et al. 2009). However, jarosite is metastable due to structural deficiencies (Swayze et al., 2008) and may undergo transformation to Fe(III) (oxy)hydroxides including goethite (eq. 29) or hematite (eq. 30):



Although these reactions release SO₄ to pore water, associated metal(loid)s are likely to be retained by association with goethite or hematite (Acero et al., 2006; Zhao and McLennan, 2013). Additionally, the co-occurrence of these phases within weathered sulfide mine tailings suggests that transformation rates are generally slow.

The metastable Fe(III) hydroxysulfate schwertmannite [Fe₈O₈(OH)_(8-2x)(SO₄)_x] is common in AMD impacted surface waters (e.g., Dold and Spangenberg, 2005; España et al., 2005, 2006; Sidenko and Sherriff, 2005; Kumpulainen et al., 2007), but less common in sulfide tailings deposits (Dold and Fontboté, 2001; Hayes et al., 2014). This metastable hydroxysulfate phase forms under acidic pH conditions (2.8–3.5) by hydrolysis of Fe(III) in the presence of SO₄ (Bigham et al., 1996; Caraballo et al., 2013):

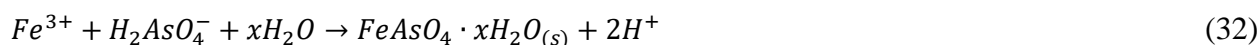


Hayes et al. (2014) also observed schwertmannite formation after ferrihydrite and gypsum with decreasing pH in a sulfide-rich tailings deposit.

Schwertmannite is a potentially important sink for metal(loid)s including Cu, As, Mo, Al and Pb (Dold and Fontboté, 2001; Carlson et al., 2002; Acero et al., 2006; Antelo et al., 2013). However, schwertmannite is metastable and transforms into jarosite and goethite with time (Acero et al., 2006). Dold and Fontboté (2001) suggested that increasing pH resulting from infiltration (i.e., dilution) and acid neutralization promoted transformation of schwertmannite to goethite within sulfide tailings at Chilean Cu-porphyry mines. Acero et al. (2006) reported that a large amounts of Cu, As, Al and Pb were incorporated into jarosite and goethite during these transformations. This finding suggests that schwertmannite could contribute to metal(loid) attenuation within sulfide tailings deposits.

5.1.3. Iron(III) arsenates

Hydrous Fe(III) arsenates are commonly observed in weathered arsenopyrite-bearing tailings deposits. These minerals can include scorodite [$\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$], kaňkite [$\text{FeAsO}_4 \cdot 3.5\text{H}_2\text{O}$], pharmacosiderite [$\text{KFe}_4(\text{AsO}_4)_3(\text{OH})_4 \cdot (6-7)\text{H}_2\text{O}$], yukonite [$\text{Ca}_7\text{Fe}_{12}(\text{AsO}_4)_{10}(\text{OH})_{20} \cdot 15\text{H}_2\text{O}$], and amorphous to poorly crystalline Fe(III) arsenates (Foster et al., 1998; Paktunc et al., 2003; Walker et al., 2009; Corriveau et al., 2011; DeSisto et al., 2011; Parviainen et al., 2012). The precipitation of hydrous Fe(III) arsenate at acidic pH combines Fe(III) and H_2AsO_4^- and generates acid:



Precipitation of hydrous Fe(III) arsenate can control As mobility in tailings pore waters characterized by acidic to circumneutral pH (Krause and Ettel, 1989). The solubility of crystalline scorodite is relatively low at pH 2 to 6, with a minimum solubility of 0.25 mg L^{-1} reported at pH 3 to 4 (Paktunc and Bruggeman, 2010). Amorphous hydrous Fe(III) arsenate can exhibit 100 to 1000 times higher solubility than scorodite depending on the Fe/As molar ratio

(Krause and Ettel, 1989; Paktunc and Bruggeman, 2010). This trend in solubility is attributed to concomitant increases in Fe/As molar ratios and crystallinity (Paktunc et al., 2008).

Although trace amounts of arsenopyrite are present in tailings from the Greens Creek and Sherridon mines (Table 1), discrete Fe(III) arsenate phases were not observed at either site. Hydrous Fe(III) arsenates were, however, an important mechanism of As attenuation in arsenopyrite-bearing tailings at the inactive Ylöjärvi Cu-W-As mine in southwest Finland (Parviainen et al., 2012). These precipitates included crystalline kaňkite, which was detected by synchrotron-based micro-focused X-ray diffraction, poorly crystalline hydrous Fe(III) arsenates identified by micro-focused X-ray absorption spectroscopy (XAS), and associated arsenical Fe(III) (oxy)hydroxides. The poorly-crystalline Fe(III) arsenates observed in the Ylöjärvi tailings contained up to 35 wt. % As(V), which corresponds to a low Fe/As molar ratio of 1.0. Similar results have been reported for highly weathered arsenopyrite-bearing gold tailings (DeSisto et al., 2011; Walker et al., 2009; Jamieson et al., this issue).

5.1.4. *Iron(II) sulfates*

Hydrated Fe(II) sulfates precipitate from acidic waters containing high dissolved concentrations of Fe(II) and SO₄ derived from sulfide-mineral oxidation (Alpers et al., 1994b; Chou et al., 2013). These efflorescent minerals commonly form due to evaporation of AMD discharging from tailings, waste rock, or mine workings (Nordstrom and Alpers, 1999). However, melanterite can also form hardpan layers within sulfide-rich tailings deposits (Fig. 7; Blowes and Jambor, 1990; Blowes et al., 1991, 1992; Dill et al., 2002; Gieré et al., 2003; Moncur et al., 2005; Sidenko et al., 2005). These hardpan layers are typically positioned within the vadose zone, below the depth of active sulfide-mineral oxidation and above the water table

(Blowes et al., 1991; Moncur et al., 2005). Melanterite precipitation can therefore store Fe(II) and SO₄ within the vadose zone of sulfide-rich tailings deposits:



The formation and stability of melanterite is highly dependent upon moisture content or relative humidity. Dehydration of melanterite can form rozenite, whereas increased moisture content will promote melanterite dissolution (Chou et al., 2013).

Melanterite can also incorporate other sulfide-mineral oxidation products including Zn, Cu, and Ni (Blowes et al., 1991; Moncur et al., 2005; Chou et al., 2013). Selective extractions performed on Camp tailings from the Sherridon mine revealed large amounts of water-soluble Fe, Zn, Cu, and Ni (Fig. 6). The highest solid-phase concentrations of these elements were observed within the upper 0.5 m of the continuous Fe(II) hardpan layer. The co-occurrence of these elements within the water-soluble fraction indicates that hydrous Fe(II) sulfates are an important, but temporary, sink for Zn, Cu and Ni within this hardpan layer. This result is consistent with electron microprobe analyses (Moncur et al., 2005) and dissolution experiments performed on melanterite samples obtained from the Sherridon mine. Alpers et al., (1994b) reported preferential uptake of Cu by melanterite relative to Zn. A similar trend is observed in the water-soluble Zn and Cu contents of the Sherridon Camp tailings, despite 10 to 40 times higher pore-water Zn concentrations relative to Cu (Fig. 6). Melanterite and rozenite are both highly soluble and, therefore, infiltration or water-table fluctuations can promote rapid dissolution and release Fe, SO₄, and associated metal(loid)s to pore water (Frau, 2000).

Copiapite [Fe²⁺Fe³⁺₄(SO₄)₆(OH)₂·7H₂O] can also precipitate due to evaporation of AMD waters discharging from mine wastes (e.g., España et al., 2005; Hammarstrom et al., 2005).

Although copiapite was associated with a groundwater seep at the Sherridon mine (Fig. 7), this Fe(II)-Fe(III) sulfate was not observed within the tailings hardpan layer.

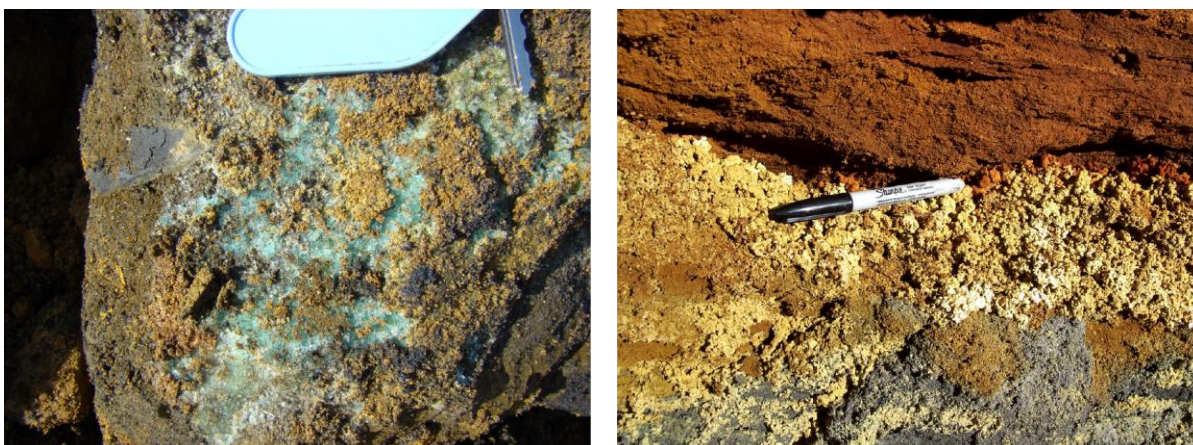


Fig. 7. Secondary iron sulfate minerals in the Camp tailings at the Sherridon mine: (left) melanterite (blue-green) accumulation within continuous hardpan in the Camp tailings (key for scale); and (right) copiapite (yellow) precipitation due to evaporation at pore-water seep from the Woods tailings (marker for scale).

5.1.5. *Gypsum*

Gypsum precipitation controls dissolved Ca and SO₄ concentrations in both AMD and NMD systems (Blowes et al., 1991; Dold and Fontboté, 2002; Moncur et al., 2005; Gunsinger et al., 2006a; Lindsay et al., 2009a). Saturation of pore water with respect to gypsum is common in tailings characterized by active sulfide-mineral oxidation and dissolution of Ca-bearing carbonates (Lindsay et al., 2009a). However, Ca release during silicate dissolution at low-pH can also promote gypsum precipitation in tailings exhibiting high dissolved SO₄ concentrations (Moncur et al., 2005). Although Ca contributed by dolomite dissolution can lead to saturation of pore water with respect to gypsum, Mg released during this reaction has little impact on dissolved SO₄ concentrations. Magnesium sulfates exhibit much higher solubility than gypsum and are, therefore, more likely to form as evaporites at tailings surfaces (Hammarstrom et al., 2005; Acero et al., 2007).

In addition to controlling pore-water Ca and SO₄ concentrations, gypsum precipitation can limit the mobility of potentially toxic elements. For example, the incorporation of As into gypsum has been reported in laboratory studies (Fernández-Martínez et al., 2006; Lin et al., 2013). Lin et al. (2013) observed incorporation of both As(V) and As(III) into the gypsum crystal lattice. The gypsum content of experimental (control) tailings cells at the Greens Creek mine reached $2.3 \pm 0.8 \text{ g kg}^{-1}$ after four years of oxidation (Lindsay et al., 2011a). The largest accumulation of gypsum was observed below the sulfide oxidation zone at a depth of 0.5 m relative to the tailings surface. Small amounts of Tl were associated with the water-soluble fraction from the Greens Creek tailings; however, neither As nor Sb were detected in these extractions (Lindsay et al., 2011a).

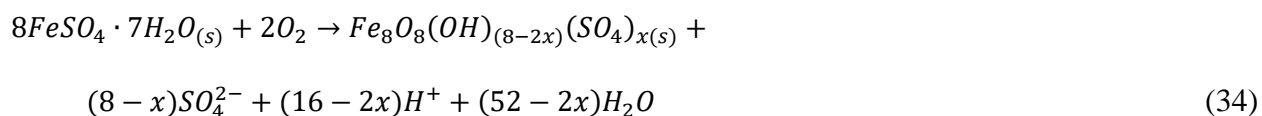
5.2. Redox processes

Sulfide-mineral oxidation is the principal source of SO₄ and metal(loid)s in tailings pore water and drainage; however, the mobility of these reaction products is strongly influenced by secondary redox reactions. The oxidation of dissolved Fe(II) or hydrous Fe(II) sulfates may promote the formation of secondary Fe(III) (oxy)hydroxide and (hydroxy)sulfate phases. However, corresponding O₂ consumption may also promote growth of anaerobic microorganisms below the oxidation zone (e.g., Benner et al., 2000; Lindsay et al., 2009a). The application of cover systems designed to limit oxygen diffusion and infiltration may also promote development of anoxic conditions within underlying tailings (Romano et al., 2003). Microbial Fe reduction can strongly influence the stability of secondary Fe(III) phases and, therefore, the mobility of associated metal(loid)s. Production of H₂S *via* microbial sulfate reduction (DSR) in the absence of O₂ can promote the formation of secondary sulfide minerals (Benner et al., 2000; Hulshof et al., 2003; Fortin et al., 2000). This process can therefore limit

pore-water concentrations and transport of SO_4 , Fe, and other sulfide-mineral oxidation products within tailings deposits (Hulshof et al., 2003, 2006; Moncur et al., 2009; Lindsay et al., 2009b, 2011a, 2011b, 2011c).

5.2.1. Iron oxidation

The oxidation of dissolved Fe(II) to Fe(III) is an important step in sulfide-mineral oxidation under acidic conditions (e.g., eqs. 8, 9, 18–20). However, the oxidation of secondary Fe(II)-bearing minerals may also impact metal(loid) mobility within sulfide tailings deposits. For example, the oxidative transformation of melanterite can promote formation of secondary Fe(III) phases and influence metal (e.g., Ni, Zn) mobility (Zhao and McLennan, 2013). Oxidation of melanterite in the presence of O_2 can lead to the formation of metastable schwertmannite:

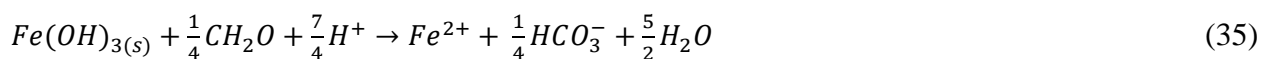


Laboratory experiments by Zhao and McLennan (2013) examined Ni and Zn partitioning during schwertmannite formation after melanterite under acidic conditions (i.e., $\text{pH} < 3$) in the presence of O_2 . Schwertmannite precipitation enhanced Ni uptake from solution, but had little impact on dissolved Zn concentrations. Although schwertmannite is metastable, this phase may serve as a temporary sink for metal(loid)s within some sulfide tailings deposits.

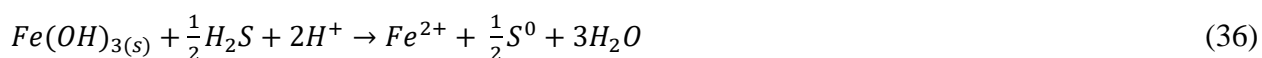
5.2.2. Iron reduction

Reductive dissolution or transformation of Fe(III) (oxy)hydroxides within weathered sulfide tailings has potential to promote release of associated metal(loid)s to pore water (Ribet et al., 1995; Paktunc, 2013). Iron (III) (oxy)hydroxides may be utilized by Fe reducing bacteria as an electron acceptor for anaerobic respiration (Lovley and Phillips, 1988; Hansel et al., 2003).

Heterotrophic Fe reducers couple organic carbon (CH₂O) oxidation with the reduction of Fe(III) (oxy)hydroxides to produce Fe(II) and alkalinity (HCO₃⁻):



Microorganisms from several genera that include Fe reducers have been identified in tailings deposits and sulfide mine wastes (Schippers et al., 2010 and references therein). However, growth of Fe reducing bacteria may be limited by carbon availability within tailings deposits characterized by elevated activity of SO₄ reducing bacteria (Praharaj and Fortin, 2008). Under these conditions, abiotic Fe(III) reduction may therefore proceed with H₂S as the electron donor (Li et al., 2006):



Iron(II) released *via* this process may also promote reductive transformation of Fe(III) (oxy)hydroxides to Fe(II,III) phases including magnetite (Hansel et al., 2003):



In tailings deposits with organic carbon additions, these reactions can have a profound influence on transport of sulfide-mineral oxidation products. In particular, these reactions may affect the mobility of metal(loid)s including Cu, Ni, Zn, As, and Sb, which are commonly attenuated by co-precipitation or sorption reactions with Fe(III) (oxy)hydroxides.

Paktunc (2013) examined the geochemical and mineralogical evolution of oxidized As-bearing sulfide tailings following application of a biosolids cover. Synchrotron-based XAS revealed association of As(V) with the secondary goethite rims on primary sulfides. Following application of the biosolids cover, Paktunc (2013) observed disappearance of these rims combined with an increase in the proportion of As(III) species. Corresponding increases in

dissolved Fe and As concentrations were attributed to reductive dissolution of these goethite rims.

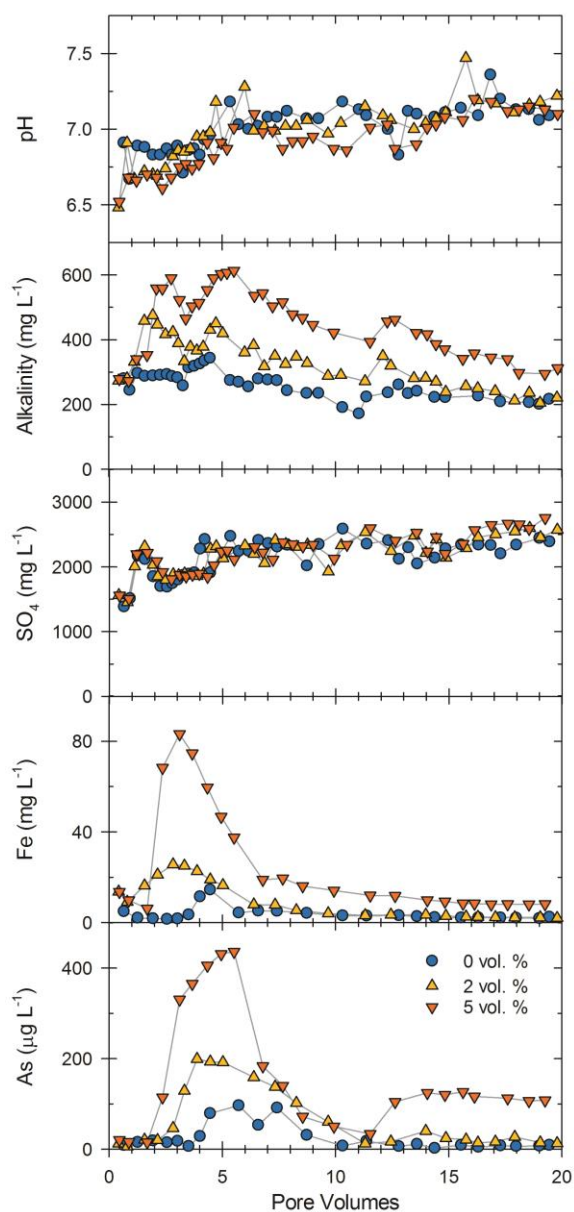


Fig. 8. Column effluent chemistry for Greens Creek tailings amended with differing amounts of organic carbon (after Lindsay et al., 2011b).

Column experiments performed by Lindsay et al. (2011b) revealed a distinct relationship between organic carbon content and effluent Fe and As concentrations (Fig. 8). Simulated NMD water was passed through three columns containing tailings from the Greens Creek mine

amended with organic carbon. Increases in the organic carbon content generally corresponded to increased alkalinity production and higher effluent Fe and As concentrations. This observation suggests that organic carbon amendments promoted the reduction of Fe(III) (oxy)hydroxides and the corresponding release of Fe and As to tailings pore water. These findings are also consistent with results of long-term field experiments to examine the potential for promoting SO_4 reduction as a tailings management strategy (Lindsay et al., 2009b, 2011a, 2011b, 2011c). In these experiments, the addition of organic carbon initially increased As and, to a lesser extent, Fe concentrations in tailings pore waters (Fig. 9). The magnitude of these increases generally corresponded to the availability of organic carbon; however, subsequent decreases in As and Fe concentrations were observed under SO_4 -reducing conditions (Lindsay et al., 2011a).

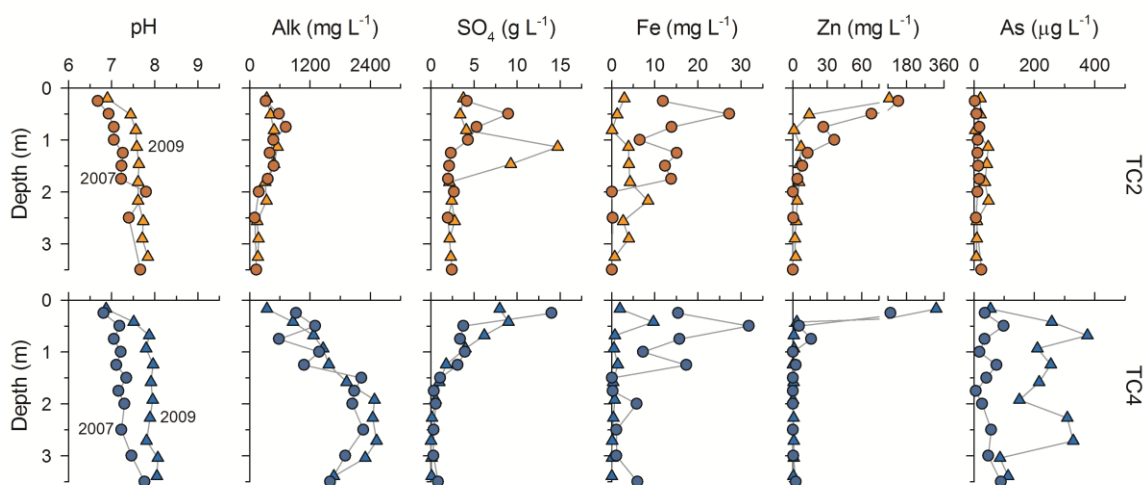


Fig. 9. Pore-water chemistry of non-amended (TC2) and organic carbon amended (TC4; 2.5 vol. % peat + 2.5 vol. % spent brewing grain) Greens Creek tailings for 2007 and 2009 sampling campaigns.

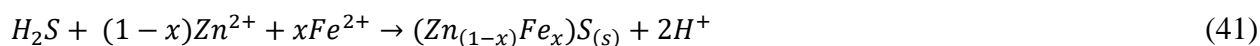
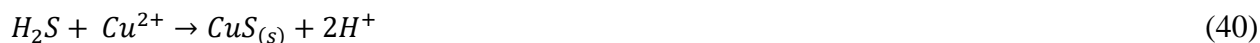
5.2.3. Sulfate reduction

Sulfate reduction can promote the attenuation of sulfide-mineral oxidation products within tailings deposits (Blowes et al., 1996; Hulshof et al., 2003, 2006; Lindsay et al., 2009b, 2011a).

Sulfate-reducing bacteria grow under anoxic conditions within sulfide mine tailings deposits over a range of pH conditions (Fortin et al., 2000; Schippers et al. 2010 and references therein). However, growth of SO_4 reducing bacteria and SO_4 -reduction rates are largely determined by physiological factors including pH, temperature, and the availability of nutrients and labile organic carbon (Praharaj and Fortin, 2008; Winch et al., 2008, 2009). Heterotrophic SO_4 -reducing bacteria catalyze SO_4 reduction coupled with organic carbon (CH_2O) oxidation to produce H_2S and alkalinity:



Many metals including Fe, Cu and Zn exhibit low solubility as sulfides. Hydrogen sulfide production can, therefore, promote the precipitation of mackinawite [FeS], covellite [CuS], sphalerite, and other secondary metal sulfides:



Secondary sphalerite and mackinawite are potentially important sinks for other metal(oids) within sulfide tailings deposits (Lindsay et al., 2011a). Mackinawite and biogenic pyrite formation have been linked to attenuation of Cu, Zn and other metal(loid)s in tailings and mining-impacted sediments (Ferris et al., 1987). The precipitation of discrete As sulfides including orpiment [As_2S_3] and realgar [$\alpha\text{-As}_4\text{S}_4$] is limited to acidic pH conditions (Eary, 1992). Therefore, As attenuation is more likely associated with co-precipitation or sorption reactions with secondary Fe sulfides including mackinawite and pyrite (Farquar et al., 2002). Biogenic

sphalerite collected from submerged circumneutral pH sulfide mine workings was also found to contain elevated As concentrations (Labrenz et al., 2000).

Secondary covellite [CuS] is commonly observed in weathered sulfide tailings (Blowes and Jambor, 1990; Blowes et al., 1991; Holmström et al., 1999b; Johnson et al., 2000; Dold and Fontboté, 2001, 2002; Moncur et al., 2005; Gunsinger et al., 2006b). Although SO₄ reduction may promote covellite precipitation, H₂S may also be derived from reduction or disproportionation of intermediate sulfur species (e.g., S⁰, S₂O₃) under anoxic conditions (Jørgensen, 1990; Thamdrup et al., 1993) or from the acid leaching of pyrrhotite (eq. 10) or sphalerite (eq. 12). The presence of covellite has been attributed to Cu(II) replacement of Fe(II) and Zn within pyrite and sphalerite, respectively (Blowes and Jambor, 1990) and Cu(II) reaction with pyrrhotite (Wang et al., 1989). Covellite may also form as an intermediate reaction product during Fe(III) leaching of chalcopyrite under acidic conditions (Córdoba et al., 2008):



Subsequent oxidation of this intermediate covellite by Fe(III) produces Cu(II), Fe(II), and elemental S (Córdoba et al., 2008):



Combining these reactions gives the overall chalcopyrite oxidation reaction (eq. 19) described by Rimstidt et al. (1994). Regardless of formation mechanism, covellite may limit Cu mobility under both AMD and NMD conditions.

Organic carbon amendment of sulfide mine tailings to promote SO₄ reduction has been evaluated as a tailings management strategy (Hulshof et al., 2003, 2006; Lindsay et al., 2009b, 2011a, 2011b, 2011c; Hwang et al., 2012). Hulshof et al. (2003, 2006) observed enhanced SO₄ reduction and the corresponding removal of dissolved Fe and Zn within sulfide tailings amended

with organic substrates. Lindsay et al. (2009b, 2011a, 2011b, 2011c) conducted longer-term field experiments at the Greens Creek mine to assess potential for SO_4 reduction and metal(loid) attenuation in tailings using amendments consisting of varied mixtures of organic carbon. These mixtures of multiple organic carbon sources sustained SO_4 reduction, alkalinity production, and metal(loid) removal for several years (Lindsay et al., 2011a). Extensive SO_4 removal was observed within tailings amended with 5 vol. % organic carbon (TC4) divided equally between peat and spent brewing grain (Fig. 9). The formation of biogenic Zn sulfides was a major sink for dissolved Zn and S within these amended tailings (Lindsay et al., 2009b, 2011a, 2011b). The development of SO_4 -reducing conditions also corresponded to Fe and As attenuation following an initial period of mobilization. The observed increase in dissolved As concentrations five years after initiating these experiments is attributed to desorption coupled with a slight increase in pore-water pH (Fig. 9). The long-term effectiveness of this tailings management strategy was limited by the availability of labile organic carbon for SO_4 reduction (Lindsay et al., 2011b). Enzyme assays performed by McDonald et al. (2012) indicated that cellulose degradation likely became a limiting factor in the availability of labile organic carbon in amended tailings at the Greens Creek mine. Nutrient availability and seasonal temperature variations may also influence SO_4 -reduction rates (Praharaj and Fortin, 2008). In summary, inducing growth of SO_4 -reducing bacteria and SO_4 reduction through organic carbon amendment of sulfide mine tailings has potential to reduce mass transport of SO_4 , Fe, Zn, and some other metal(loid)s.

Conclusions

Research conducted at the Greens Creek, Nickel Rim, and Sherridon mines over the past 20 years has contributed to our understanding of the geochemical and mineralogical evolution of sulfide mine tailings. These and other studies discussed in this review highlight the complex

array of geochemical and mineralogical processes that occur within sulfide tailings deposits. The oxidation of pyrite, pyrrhotite and other sulfide minerals releases SO_4 , Fe and associated metal(loid)s to tailings pore water. Acid generation associated with this process is neutralized in the presence of carbonate minerals to maintain circumneutral pH conditions. Consumption of carbonate minerals due to ongoing sulfide-mineral oxidation often precedes a transition to acidic pH conditions. The resulting pH strongly influences concentrations and mobility of metal(loid)s released during sulfide mineral oxidation. Metals including Fe, Al, Zn, Cu, and Pb generally exhibit greater mobility under acidic pH conditions. In contrast, weakly hydrolyzing metals (e.g., Fe(II), Zn, Cd) and (hydr)oxyanion-forming elements (e.g., As, Se, Sb) tend to exhibit greater mobility under circumneutral pH conditions. Finally, a series of secondary redox reactions, including Fe(II) oxidation, Fe(III) reduction, and SO_4 reduction can strongly influence the mobility of metal(loid)s within tailings deposits. Understanding how the complex interactions between these processes impact the release, transport and attenuation of sulfide-mineral oxidation products is critical for anticipating and mitigating potential environmental impacts associated with sulfide tailings.

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