Mine drainage from the weathering of sulfide minerals and magnetite

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A B S T R A C T
Pyrite and pyrrhotite are the principal minerals that generate acid drainage in mine wastes. Low-pH conditions derived from Fe-sulfide oxidation result in the mobilization of contaminant metals (such as Zn, Cd, Ni and Cr) and metalloids (such as As) which are of environmental concern. This paper uses data from detailed mineralogical and geochemical studies conducted at two Canadian tailings impoundments to examine the mineralogical changes that pyrite, pyrrhotite, sphalerite and magnetite undergo during and after sulfide oxidation, and the subsequent release and attenuation of associated trace elements. The stability of sphalerite in tailings impoundments generally is greater than that of pyrrhotite, but less than pyrite. Dissolved Ni and Co derived from Fe sulfides, and to a lesser extent, dissolved Zn and Cd from sphalerite, are commonly attenuated by early-formed Fe oxyhydroxides. As oxidation progresses, a recycling occurs due to continued leaching from low-pH pore waters and because the crystallinity of Fe oxyhydroxides gradually increases which decreases their sorptive capacity. Unlike many other elements, such as Cu, Pb and Cr, which form secondary minerals or remain incorporated into mature Fe oxyhydroxides, Zn and Ni become mobile. Magnetite, which is a potential source of Cr, is relatively stable except under extremely low-pH conditions. A conceptual model for the sequence of events that typically occurs in an oxidizing tailings impoundment is developed outlining the progressive oxidation of a unit of mine waste containing a mixed assemblage of pyrrhotite and pyrite.

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1. Introduction

Pyrite [FeS₂] is the most abundant metal sulfide associated with the Earth’s crust (Rimstidt and Vaughan, 2003; Murphy and Stron- gin, 2009) and contributes significantly to the world’s acid drainage through natural weathering or from anthropogenic activities. However, in many mineral deposits, pyrrhotite [Fe₁₋ₓS] is also a significant contributor of acid drainage. The oxidation of Fe-sulfide minerals and the subsequent generation of acidity may lead to destructive impacts to receiving ground and surface waters (Blowes and Jambor, 1990; Nordstrom and Alpers, 1999; Johnson et al., 2000; Levings et al., 2005; Moncur et al., 2006). Low-pH effluent is the primary concern in wastes from sulfide-bearing metalliferous deposits where potentially toxic metals and metalloids are solubilized and become mobile in the low-pH pore waters. This paper presents a review of the behavior of pyrite, pyrrhotite, sphalerite [ZnS], and magnetite [Fe²⁺Fe³⁺O₄] based on geochemical and mineralogical data from over 30 tailings impoundments studied by the authors worldwide with specific examples from the Sherritt–Gordon tailings in Sherridon, Manitoba, Canada, where detailed mineralogical and geochemical characterization has been conducted (Fig. 1). The focus of this paper is primarily on the mineralogical changes that develop during sulfide oxidation, and on the behavior of the principal trace elements that are released by the oxidation of the sulfide minerals.

2. Oxidation of the sulfide minerals

The oxidation of pyrite, pyrrhotite, sphalerite and magnetite may be written as follows:

\[
\begin{align*}
\text{pyrite:} & \quad \text{FeS}_2 + \frac{15}{4} \text{O}_2 + \frac{7}{2} \text{H}_2\text{O} \rightarrow 2\text{SO}_4^{2−} + \text{Fe(OH)}_3 + 4\text{H}^+ \\
\text{pyrrhotite:} & \quad \text{Fe}_1\text{–xS} + \left(2 - \frac{x}{2}\right) \text{O}_2 + x\text{H}_2\text{O} \rightarrow \text{SO}_4^{2−} + (1-x)\text{Fe}^{2+} + 2x\text{H}^+ \\
\text{sphalerite:} & \quad \text{ZnS} + 2\text{O}_2 \rightarrow \text{Zn}^{2+} + \text{SO}_4^{2−} \\
\text{magnetite:} & \quad \text{Fe}^{2+}\text{Fe}^{3+}\text{O}_4 + \frac{9}{2} \text{H}_2\text{O} \rightarrow 3\text{Fe(OH)}_3
\end{align*}
\]

These simplified equations, where Fe(OH)₃ is a replacement for ferrihydrite [5Fe₂O₃·9H₂O], do not adequately describe the complex reactions that occur in the oxidation process. For example, the oxidation of pyrite involves a series of multiple reactions to achieve the end product in Eq. (1) (Garrels and Thompson, 1960; Nordstrom and Southam, 1997; Druschel et al., 2004). Reactions involving pyrrhotite in Eq. (2) are similarly complex and do not always express...
the amount of acid generated by the mineral (Nicholson and Scherer, 1994; Janzen et al., 2000). Crystal-structure vacancies related to the Fe deficiency in pyrrhotite may allow the vacancy-associated Fe$^{2+}$ to waiver between Fe$^{2+}$ and Fe$^{3+}$ valence states, thereby potentially destabilizing defect structures that are more easily broken than those of pyrite and oxidize more rapidly than pyrite (Jambor, 2003; Murphy and Strongin, 2009). The presence of Fe$^{3+}$ in pyrrhotite may increase the rate of oxidation of Fe$^{2+}$ to Fe$^{3+}$ which in turn will accelerate the oxidation of pyrite and pyrrhotite by Fe$^{3+}$ through:

$$\begin{align*}
\text{Fe}_{(1-x)}S + (8-2x)\text{Fe}^{2+} + 4\text{H}_2\text{O} &\rightarrow (9-3x)\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 8\text{H}^+ \\
\text{Fe}_2\text{S}_2 + 14\text{Fe}^{3+} + 8\text{H}_2\text{O} &\rightarrow 15\text{Fe}^{3+} + 2\text{SO}_4^{2-} + 16\text{H}^+ 
\end{align*}$$

(5)

(6)

The oxidation of pyrite and pyrrhotite in Eqs. (5) and (6) is more rapid than oxidation by atmospheric O$_2$ in Eqs. (1) and (2) (Nordstrom, 1982), and with the dissolution of pyrrhotite, Fe$^{3+}$ may be released.

Although pyrite and pyrrhotite are the primary concerns with regard to the dissolution of Fe-bearing sulfide minerals, sphalerite, magnetite and other Fe-bearing minerals are commonly overlooked as potential candidates for contributing to mine drainage. Sphalerite is commonly Fe-bearing, magnetite contains both Fe(II) and Fe(III), and other minerals that contain Fe (e.g., siderite [FeCO$_3$]; biotite [K(Fe)$_3$AlSi$_3$O$_{10}$(OH)$_2$]), may provide an additional input to acid generation through the oxidation of Fe(II) and hydrolysis of Fe(III) as described by the reactions:

$$\begin{align*}
\text{Fe}^{2+} + \frac{1}{4}\text{O}_2 + \text{H}^+ &\rightarrow \text{Fe}^{3+} + \frac{1}{2}\text{H}_2\text{O} \\
\text{Fe}^{3+} + 3\text{H}_2\text{O} &\rightarrow \text{Fe(OH)}_3 + 3\text{H}^+
\end{align*}$$

(7)

(8)

where one mole of acid is consumed in Eq. (7), but three are released in Eq. (8).

2.1. Trace-element mineral associations

Trace elements associated with pyrrhotite are Ni and, to a lesser extent, Co (Gunsinger et al., 2006b). The same association applies to pyrite, however, pyrite may be arsenical (Paktunc, 2008). The association of Au with As-bearing pyrite (Cook and Chryssoulis, 1990; Fleet et al., 1993; Palenik et al., 2004) results in ineffective cyanidation unless the pyrite is artifically oxidized (McCreadie et al., 2000). Following ore processing, the arsenical pyrite and arsenical residues are commonly stored within tailings facilities, and subsequent dissolution and mobilization of the As is an environmental concern.

Sphalerite is the principal source of Zn and Cd in mine tailings. Sphalerite may be present in percentages at sites, where Zn recovery was not included in the concentration process, as was the case in the early years of milling at the former Sherritt–Gordon Mine in Manitoba, Canada (Farley, 1949). Also, Fe typically substitutes partially for Zn in sphalerite (Pring et al., 2008) and can affect the flotation process potentially decreasing recoveries (Walker, 1930; Gigowski et al., 1991; Zieliński et al., 2000). The oxidation and dissolution rates of sphalerite also have been observed to increase with increasing Fe content in the mineral (Perez and Dutrizac, 1991; Weisener, 2002; Blowes et al., 2003). In laboratory studies, both low-Fe and high-Fe sphalerites have been observed to show a rapid initial dissolution rate with release of Zn from the mineral surface, followed by a much slower rate of reaction (Buckley et al., 1989; Giudici et al., 2002; Weisener et al., 2003; Stanton et al., 2008).

The structure of sphalerite can lead to substitution by a wide variety of ions in percentage amounts, such as Cu, Mn, In, Fe and Cd (de Giudici et al., 2002). Up to 13.4 mol% Cd has been incorporated in synthetic sphalerite at 600 °C (Maurel, 1978), but in most natural occurrences the Cd content is <1 wt.% (Doménech et al., 2002; Moncur et al., 2005; Koski et al., 2008; Pring et al., 2008). The larger atomic radius of Cd relative to that of Zn prefers the wurtzite-type structure (hexagonal ZnS) over that of sphalerite (Patrick et al., 1998).
Magnetite in sulfide-bearing mine wastes is of interest because the mineral forms a solid-solution series with chromite \([\text{Fe}^{2+}\text{Cr}_2\text{O}_4]\) and other members of the spinel group, and can be Cr-bearing (Kadziella-Kofmold et al., 2008). Although the common rock-forming minerals such as chlorite, mica, amphibole and pyroxene may contain trace amounts of Cr (Tischendorf et al., 2001; Jambor et al., 2002), in most of the oxidized tailings impoundments investigated by the authors, the presence of dissolved concentrations of Cr have been observed to coincide with the presence of Cr-bearing magnetite in the tailings (e.g., Moncur et al., 2005; Gunsinger et al., 2006b).

3. Mineralogical and geochemical behavior

The relative resistance of various sulfide minerals to oxidation in tailings impoundments has been documented previously (Jambor, 1994; Jambor and Blowes, 1998; Plumlee, 1999; Gunsinger et al., 2006a; Koski et al., 2008). An updated version of the relative resistance, as observed by optical microscopy of field samples from several tailings sites is presented in Table 1. The listing serves as a guide to the susceptibility of the sulfide mineral to oxidation where the textures and grain sizes are similar. It is also important to recognize that: (i) a ‘persistence’ effect may be present and (ii) the order applies to primary minerals. An example of the persistence effect would be the opposite behaviors of galena \([\text{PbS}]\) and sphalerite during oxidation. Although exceptions are common in carbonate-rich environments, where the replacement of Fe-bearing sphalerite is by Fe oxhydroxides (Bertorino et al., 1995; Fanfani et al., 1997; Boulet and Larocque, 1998) or Fe oxhydroxides and sulfur (Jeong and Lee, 2003), in sulfate-rich systems derived from sulfide mine wastes that generate acid drainage, the dissolution of sphalerite typically occurs without the formation of alteration rims that partly or completely pseudomorph the sphalerite. The solubilization of sphalerite typically occurs by particle-size reduction rather than replacement by secondary minerals. Sphalerite dissolution and the subsequent precipitation of smithsonite \([\text{ZnCO}_3]\) has been suggested as a control for dissolved Zn concentrations (e.g., Nordstrom and Alpers, 1999; Bain et al., 2001; Malmstrom et al., 2008), however, secondary smithsonite has not been identified in sulfide-containing tailings impoundments. The absence of secondary smithsonite in sulfide tailings could be due to difficulties in identifying minute masses of secondary smithsonite or due to the high solubility of smithsonite in low-pH waters. Alternatively, Zn concentrations could also be controlled by the precipitation of other Zn bearing minerals, such as Fe oxhydroxides. The behavior of magnetite seems to be similar to that of sphalerite, but because the magnetite content of most non-calcareous sulfide deposits is low, the first appearance of magnetite is typically below the zone of intense oxidation.

The ‘persistence’ effect is demonstrated by galena, when compared to sphalerite, which forms a rim of anglesite \([\text{PbSO}_4]\) during oxidation. Due to the lower solubility of galena, the formation of secondary anglesite rims slows the progress of further replacement but does not completely retard it. Therefore, although galena and sphalerite are similar in reactivity, galena may persist in a strongly oxidized environment that has removed sphalerite. Similar alteration rim or retardation applies to other minerals, such as pyrrhotite and arsenopyrite, except for enargite \([\text{Cu}_3\text{AsS}_4]\), where the effects are much less pronounced.

The limitation concerning the oxidation of primary minerals is marcasite \([\text{FeS}_2]\). Laboratory experiments have shown a similar (Wiersma and Rimstidt, 1984) or greater reactivity for marcasite than for pyrite (Rinker et al., 1997; McGuire et al., 2001; Uhlig et al., 2001; Elsetinow et al., 2003) but the reaction rates vary widely. The placement of marcasite in Table 1 refers only to primary marcasite of a homogeneous texture and grain size similar to that of the associated pyrite. This condition is stressed because marcasite is commonly a secondary mineral that forms rims and pseudomorphs after pyrrhotite in the early stage of oxidation (Blowes and Jambor, 1990). This type of marcasite is typically heterogeneous on a μm or finer scale, and in this form it seems to be a metastable transitional mineral that very readily alters to goethite (Jambor, 2003).

The stabilities of the various sulfide minerals can be illustrated by the sulfide alteration index (SAI), which is a practical method of mapping the changes observed in the appearance and disappearance of the sulfide minerals through a vertical profile of a tailing impoundment. The SAI was first constructed by Blowes and Jambor (1990) for a series of cores through the Waite Amulet tailings impoundment near Noranda (Quebec, Canada). An example of a SAI for the tailings from the Sherritt–Gordon mine at Sherridon (Manitoba, Canada) is described and illustrated in Table 2 and Fig. 2. At both sites the ore deposit consisted of volcanogenic massive sulfides and the tailings contain pyrite and pyrrhotite. The Sherridon site is used to illustrate the mineralogical and geochemical changes that typically occur in a sulfide oxidation profile.

The Sherritt–Gordon mine at Sherridon operated from 1931–1932, and from 1937–1951, during which 7.7 Mt of pyritic ore grading 2.45% Cu, 2.97% Zn, 19.9 g tons\(^{-1}\) Ag and 0.62 g tons\(^{-1}\) Au were milled, however a Zn concentrate was not produced until 1942 (Farley, 1949). The sulfide assemblage consisted of mainly pyrite and pyrrhotite with lesser amounts of chalcopyrite, sphalerite, and minor amounts of only a few other minerals, including arsenopyrite \([\text{FeAsS}]\), cubanite \([\text{CuFeS}_2]\) and local occurrences of galena. The tailings were discharged into two impoundments, the older of the two is briefly referred to in the following; a more detailed description is in Moncur et al. (2005).

The tailings, with groundwater temperatures ranging from 6.0–15.5 °C, have been oxidizing for over 70 a and have formed a continuous ochreous hardpan that is >1 m thick. Near the center of the impoundment the tailings extend to a depth of 7 m and the water table is at a depth of approximately 4 m, however the top of the hardpan located at 0.90 m marks the zone where the tailings are variably water-saturated. The unsaturated zone above the hardpan has a high SAI, is depleted in sulfides and carbonates, and the pore gas-phase \(\text{O}_2\) concentrations show a rapid downward decrease to a depth of 0.5 m that reflects \(\text{O}_2\) consumption by sulfide oxidation (Fig. 3). In contrast to the deeper continuous hardpan that begins at 0.90 m, the unsaturated, near-surface zone contains only thin (1–10 cm) layers of Fe oxhydroxide precipitates lacking lateral continuity, and which can be categorized as a discontinuous hardpan. The bulk-sample X-ray data indicate that the zone is rich in gypsum \([\text{CaSO}_4\cdot2\text{H}_2\text{O}]\), jarosite \([\text{(KNa})\text{AlFe}(\text{SO}_4)\text{OH})_2]\), native sulfur (from the oxidation of pyrrhotite), and goethite \([\alpha-\text{FeOOH}]\) (Fig. 4). Optical microscopy revealed that phlogopite \([\text{K(Mg,Fe)}_2\text{AlSi}_3\text{O}_{10}(\text{OH})_2]\) and plagioclase \([\text{(Na,Ca})\text{Al(Si,Al)}_3\text{O}_8]\) have been substantially al-

| Pyrrhotite | Fe\(_1\cdot5\)S | Low resistance |
| Galena | PbS | |
| Sphalerite | (Zn,Fe)_3S | |
| Bornite | CuFeS | |
| Pentlandite | (Fe,Ni)_3S | |
| Arsenopyrite | FeAsS | |
| Marcasite | FeS\(_2\) | |
| Pyrite | FeS | |
| Chalcopyrite | CuFeS\(_2\) | |
| Magnetite | FeO\(_4\) | High resistance |
| Molybdenite | MoS\(_2\) | |
tered, and the X-ray data indicate that chlorite and biotite are depleted (Fig. 4). Replacement of Al-bearing silicates, mainly albite and biotite, by amorphous silica is common in this near-surface zone of the tailings.

Table 2

<table>
<thead>
<tr>
<th>Index</th>
<th>Sulfide alteration index (SAI) of the Sherridon tailings (revised after Blowes and Jambor, 1990; Moncur et al., 2005).</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>Almost complete oxidation of sulfides; traces of chalcopyrite ± pyrite</td>
</tr>
<tr>
<td>9</td>
<td>Only sparse pyrite and chalcopyrite; no pyrrhotite or sphalerite</td>
</tr>
<tr>
<td>8</td>
<td>Pyrite and chalcopyrite common, but chalcopyrite proportion higher than normal possibly because of pyrite dissolution; no pyrrhotite or sphalerite</td>
</tr>
<tr>
<td>7</td>
<td>Pyrite and chalcopyrite proportions normal; pyrrhotite absent but sparse sphalerite present</td>
</tr>
<tr>
<td>6</td>
<td>Pyrrhotite absent but sphalerite common</td>
</tr>
<tr>
<td>5</td>
<td>Pyrrhotite represented by marcasite pseudomorphs</td>
</tr>
<tr>
<td>4</td>
<td>First appearance of pyrrhotite, but only as remnant cores</td>
</tr>
<tr>
<td>3</td>
<td>Cores of pyrrhotite abundant</td>
</tr>
<tr>
<td>2</td>
<td>Well-developed cores of pyrrhotite, with narrower alteration rims; replacement by marcasite decreasing, and pseudomorphs are absent</td>
</tr>
<tr>
<td>1</td>
<td>Alteration restricted to narrow rims on pyrrhotite</td>
</tr>
</tbody>
</table>

Fig. 2. Cross-section through the center of the older Sherridon tailings impoundment, showing the mineralogical changes rated according to a sulfide alteration index (SAI) (after Moncur et al., 2005), which is a relative scale of alteration intensity. At SAI = 10, the sulfides have been almost completely obliterated (Fig. 5); at SAI = 3, remnant cores of pyrrhotite are abundant; at SAI = 1, the alteration occurs only as narrow rims on pyrrhotite (Fig. 6e). A continuous hardpan extends from 90 cm to 2 m. The photo to the right of the SAI plot shows fresh exposed tailings on the left adjacent to extensive development of surface blooms of tertiary rozenite (white mineral) that formed shortly after the Fe²⁺-rich continuous hardpan was exposed to O₂ (right half of the photo). Analysis of the rozenite showed that Zn is present in trace amounts. The static water table is at approximately 4 m below ground surface.

Fig. 3. Variation in O₂ and CO₂ gas, percent sulfur and CaCO₃, volumetric moisture content (Θ) [where Θ = (mass_water/density_water)/volume_total], porosity (n), and saturation, and pore water density, in the Sherridon tailings. The solid horizontal line shows the top of the main hardpan. The static water table is at approximately 4 m below ground surface. Data from Moncur et al. (2005).
The main continuous hardpan zone extends from 0.9 to 2.0 m. Compared to the ochreous, Fe(III)-rich overlying tailings, the main hardpan is blackish and solidly cemented; although the same secondary minerals that have formed in the near-surface zone are also present. The main hardpan is characterized by an enrichment in Fe(II)-sulfate minerals (melanterite \([\text{FeSO}_4 \cdot 7\text{H}_2\text{O}]\) and rozenite \([\text{FeSO}_4 \cdot 4\text{H}_2\text{O}]\) (Fig. 4), and by decreased porosity (Fig. 3) related to the cementation by secondary minerals. Similar enrichments of Fe(II)-sulfate minerals in hardpan layers have been observed in the tailings impoundment at the Heath Steele mine, Newcastle, NB (Blowes et al., 1992), the Renison Bell Tin Mine, Tasmania, Australia (Gilbert et al., 2003) and in mine-waste piles at the Elizabeth Mine, Strafford, VT (Hammarstrom et al., 2005).

4. Progression of sulfide alteration

The unaltered Sherridon tailings contain up to 60 wt.% of combined pyrite and pyrrhotite, with the relative proportion variable from 1:1 to 1:2, respectively. Mineralogical examination of samples from the oxidized zone above the main hardpan shows that the sulfides have been almost completely replaced in the most oxidized material near the surface (Fig. 5). The downward progression is marked by the initial appearance of pyrite, then by the additional appearance of sphalerite and by marcasite pseudomorphs after pyrrhotite (Fig. 6a and b). In other tailings impoundments, Fe oxyhydroxide replacement rims on pyrite are common (Jambor, 2003). At the Sherridon tailings, the oxidation of pyrite is marked by depletion of the mineral. Extensively altered pyrrhotite is first observed at the top of the hardpan layer. The thickness of the alteration rims on pyrrhotite gradually decreases toward the bottom of the hardpan (Fig. 6c and d). The hardpan is a zone of accumulation of secondary minerals, including small amounts of covellite \([\text{CuS}]\). The accumulation zone forms in advance of the sulfide-oxidation front and appears to be migrating downward. The near-surface, Fe(II)-rich zone represents a slightly older and more advanced stage of oxidation which is expected to gradually expand downward approaching the Fe(III)-rich hardpan. Various Fe-sulfate minerals undergo this progression of Fe(II) to Fe(III) transformation as oxidation progresses (Nordstrom and Alpers, 1999; Jambor et al., 2000a).

5. Geochemical variations with depth

Within the Sherridon tailings, sulfide minerals below the permanent water table do not show signs of alteration (SAI = 0). The unaltered tailings solids average 246 mg g\(^{-1}\) Fe, 7.7 mg g\(^{-1}\) Zn, 2.2 mg g\(^{-1}\) Cu, 0.01 mg g\(^{-1}\) Ni, 0.08 mg g\(^{-1}\) Co, 0.005 mg g\(^{-1}\) Cr and 31 mg g\(^{-1}\) Al. Pore waters from the unsaturated zone in the Sherridon tailings locally contain up to 280 g L\(^{-1}\) SO\(_4\), 129 g L\(^{-1}\) Fe, 55 g L\(^{-1}\) Zn, 1.6 g L\(^{-1}\) Cu, 0.02 g L\(^{-1}\) Ni, 0.11 g L\(^{-1}\) Cr, 0.003 g L\(^{-1}\) Co, 0.003 g L\(^{-1}\) Cd and 7.2 g L\(^{-1}\) Al, which in mine-waste settings are among the highest documented values in the world (Moncur et al., 2005). The pH, Eh and distribution of trace elements in the pore waters above and below the permanent water table are illustrated in Fig. 7. High concentrations of Fe, SO\(_4\), and many of the metals coincide with low-pH conditions above the main hardpan and above the permanent water table.

Dissolved Cu in the pore waters is derived from chalcopyrite. Concentrations are highest at the top of the main hardpan, decreasing rapidly to <1.2 mg L\(^{-1}\) at depth. The decrease coincides with the appearance of secondary covellite and melanterite (0.25 wt.% Cu), which appear to act as controls on dissolved Cu.

Dissolved concentrations of Zn and Cd, which are attributed to the dissolution of sphalerite, behave differently. Although Zn was commonly detected in electron-microprobe analyses of the secondary Fe oxyhydroxides (0.10–0.33 wt.% Zn in six samples), the high mobilility and only limited attenuation of Zn is reflected by the high concentrations in the pore water beneath the main
hardpan, as also observed in other sulfide tailings (Blowes et al., 1991; Gunsinger et al., 2006a). Values for Cd, however, are highest within the hardpan, and the distribution is similar to that of dissolved concentrations of Pb and Cr (Fig. 7).

Dissolved Co and Ni concentrations are derived from the oxidation of pyrite and pyrrhotite. Concentrations of dissolved Co, like those of Cu, are highest near the top of the main hardpan, decrease progressively within the hardpan, and are negligible beneath it. The distribution pattern indicates solid-phase attenuation, most likely by sorption or coprecipitation with the Fe oxyhydroxides. In contrast, dissolved Ni is mobile and largely unattenuated.

Chromium has multiple primary sources as it was detected by electron-microprobe analyses in magnetite, biotite and amphibole. As well, almandine garnet \([\text{Fe}^{2+}_7\text{Al}_2(\text{SiO}_4)_3]\) is present in the tailings from the Sherridon sulfide-depleted zone at 20 cm depth. Photo to the left, in plain reflected light, width of field 2.6 mm, shows two adjacent residual grains of chalcopyrite (cp), which are the only remaining sulfides (the whitish grain 'il' on the left is ilmenite \(\text{FeTiO}_3\)). The narrow grey rims, as at the arrow, are Fe oxyhydroxides, mainly goethite. Photo to the right is of the same field, but in plain transmitted light. The black areas are Fe oxyhydroxides that have formed as rims and pseudomorphs after Fe sulfides.

**Fig. 5.** Photomicrographs of the Sherridon tailings; (a–e) are for plain reflected light. (a) Oxidized zone at 60 cm depth, showing complete replacement of pyrrhotite, now represented by blackish pseudomorphs, but with no alteration evident for the whitish grains of pyrite. Width of field is 2.1 mm. (b) Top of the hardpan contact at 90 cm depth, showing unaltered pyrite (py), sphalerite (s, at center), and a grain of chalcopyrite (cp). The zoned grains, as at the arrow, are pseudomorphs after pyrrhotite, wherein the whitish rims are secondary marcasite. Width of field is 2.1 mm. (c) Hardpan contact at 90 cm depth; width of field is 0.625 mm. The white, homogeneous grains are pyrite (py). Pyrrhotite (po, and at the core of the triangular particle at the top) is variably rimmed by marcasite (mr); in the particle at the bottom right no pyrrhotite remains. The large grey grain is sphalerite (sp) containing, at the arrow, an inclusion of former pyrrhotite, now altered to marcasite. (d) Hardpan zone at 116–126 cm depth, showing white unaltered pyrite (py) and weak alteration of pyrrhotite (po) along the rim and basal parting, with a narrow outermost rind of marcasite. Width of field is 0.625 mm. (e) Hardpan zone at 112–118 cm depth, showing cores of pyrrhotite with a thin exterior of marcasite; the intermediate zone is a Fe sulfate, as is indicated by its low reflectance and spectrally high S content. Width of field is 0.625 mm. (f) Basal part of the hardpan zone at 185 cm depth; reflected light, internal reflection, polarizers almost crossed, width of field 0.625 mm. The grains showing the basal parting are marcasite after pyrrhotite, a few remnants of which are present, as at the arrow. The cementing material is yellowish in plain light (whitish in the reproduction), and is apparently a mixture of Fe oxyhydroxide and Fe sulfate. The unaltered grains at the top right and lower left are pyrite (py).
ings, and the Cr-dominant species uvarovite \([\text{Ca}_3\text{Cr}_2(\text{SiO}_4)_3]\) is known to occur in outcrops near the mine (Froese and Goetz, 1981). Although Cr was detected in the Fe oxyhydroxides within the hardpan, the concentrations of dissolved Cr below the hardpan are not substantially lower than those within it (Fig. 7).

Small amounts of arsenopyrite are the principal primary source of As. Speciation of dissolved As concentrations indicates that As(III) is more abundant than As(V), but the distribution of both is similar. The downward profile for \(\text{As}_{\text{total}}\) is like that of Cu, indicating distinct attenuation at the top of the hardpan (Fig. 7). Although a discrete secondary As mineral was not identified in the Sherridon tailings, in other impoundments the sorption of As by Fe oxyhydroxides (Figs. 8 and 9) and substitution in jarosite are of common occurrence (Alpers et al., 1994; Jambor, 1999; Jambor et al., 2000b; Savage et al., 2000; Paktunc and Dutrizac, 2003).

The tailings profile of pore water pH and the downward mobility of dissolved \(\text{SO}_4\) and the metal concentrations is well illustrated in Fig. 7. The oxidation front and the hardpan will continue to move downward over time. For example, covellite that currently serves as a solid-phase sink for Cu will be exposed to oxidizing acid conditions, releasing Cu to the pore waters along with the remobilization of other temporarily attenuated species bound in soluble mineral phases. An example of this type of recycling, specifically for As, has been documented by Courtin-Nomade et al. (2003) for As-rich tailings that have oxidized along a slipped topography. Early attenuation of As occurs in association with amorphous and poorly crystalline Fe oxyhydroxides, such as ferrihydrite (Jambor and Dutrizac, 1998), and As decreases in the solid phase through desorption as goethite becomes the dominant Fe oxyhydroxide mineral phase.

6. Generalized paragenesis

Table 3 shows a simplified sequence of the paragenesis that occurs within a sulfide tailings impoundment. The table shows that most reactions proceed concurrently, however the transformation of some minerals is more distinct than others. For example, laboratory examinations of freshly exposed surfaces of pyrite and other sulfide minerals have shown that the minerals react almost instantaneously to produce secondary mineral phases, however the secondary minerals at that stage are present in minute amounts and are not observable megascopically or by standard optical microscopy (Jambor, 2003). The replacement of pyrrhotite by secondary minerals in Table 3 is the first indicator of alteration in the ‘earliest’ stage of the oxidation of a sulfide tailings impoundment. The alteration of pyrrhotite is preceded by the diffusion of S to the grain surface which forms a S-enriched alteration rim where the Fe has departed (Pratt et al., 1994a,b; Mycroft et al., 1995). The released Fe oxidizes to form Fe oxyhydroxide and the S-enriched alteration rim typically forms marcasite (Jambor, 1994). In some cases the boundary between the pyrrhotite core and the marcasite rim is also S-enriched and through microprobe analysis, reveals a mineral that has a composition that is approximately \(\text{Fe}_3\text{S}_5\), also observed by Murphy and Strongin (2009). This Fe sesquisulfide phase is interpreted by the authors to be less stable than either pyrrhotite or marcasite, and it oxidizes much more rapidly producing an interior zone that is blackish in reflected light as illustrated in Fig. 6e. The oxidation of pyrrhotite may also form native sulfur (Fig. 4) and Fe(II)-sulfate minerals that may dissolve and crystallize seasonally as sulfates containing both Fe(II) and Fe(III), as is the case in the Sherridon tailings.
During the 'early' oxidation of pyrrhotite, acid and Fe(III) are released which increases the oxidation of other Fe sulfides and decreases the pore water pH. The presence of carbonate minerals within the tailings may neutralize the acidity, however if carbonate minerals are not present or have become consumed, the pH will continue to decrease because most of the common rock-forming minerals have a slow reaction rate and poor neutralizing capacity (Jambor et al., 2000c, 2002; Jurjovec et al., 2002). The silicate minerals observed to be the most susceptible to low-pH dissolution within oxidized tailings are micas (e.g., biotite) and chlorite (e.g., Sherridon, Fig. 4). In low-pH conditions the incongruent early release of K from biotite (Kalinowski and Schweda, 1996; Malmström et al., 1996) provides the main source of K for jarosite precipitation (Jambor, 1994). Although other silicate minerals such

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Fig. 8. Examples of well-developed alteration rims of Fe oxyhydroxide on pyrite in tailings from the Yellowknife gold-producing area, Northwest Territories, Canada. Photos (a) and (b) are backscattered-electron (BSE) images of oxyhydroxide-rimmed pyrite (py) and the corresponding X-ray maps that show the distribution of Fe, As and S. The residual pyrite is outlined well by the maps for S. Note that As is concentrated in the Fe oxyhydroxides and has been sorbed from the pore waters rather than from the low-As host pyrite. The bar scales are 45 μm for (a) and 35 μm for (b).
as K feldspar, muscovite and illite also release K during weathering, concentrations are much lower due to the low solubility of the minerals (Jambor et al., 2002). As the tailings 'mature', pyrrhotite will be depleted long before pyrite is consumed. During the final or 'late' stage, the tailings will take on the characteristics of a mature gossan (Blowes et al., 1992) and as the pore water pH rises due to the absence of sulfide minerals, jarosite will become unstable. During this evolution of tailings weathering, there is a continuous recycling of trace elements often resulting in the temporary formation of fine-grained poorly crystalline Fe oxyhydroxides (Fig. 8 and 9; tailings samples from the Yellowknife Au-producing area, Northwest Territories, Canada) or precipitation of soluble sulfate minerals. However, the high sorptive and retentive capacities of the Fe oxyhydroxides decline as their crystallinity improves by increasing the grain sizes and decreasing their surface areas (Courtin-Nomade et al., 2003), and goethite becomes the dominant Fe oxyhydroxide because it is a stable phase relative to species such as ferricydrite or lepidocrocite.

Fig. 9. (a) BSE image of remnant arsenopyrite (asp) and (b) a pseudomorph of Fe oxyhydroxide after arsenopyrite in tailings from the Yellowknife area, Northwest Territories, Canada. The bar scales are 50 μm and 25 μm, respectively. The black areas within the pseudomorph are voids. The relatively homogeneous distribution of As in the X-ray maps of both (a) and (b) suggests sorption of As rather than the presence of mixtures containing discrete As mineral species. Electron-microprobe analyses of the rims in Fig. 8 gave up to 5.3 wt.% As₂O₅, and analyses of the rims in Fig. 9 range from 5.6 to 7.1 wt.% As₂O₅.
The 4 stages of tailings oxidation presented in Table 3 are not of equal duration. The initial oxidation ‘earliest’ stage is almost instantaneous upon atmospheric exposure, and the effects become evident in pyrrhotite-rich environments. The progression through the ‘earliest’ and ‘early’ stages may occur within a few months or a few years, whereas, the ‘maturing’ and ‘late’ stages may require many centuries.

7. Conclusions

Geochemical and mineralogical data for pore water, primary and secondary minerals from tailings impoundments has provided a great deal of insight into the processes occurring during the oxidation of sulfide-rich tailings. The behavior of pyrite, pyrrhotite, sphalerite and magnetite are particularly important in controlling the release and attenuation of metals. In the earliest stage oxidation, the secondary products are formed predominantly from the alteration of pyrrhotite, with native sulfur, marcasite, Fe sulfate and Fe oxyhydroxides derived from pyrrhotite during which pyrite shows little or no evidence of alteration. Iron oxyhydroxides may include amorphous material and ferrhydrite, but typically consist of very fine-grained goethite with a high sorptive capacity. The relative stability of sphalerite is greater than that of pyrrhotite but is less than that of pyrite. Dissolved Ni and Co derived from solid solution in the Fe sulfides, and to a much lesser extent, dissolved Zn and Cd from sphalerite, commonly co-precipitate or absorb into early-formed Fe oxyhydroxides, however, as the tailings system matures, a recycling occurs due to continued leaching from low-pH pore water and because the gradually increased crystallinity of the Fe oxyhydroxides decreases their sorptive capacity. Unlike many other elements, such as Cu, Pb, and Cr, which either form secondary minerals or are readily incorporated as solid solutions, Zn and Ni remain mobile. During the late stage of oxidation within a tailings impoundment following consumption of the sulfide minerals, the pore water pH will eventually rise and jarosite will therefore be unstable leaving goethite as the dominate secondary mineral.

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