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BY

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Evaluation of long-term sulfide oxidation processes within pyrrhotite-rich tailings, Lynn Lake, Manitoba

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Abstract

Oxidation reactions have depleted sulfide minerals in the shallow tailings and have generated sulfate- and metal-rich pore water throughout the East Tailings Management Area (ETMA) at Lynn Lake, Manitoba, Canada. Information concerning the tailings geochemistry and mineralogy suggest the sulfide oxidation processes have reached an advanced stage in the area proximal to the point of tailings discharge. In contrast, the distal tailings, or slimes area, have a higher moisture content close to the impoundment surface, thereby impeding the ingress of oxygen and limiting sulfide oxidation. Numerical modelling of sulfide oxidation indicates the maximum rate of release for sulfate, Fe, and Ni occurred shortly after tailings deposition ceased. Although the sulfide minerals have been depleted in the very shallow tailings, the modelling suggests that sulfide oxidation will continue for hundreds and possibly thousands of years. The combination of sulfide minerals, principally pyrrhotite, that is susceptible to weathering processes and the relatively dry, coarse-grained nature of the tailings have resulted in the formation of a massive-hardpan layer in the proximal area of the ETMA. Because extensive accumulations of secondary oxyhydroxides of ferric iron are already present, remediation strategies for the ETMA should focus on mitigating the release of sulfide oxidation products rather than on preventing further oxidation.

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Keywords: Tailings; Sulfide oxidation; Acid mine drainage; Pyrrhotite; Gaseous diffusion; Geochemical models

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1. Introduction

Oxidation of sulfide minerals in mine tailings impoundments releases H^+ , SO_4 , Fe, and other metals, such as Ni, Al, Cu, Co and Cr, to the tailings pore water. Low-pH pore water, along with dissolved constituents, can migrate out of the tailings impoundment and into adjacent aquifers and surface waters, detrimentally affecting these resources. It is important, therefore, to understand controls on sulfide oxidation to predict the long-term release and fate of dissolved H^+ , sulfate, Fe, and other metals.

Mine tailings are composed of aluminosilicate, carbonate, oxide (especially quartz), and metal-sulfide gangue minerals that are separated from the ore concentrate and are deposited into a containment facility. Tailings are typically ground into fine-sand to silt-size particles to increase ore beneficiation. However, because no separation technique is perfectly effective, some ore minerals along with the non-economic sulfide minerals are routinely deposited into tailings impoundments. Sulfide minerals weather upon exposure to atmospheric oxygen, resulting in a series of reactions that produces acidic pore water and liberates sulfate, Fe, and other metals. In the absence of preventative or remediation strategies, the result may be the discharge of low-quality pore water from the impoundment into adjacent bodies of surface water and to nearby aquifers (Blowes and Jambor, 1990; Blowes et al., 1991, 1992; Johnson et al., 2000; Moncur et al., 2005).

Field investigations were carried out on the East Tailings Management Area (ETMA) at Lynn Lake, Manitoba, Canada, during the summer of 2002. The objective of these investigations was to determine the mechanisms controlling the release and transport of dissolved metals from the tailings impoundment. Approximately 21.8 million tonnes of tailings were deposited into the ETMA from 1952 until 1976 (Acres, 1986). The tailings were separated into two fractions, a coarser sandy fraction and a silty-slime fraction, using a cyclone process (MacLellan and George, 1957; Acres, 1986). The sandy fraction was deposited in the area proximal to the point of tailings discharge or within the relative vicinity of the spigots. The finer tailings or slimes settled around the fringe of the proximal area (Hawthorne and Kennedy, 1987). Since tailings deposition ceased, the wastes have oxidized extensively, producing acidic pore waters that contain elevated concentrations of SO_4 , Fe, Ni, Zn, Al, and other metals.

This paper focuses on the sulfide oxidation processes that have occurred over the past 28 years. Sulfide oxidation modelling was performed to approximate sulfide oxidation processes in the near and distant future. This modelling was conducted using information that is specific to the Lynn Lake ETMA. These conditions, however, are similar to those that prevail at many other tailings impoundments worldwide. The results, therefore, are representative of the processes that occur at many mine-waste sites, and the results provide insights that are widely applicable.

2. Methods

During the summer of 2002, samples of tailings solids, pore water, and pore gas were collected and analyzed to determine the physical properties of the tailings and the effect of sulfide oxidation within the ETMA. This study focuses on 12 sampling locations within the main tailings area, the adjacent ponds, and discharge zones as shown in Fig. 1. At these locations, 1 to 4 drive-point and (or) mini-piezometers were installed at different depths. Drive-point piezometers were constructed of stainless steel or PVC drive-point tips that were machined to fit onto threaded 1.27 cm steel pipe or 3.17 cm schedule 80 PVC pipe, respectively. A direct-push technique, using a gas-powered vibrating rock hammer, was used to drive the piezometers

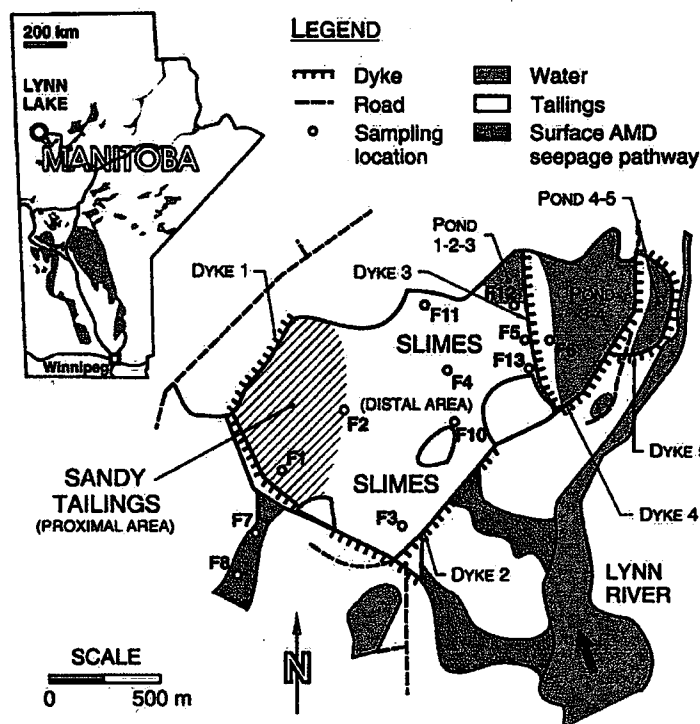


Fig. 1. Schematic map of the ETMA, distinguishing the sandy tailings (proximal area) from the slimes (distal area). The provincial map, top left, shows the location of Lynn Lake, Manitoba, Canada.

into the tailings. From the sampling locations, information concerning the tailings geochemistry and mineralogy was obtained and integrated to determine the extent of sulfide oxidation.

2.1. Tailings solids

Tailings solids were collected using a minor modification of the piston-coring technique described by Starr and Ingleton (1992). Samples of continuous core were collected in aluminum tubing within a piston-core barrel that is driven into the tailings using a gas-powered vibrating hammer. The cores were cut into 0.3 to 0.5 m sections, which were then immediately capped and frozen to minimize exposure to atmospheric oxygen. Cores for solid-phase geochemical and mineralogical analysis were 5.05 cm in diameter, and those used to obtain samples of the pore waters in the vadose zone were 7.62 cm in diameter.

Core sections were thawed in an anaerobic chamber, and sub-samples of tailings were collected along the core length for analysis of total sulfur. Non-sequential extractions that target specific metal-rich minerals within the tailings solids were completed on corresponding sub-samples. The total-sulfur content of the tailings was determined by LECO sulfur analysis at Activation Laboratories Ltd. in Ancaster, Ontario, Canada. A strong-basic extraction, 0.3 M NaOH, was used to target sulfate-containing secondary Fe(III) hydroxides (Yin and Catalan, 2003). This fraction of the tailings represents both the water-soluble sulfate and insoluble-sulfate minerals. Sulfate extracted by the 0.3 M NaOH extractions was quantified using ion

chromatography. The total-insoluble sulfate was subtracted from the measured total sulfur to determine the total mass of sulfide minerals in the tailings. Moisture contents were determined both gravimetrically and volumetrically. Moisture contents were used to determine the dry masses of tailings solids, which, in turn, were used to correct the extraction results.

Mineralogical study of the tailings was completed in detail at location F1 (Fig. 1), where sulfide oxidation is the most extensive. The tailings were examined using transmitted- and reflected-light optical microscopy, scanning electron microscopy with an energy dispersion X-ray analysis system (SEM–EDX), and qualitative X-ray diffraction (XRD). Polished thin-sections were made by Vancouver Petrographics Ltd. in Langley, British Columbia. The thin-sections examined by SEM were coated with 15 μm of gold or with carbon to prevent charge build-up. SEM images were taken with a LEO 1530 FE–SEM, and EDX data were collected using an EDAX Pegasus 1200 integrated EDX/OIM. The EDX detector quantifies specific elements on the basis of the characteristic wavelength of X-rays radiated from the sample as a result of electron bombardment. Thin-sections were also examined by SEM using a Philips XL-30 with a Princeton Gamma IMX-4 EDS system.

Physical characterization of the tailings included measurements of grain size, bulk density, particle density, and volumetric water content. Grain-size distribution curves were generated from sieve and laser analyses performed at University of Waterloo and Activation Laboratories Ltd., respectively. From these plots, the grain size at which 50% of the sample passes (d_{50}) was determined. The graphic-mean grain size, graphic-standard deviation, and the sorting class were calculated using the method of Folk and Ward (1957). An air-comparison pycnometer Beckman model 930 was used to determine the particle density of the tailings samples. Porosity values were calculated from the measured bulk densities and particle densities.

2.2. Tailings pore water

Pore water in the vadose zone was sampled at locations F1, F2, F3, F4, and F5 (Fig. 1). An immiscible-displacement technique, using the method described by Smyth (1981), was used to extract pore water from the vadose zone. This method is advantageous because it minimizes exposure of the pore water to atmospheric O_2 . The samples were eluted into 60 mL syringes and filtered through 0.45 μm cellulose acetate filters and into two separate polyethylene bottles, one for cation analysis and the other for anion analysis. The cation samples were immediately acidified for preservation using 12 N Trace Grade HCl to a $\text{pH} < 1$, and both the cation and anion samples were maintained at 4 °C until analyzed.

Samples of groundwater were collected, using a peristaltic pump and polyethylene tubing, from all piezometers at locations F1, F2, and F4. All piezometers were bailed dry and allowed to recover prior to collecting a fresh sample through in-line 0.45 μm filters. Measurements of pH and Eh were made in the field using sealed flow-through cells maintained at groundwater temperature. Measurements of alkalinity were determined on filtered samples in the field. Two filtered samples were collected from each piezometer for cation and anion analyses. Cation samples were acidified with 12 N HCl. All samples were maintained at 4 °C prior to analysis.

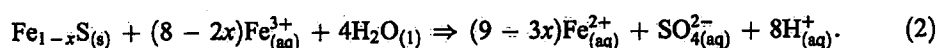
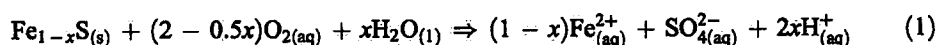
2.3. Pore-gas analysis

A modified technique of Reardon and Poscente (1984) was used to sample the pore gas in the vadose zone. Stainless steel sampling tubes 0.63 cm in diameter were driven into the tailings at

10 cm intervals. The pore gas was extracted and measured using a Nova model L8D50 portable $O_{2(g)}$ analyzer. Measurements were terminated at the depth where hardpan or saturated conditions were encountered. The gas analyzer was calibrated in the laboratory using known concentrations of $O_{2(g)}$. The performance of the gas analyzer was checked in the field using atmospheric $O_{2(g)}$ concentrations as a reference.

3. Sulfide oxidation

Solid-phase analysis indicates the fresh tailings consist of 0.46 to 14.70 wt.% total sulfur, and 0.013 to 1.59 wt.% carbonates as acid-soluble $CaCO_3$. Trace amounts of calcite [$CaCO_3$] were observed in the tailings. Mineralogical examination identified two main types of unaltered tailings: 1) proximally derived tailings that are characteristically blackish, of relatively coarser grain size, and are sulfide-rich, and 2) distal tailings that are characteristically gray, sulfide-poor, and amphibole-rich. In general, the non-carbonate gangue assemblage in the tailings of the ETMA consists of, in decreasing order of abundance, actinolite [$Ca_2(Mg,Fe^{2+})_5Si_8O_{22}(OH)_2$], plagioclase [$(Na,Ca)(Si,Al)_4O_8$], chlorite [$(Mg,Fe^{2+})_5Al(Si_3Al)O_{10}(OH)_8$], talc [$Mg_3Si_4O_{10}(OH)_2$], quartz [SiO_2], cummingtonite [$Mg_7Si_8O_{22}(OH)_2$], biotite [$KMg_3AlSi_3O_{10}(OH)_2$], and small amounts of K-feldspar [$KAlSi_3O_8$] and diopside [$CaMgSi_2O_6$]. Sulfide minerals present in the tailings consist principally of pyrrhotite (>99%) [$Fe_{1-x}S$], with lesser amounts of chalcopyrite [$CuFeS_2$] and pentlandite [$(Fe,Ni)_9S_8$], and trace amounts of pyrite [FeS_2]. Pyrrhotite has a disordered structure that gives rise to non-stoichiometric and stoichiometric compositions. The formulae can be represented as $Fe_{1-x}S$, with the value of x varying from 0.125 [Fe_7S_8] to 0 [FeS], where FeS is troilite. Metals, such as Ni and Co, can be incorporated as a solid solution into the structure of pyrrhotite. The oxidation of pyrrhotite, therefore, results in the release of the usual sulfide oxidation products along with any trace metals that substitute in the crystal structure of the pyrrhotite. The following is the overall reactions when O_2 and $Fe(III)$ are the oxidants (Nicholson and Scharer, 1994; Janzen et al., 2000):

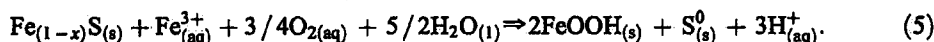
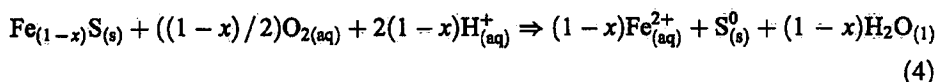


The number of moles of H^+ produced is dependent on the mineral stoichiometry (Jambor, 2003). These reactions can lead to low-pH conditions. At $pH < 4.0$, the primary mechanism of sulfide oxidation is the oxidation by $Fe(III)$, as in Reaction (2). Furthermore, pyrrhotite is unstable under acidic conditions. The development of low-pH conditions can cause pyrrhotite to be directly dissolved through the reaction:

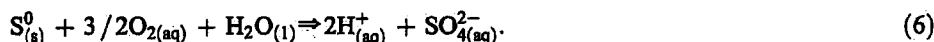


These weathering processes can be catalyzed by sulfide-oxidizing bacteria from groups such as *Acidithiobacillus*. Documentation of the presence and effects of various types of bacteria in tailings environments suggests that bacteria are abundant and of considerable importance with respect to sulfide oxidation processes (Gould et al., 1994; Gould and Kapoor, 2003; Blowes et al., 2004). Furthermore, Norris and Parrott (1985) confirmed that *A. ferrooxidans* catalyzes the oxidation of ferrous iron in tailings rich in pyrrhotite and pentlandite.

Pyrrhotite can partially oxidize to form secondary sulfur. The partial oxidation of pyrrhotite, by either O_2 or $Fe(III)$, may result in the formation of native sulfur [S^0] (Janzen et al., 2000):



Qualitative X-ray diffraction analysis detected the presence of native sulfur as pseudomorphs after pyrrhotite in the ETMA tailings. Native sulfur can then be oxidized to release H^+ and sulfate through the reaction:



The release and oxidation of $Fe(II)$ can result in further production of H^+ via the precipitation of minerals rich in $Fe(III)$, such as goethite [α - $FeOOH$] and jarosite [$KFe_3(SO_4)_2(OH)_6$]:



The secondary mineral assemblage in the tailings consists principally of goethite, with lesser amounts of gypsum [$CaSO_4 \cdot 2H_2O$] and jarosite. The formation of $Fe(III)$ oxyhydroxides and hydroxysulfates is, therefore, likely an additional source of H^+ in the shallow tailings.

Tailings that have undergone oxidation are ochreous in colour and are apparent across the impoundment. Depletion of sulfide minerals in the shallow tailings, abrupt declines in gaseous-oxygen concentrations in the vadose zone, and elevated concentrations of dissolved sulfide-oxidation products in the tailings pore water are all indicative of sulfide oxidation. The pore-water geochemistry for location F1 is presented in Fig. 2. Elevated concentrations of dissolved SO_4 (max. 9760 $mg\ L^{-1}$), Fe_{Total} (max. 4220 $mg\ L^{-1}$), Ni (max. 3870 $mg\ L^{-1}$), Al (max. 2390 $mg\ L^{-1}$), Cu (max. 270 $mg\ L^{-1}$), Zn (max. 226 $mg\ L^{-1}$), Co (max. 156 $mg\ L^{-1}$), Pb (max. 4.75 $mg\ L^{-1}$), Cr (max. 0.85 $mg\ L^{-1}$), and Cd (max. 0.54 $mg\ L^{-1}$) were detected in the tailings pore waters. An alteration intensity that is classified on a relative scale from 0 to 10 was determined through mineralogical analysis (Sulfide Alteration Index or SAI, Table 1). In general, the SAI values increase moving up from the depth of active oxidation. High SAI values, 9 to 10, near the impoundment surface confirm that considerable oxidation has occurred in the shallow tailings. Profiles of gaseous-oxygen concentrations and total-sulfide content demonstrate a close relationship with the degree of sulfide alteration (Fig. 3).

3.1. Proximal area of the ETMA

Gaseous oxygen was detectable at greater depths below the impoundment surface in the proximal area of the ETMA. Measurable gaseous-oxygen concentrations were detected to a depth of 1.1 m at location F1 (Fig. 3). This depth corresponds to high water-saturation values and fresh tailings that have a higher sulfide content. However, the vadose zone extends approximately 3 m below the greatest depth that gaseous oxygen was measurable at location

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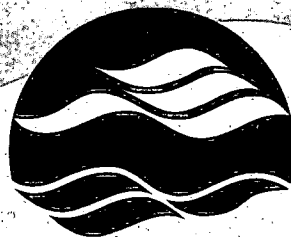
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