The Environmental Effects of Mine Wastes

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ABSTRACT

The oxidation in sulfide minerals in waste rock piles and mine tailings impoundments generates acidic waters containing high concentrations of $\text{SO}_4^{2-}$, $\text{Fe(II)}$ and other metals. The water affected by sulfide oxidation is displaced downward through the wastes into underlying geological materials, or it is discharged directly to the adjacent surface-water flow system. As the water affected by sulfide oxidation flows through the waste material, geochemical reactions with the gangue minerals result in progressive increases in the pH, and the attenuation of some dissolved metals. The sequence of geochemical reactions occurring in the mine waste pile, and in underlying aquifers, result in profound changes in the electromagnetic properties of the mine waste materials and the water flowing through the pile. The changes in these properties are discernable using geophysical techniques that are available widely. The use of geophysical investigations as reconnaissance surveys in the characterization of mine wastes has been demonstrated to be both inexpensive and effective. These surveys are rapidly becoming accepted as integral parts of mine waste characterization programs.

INTRODUCTION

The release of acidic drainage from abandoned mines, mine tailings impoundments, and waste rock piles is the largest environmental problem facing the North American mining industry (Feasby et al., 1991). In Ontario, there are more than 1000 inactive mines. There are estimated to be between 20,000 and 50,000 mines generating acidic drainage on United States Forest Service lands (USDA, 1993). The estimated costs of remediating and reclaiming waste sites affected by acidic drainage are in the billions of dollars (Feasby et al., 1991).

Acidic drainage waters, containing high concentrations of dissolved metals, result from the oxidation of sulfide minerals within mines and mine wastes. The most abundant sulfide minerals in mine wastes are the iron sulfide minerals pyrite ($\text{FeS}_2$) and pyrrhotite ($\text{Fe}(1-x)\text{S}$). Because of their low commercial value, these minerals are excluded from concentrates in the ore beneficitation process and are deposited in waste rock piles and mine tailings impoundments.

MINE WASTE HYDROLOGY

Waste rock hydrology

The two most common forms of mine waste are waste rock and mine tailings. Waste rock is the large volume of broken rock, excavated in order to gain access to the ore deposit, and low grade ore materials that cannot be processed commercially. Waste rock is commonly deposited in large piles that are typically 10 to 30 m high, but range up to 150 m in height, and up to several square kilometers in area. These waste rock piles may be deposited in successive lifts or benches, or the waste rock may be end-dumped from the top of the pile, enhancing sorting and segregation according to particle size. The selection of disposal technique varies depending on the site conditions, economic considerations and environmental policy.

Waste rock materials vary in grain size from fine-grained sand- and gravel-sized materials, to large blocks up to several meters in diameter (Ritchie, 1994). The coarse nature of waste rock leads to a relatively large, free-draining porosity. The free-draining nature of waste rock results in a low residual moisture content, and rapid flow of water through the waste rock pile. Ritchie (1994) summarized the characteristics of waste rock piles (Table 1). This summary indicates that the travel time for vertical transport of water from the surface through a 15 m high waste rock pile to its base is approximately three years. At many locations, waste rock piles are constructed on permeable geological materials (Ritchie, 1994). At these locations, pore water affected by geochemical reactions within the waste rock pile may be displaced into the underlying geological materials. Travel through the base of a waste rock pile, 25 ha in area and under saturated flow conditions, is anticipated to require five years.
The nature and mechanisms of water flow through a waste rock pile are poorly understood, and are the focus of active research (Gelinhas et al., 1992; Ritchie, 1994). Groundwater velocities, calculated assuming continuum or Darcian flow and the travel time and porosity provided by Ritchie (1994), are on the order of 100 m/a. If flow occurs in two or more regions within the waste rock pile; that is if there are channels of rapid flow within larger regions of low flow, the maximum velocities would be greater.

**Mine tailings hydrology**

Mine tailings are the finely ground residual from ore beneficication. Although the grain size of the tailings depends on the nature of the ore, and the milling process, they are typically fine sand to silt grain size. Tailings are transported from the mill, and discharged into the tailings impoundment as a slurry. The method of deposition affects the distribution of tailings particles within the impoundment. In most tailings impoundments, tailings are discharged from elevated perimeter dams as a slurry of approximately 30 wt.% solids. Using this deposition technique, there is potential for extensive hydraulic sorting, with coarser fractions settling near the discharge point, and finer fractions settling out in distal portions of the impoundment (Robertson, 1994). At some sites tailings are thickened to 60 wt.% solids prior to deposition. Thickening the tailings results in more rapid settling of the tailings solids, and provides less potential for hydraulic sorting, resulting in a more uniform grain-size distribution than is observed in conventional tailings areas (Robinsky, 1978; Al, 1996).

Water flow in saturated mine tailings is considered to be continuum flow, and can be described, by the equation:

\[
\frac{\partial}{\partial x} \left( K_{xx} \frac{\partial h}{\partial x} \right) + \frac{\partial}{\partial y} \left( K_{yy} \frac{\partial h}{\partial y} \right) + \frac{\partial}{\partial z} \left( K_{zz} \frac{\partial h}{\partial z} \right) = 0
\]  

where \( h \) is the hydraulic head [L], and \( K_{xx}, K_{yy}, K_{zz} \) [L/T] are the principal components of the hydraulic conductivity tensor. The fine grain size of tailings results in slow to moderate hydraulic conductivities of \( 10^{-7} \) to \( 10^{-4} \) cm/s. In conventional tailings impoundments, hydraulic conductivities are observed to vary as a result of grain-size segregation, with higher hydraulic conductivities observed near the discharge point, and lower hydraulic conductivity materials observed in distal areas. In tailings areas where thickened-discharge techniques are employed, the hydraulic conductivity is observed to be relatively uniform.

During tailings disposal, water is added to the impoundment continually, and the water table remains near the impoundment surface. After tailings deposition ceases, precipitation becomes the dominant source of recharge to the tailings impoundment. The water table falls to an equilibrium position controlled by the rate of precipitation, the rate of evapotranspiration, and the hydraulic properties of the tailings and the underlying materials. The annual recharge determined for tailings areas in northern Canada ranges from 0.02 m/a to 0.3 m/a (Coggans et al., 1991; McCreadie, 1996).

The fine grain size of mine tailings results in a high moisture retaining potential for these materials. The moisture retaining potential of mine tailings leads to distinct differences between mine tailings impoundments and waste rock piles. Whereas waste rock piles tend to have a large open and free draining porosity, mine tailings drain slowly, maintaining a large residual moisture content under gravity drainage. Measured moisture contents of conventional tailings impoundments vary from 10 to 100 % saturation (Smyth, 1981; Blowes, 1990). The residual moisture content of thickened tailings is greater than observed for conventional tailings (Robinsky et al., 1991; Al and Blowes, 1996).

The high residual moisture content of mine tailings results in a low gas-filled porosity, and rapid changes in hydraulic gradient in response to precipitation (Blowes and Gillham, 1988; Al and Blowes, 1996).

Precipitation that falls on the impoundment surface migrates downward and laterally through the tailings impoundment into underlying geological materials (Figure 1). Groundwater velocities in tailings impoundments are relatively low. Coggans et al. (1997) used tritium dating to estimate the rate of groundwater flow through the Inco Ltd. Copper Cliff Central Tailings area. Estimates of vertical velocity ranged from 0.2 to 1.0 m/a, depending on the location within the impoundment. Horizontal velocities at this site were estimated to be on the order of 10 to 15 m/a. At the Nickel Rim tailings impoundment near Sudbury, Johnson (1993) estimated the horizontal groundwater velocity ranges from 1 m/a up to 16 m/a. Vertical velocities, estimated through tritium age dating, and through numerical modelling, range from 0.1 to 0.5 m/a.

Tailings impoundments vary in size from less than 10 ha up to several square kilometers in area. Thicknesses of tailings deposits vary from a few meters up to more than 50 m. The relatively low groundwater velocities, and the large areal extent of tailings impoundments, result in long
time intervals between the time of groundwater infiltration to the time of discharge of that groundwater to an underlying aquifer, or the surface water environment. These long travel times result in the delay of measurable environmental degradation at the groundwater discharge point until long into the life of the impoundment. The severity of the negative environmental effects associated with a tailings impoundment may not be evident until long after mine closure and tailings impoundment decommissioning. At this time prevention and remediation of low quality drainage waters is more difficult than during the active mining. The long travel distances and low groundwater velocities also result in the potential for prolonged release of contaminants from the tailings impoundment, and large long-term treatment costs.

**MINE-WASTE GEOCHEMISTRY**

**Sulfide mineral oxidation**

The principal environmental concerns associated with tailings impoundments and waste rock piles result from the oxidation of sulfide minerals within the waste materials, and the transport and release of oxidation products. The principal sulfide minerals in mine wastes are pyrite and pyrrhotite. The oxidation of pyrite can be described through the equation:

$$FeS_2 + \frac{7}{2}O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$$  \[2\]

This reaction consumes pyrite, oxygen and water and generates low pH conditions, and releases Fe(II) and SO$_4^{2-}$ to the water flowing through the mine waste. The Fe(II) released by sulfide oxidation may be oxidized to Fe(III) through the reaction:

$$Fe^{2+} + \frac{1}{2}O_2 + H^+ \Leftrightarrow Fe^{3+} + \frac{1}{2}H_2O$$  \[3\]

The resulting Fe(III) may precipitate as a ferric oxyhydroxide phase, through a reaction of the form:

$$Fe^{3+} + 3H_2O \Leftrightarrow Fe(OH)_3 + 3H^+$$  \[4\]

Alternatively, Fe(III) may oxidize additional pyrite or other sulfide minerals through reactions of the form:

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+$$  \[5\]

Within mine wastes, sulfide oxidation proceeds rapidly, and is catalyzed by chemolithotrophic bacteria of the Thiobacillus group (Boorman and Watson, 1976).

In addition to the iron-sulfide minerals, other metal-sulfide minerals are susceptible to oxidation, releasing elements such as As, Cd, Co, Cu, Ni, Pb and Zn to the water flowing through the mine waste.

**Sulfide oxidation in waste rock piles**

Under conditions that prevail in most waste rock piles, the supply of oxygen limits the rate and extent of sulfide-mineral oxidation (Ritchie, 1994). Initially, oxygen contained in the waste rock pile upon deposition is consumed. This oxygen is gradually replenished by oxygen from the surface of the pile. Three gas-transport mechanisms replenish gas-phase oxygen into waste rock piles: diffusion, advection, and convection. Transport and consumption of oxygen within waste rock piles can be described by the equation (Ritchie, 1994):

$$\frac{\partial (\rho_s \omega_0)}{\partial t} + \nabla (\rho_s \omega_0 \mathbf{v}_g - \rho_g \nabla \omega_g) = \varepsilon S_s (\omega_0, \omega_g, T)$$  \[6\]

where \(\rho_s\) is the gas density, \(\omega_0\) is the mass fraction of oxygen in the gas phase, \(\omega_g\) is the mass fraction of oxidizable material in the solid phase, \(\mathbf{v}_g\) is the gas-phase velocity [L/T], \(D\) is the gas-phase diffusion coefficient, \(\varepsilon\) is mass of oxygen consumed per mass of sulfide reacted, \(S_s\) is the oxidation rate of oxidizable material, \(t\) is time [t], and \(T\) is temperature.

The rate of oxygen diffusion is proportional to the diffusivity of the waste rock pile. Although the diffusivity of waste rock is high, due to the low moisture content of the waste rock, diffusive transport of oxygen is relatively slow, relative to advective transport, limiting the rate of sulfide oxidation. In sulfide-rich waste rock piles, in which oxygen transport is dominated by diffusive processes, the zone of active sulfide oxidation can be quite narrow (Ritchie, 1994).

Advective transport of oxygen results from changes in gas pressure between the waste rock pile and the adjacent atmosphere. Wind blowing onto the dump batters has the potential to drive oxygen deeper into the pile than would occur under diffusive transport mechanisms alone (Ritchie, 1994). The oxidation of pyrite is exothermic, releasing heat as pyrite oxidizes. As sulfide oxidation proceeds, the accompanying release
of heat can result in the generation of high temperatures in zones of waste rock undergoing intense oxidation. Temperatures in excess of 60°C have been observed in oxidizing waste rock piles. These increased temperatures induce convective transport of atmospheric oxygen into the waste rock pile (Figure 2). Convective transport of oxygen results in the penetration of oxygen deep into the waste rock pile, accelerating the rate of oxidation of sulfide minerals within the pile, reinforcing the development of the convection cell (Cathles 1979; Cathles, 1994). Convective transport of oxygen accelerates the rate of oxidation of the waste rock near the pile margins, increasing the short-term release of contaminants, and decreasing the overall duration of sulfide oxidation. Although dramatic in appearance, the convective transport of atmospheric gases is relatively limited in importance, affecting a zone of about 100 m inward from the pile margins (A.I.M. Ritchie, 1997; personal communication). Based on model calculations, Ritchie (1994) estimates approximately 150 years are required to fully oxidize the pyrite content of a typical waste rock pile which initially contains 2 wt.% pyrite. The duration of oxidation is longer for waste rock piles with a greater sulfide content.

**Figure 2: Schematic diagram of a waste rock dump.**

### Sulfide oxidation in mine tailings impoundments

The fine grain size and the high moisture content of mine tailings results in lower gas permeability than is observed in waste rock. The permeability of tailings materials is typically too low to permit significant advective or convective transport of gas-phase oxygen. In coarse-grained tailings at locations where the water table is greater than 10 m below the tailings surface, barometric pumping due to atmospheric pressure changes may result in advective transport of oxygen into the near-surface tailings. These conditions are most likely to be encountered in arid climates, where potential evaporation exceeds the precipitation rate, and where dessication cracking may facilitate the advective transport of gases.

In most tailings impoundments in Canada, gaseous diffusion is the most significant oxygen transport mechanism (Figure 1). The rate of oxygen gas diffusion is dependent on the concentration gradient and the diffusion coefficient of the tailings material. The diffusion coefficient of tailings is dependent on the air-filled porosity of the tailings, with the diffusion coefficient increasing as the air-filled porosity increases, and decreasing as the moisture content increases. Several empirical relationships have been developed to describe the dependence of the gas diffusion coefficient on the tailings moisture content. Reardon and Moddle (1985) determined the relationship:

\[
D_{O_2} = (3.98 \cdot 10^{-9})[(e - 0.05)/0.95]^{1.7} T^{3/2}
\]  

where \( D_{O_2} \) is the oxygen diffusion coefficient, \( e \) is the air-filled porosity, and \( T \) is the temperature in degrees Kelvin. The relationship between moisture content and diffusion coefficient results in rapid oxygen diffusion in the shallow portion of the vadose zone of a tailings impoundment, where the moisture content is low. The rapid supply of oxygen in this zone can supply rapid oxidation of sulfide minerals. As the sulfide minerals in the shallow portion of the tailings are depleted the rate of sulfide oxidation decreases due to the longer diffusion distance, and the higher moisture content of the deeper tailings.

The rate of sulfide oxidation in mine tailings can be described by numerical models that couple oxygen transport mechanisms with consumption of oxygen by sulfide mineral oxidation. Davis and Ritchie (1986) developed a series of numerical models that couple oxygen gas transport through the pore space of the tailings impoundment by diffusion, with oxygen transport through an alteration rim surrounding the primary sulfide grain. Comparison of the model calculations with field data suggest that this model provides a reasonable description of sulfide-mineral oxidation in mine tailings impoundments (Blowes and Jambor, 1990; Blowes et al., 1991). Calculations conducted using this model suggest that the peak period of oxidation occurs shortly after tailings deposition, as sulfide minerals near the impoundment surface are consumed rapidly. The rate of sulfide oxidation gradually decreases as the depth to unaltered tailings increases, and as alteration rims accumulate on particle surfaces. The duration of sulfide oxidation is dependent on the thickness of the vadose zone, and the sulfide content of the tailings. Blowes and Jambor (1990) estimated that sulfide oxidation will continue at the Waite Amulet tailings impoundment Noranda, Quebec, for more than 500 years.

### Acid neutralization mechanisms

The oxidation of sulfide minerals results in the acidification of the pore water of the waste rock pile or the tailings impoundment, and releases high concentrations of dissolved metals. This acidic water reacts with the non-sulfide gangue minerals within the mine wastes. Acid-neutralization reactions consume \( H^+ \), resulting in a progressive increase in the pH along the groundwater flow path. The most significant pH-buffering reactions are the dissolution of carbonate minerals, aluminum hydroxide and ferric oxyhydroxide minerals, and aluminosilicate minerals.

The most abundant carbonate minerals in mine wastes are calcite (CaCO\(_3\)) and dolomite (CaMg(CO\(_3\))\(_2\)). The dissolution of calcite can be described as:

\[
CaCO_3 + H^+ \leftrightarrow Ca^{2+} + HCO_3^-
\]  

Dissolution of these minerals has the potential to raise the pH of the pore water to near neutral. Carbonate mineral dissolution releases Ca, Mg, and cations such as Mn that are included as impurities, and increases the alkalinity of the water. At many sites, the mass of carbonate minerals contained in the mine wastes is large when compared to the mass of sulfide minerals, and the rapid dissolution of carbonate minerals is sufficient to maintain neutral pH conditions through the mine waste pile. Neutral pH conditions have been observed in tailings impoundments derived
from processing of vein-type gold deposits in the Timmins and Red Lake areas of Ontario (Blowes, 1990; McCreadie, 1996).

The wastes derived from the processing of massive sulfide ores frequently contains a sulfide content in excess of the carbonate neutralization capacity. At these sites the available carbonate content is quickly consumed, with the most soluble and most reactive carbonate minerals depleted first. At many sites, calcite is depleted initially, followed by dolomite/ankerite and siderite (Blowes and Ptacek, 1994). As the carbonate content of the waste dissolves, the pH is buffered to near neutral. Under the neutral pH conditions maintained by carbonate mineral dissolution the precipitation of crystalline and amorphous metal hydroxide phases is favoured. After the carbonate minerals contained in the waste are depleted, the pH of the pore water falls until equilibrium with the most soluble of the secondary hydroxide minerals is attained. Field studies at several mine tailings impoundments have indicated that the initial hydroxide mineral to dissolve is Al(OH)$_3$ buffering the pH in the region of 4.0 to 4.5 (Dubrovsky, 1986; Blowes and Jambor, 1990; Johnson, 1993). After the secondary Al(OH)$_3$ present in the tailings has been depleted, the pH falls to until equilibrium with an iron oxyhydroxide mineral, typically ferrihydrite or goethite, has been attained. Dissolution of ferric oxyhydroxide minerals typically maintains pH values in the range of 2.5 to 3.5.

Throughout the period of carbonate and hydroxide mineral dissolution, the aluminosilicate gangue minerals also dissolve, consuming H$^+$, and releasing H$_2$SiO$_4$, Al$^{3+}$, and other cations such as K, Ca, Mg and Mn to the pore water. Although aluminosilicate dissolution is generally not rapid enough to buffer the pore water to a specific pH, these reactions consume H$^+$. In addition, Al and other metals released from aluminosilicate minerals may accumulate in secondary minerals that act as secondary pH buffers.

The sequence of pH buffering reactions observed within mine tailings impoundments results in a progressive increase in the pore-water pH along the groundwater flow path. These changes in pH occur as long zones of relatively uniform pH, which are dominated by a single pH buffering reaction, separated by fronts or relatively sharp changes in pH as a buffering phase is depleted (Figure 3).

**Formation of secondary minerals and attenuation of dissolved metals**

Sulfide oxidation and acid neutralization reactions occurring in mine tailings impoundments and waste rock piles generate high concentrations of dissolved constituents. At many locations throughout these wastes the concentrations of dissolved constituents exceed the solubilities of secondary minerals, which accumulate in the wastes or in underlying aquifers. The precipitation of secondary minerals limits the concentrations of dissolved major ions and dissolved metals in the waste-derived waters, and in some cases, accumulations of secondary minerals are sufficient to decrease the porosity and permeability of the waste materials or underlying aquifers (Blowes et al., 1991).

The most abundant dissolved constituents derived from sulfate oxidation and acid neutralization reactions are SO$_4$$^{2-}$, Fe$^{(II)}$, Fe$^{(III)}$, and the major cations Ca, Mg, K, Na, and HCO$_3$$. These dissolved constituents react in the effluent waters, resulting in the precipitation of a number of secondary minerals including gypsum (CaSO$_4$$\cdot$2H$_2$O), jarosite (KFe$_3$(SO$_4$)$_2$(OH)$_6$), geothite (FeOOH), ferrihydrite (Fe$_3$(OH)$_8$), siderite (FeCO$_3$), and rarely melanterite (FeSO$_4$$\cdot$7H$_2$O). The precipitation and dissolution of these phases limits the dissolved concentrations of the major ions in the pore water and provides substrate for the attenuation of dissolved metals.

In addition to affecting the aqueous concentrations of the major ions, precipitation and dissolution reactions limit the concentrations of some dissolved metals. The formation of the lead sulfate mineral anglesite has been observed to limit dissolved Pb concentrations at several mine sites (Boorman and Watson, 1976; Blowes and Jambor, 1990). The formation of secondary covellite (CuS) on the surfaces of pyrrhotite and sphalerite has been observed to limit dissolved copper concentrations (Boorman and Watson, 1976; Johnson, 1993). In addition to solubility limitations, dissolved metal concentrations are also limited by adsorption on the surfaces of secondary iron and aluminum hydroxide minerals. Jambor and Owens (1993) indicated that goethite precipitated in the vadose zone of the Nickel Rim mine tailings impoundment contained up to 0.9 wt.\% Ni. Jambor and Blowes (1991) identified goethite as the primary host for adsorbed As in the inactive mine tailings impoundment at the Delnite gold mine near Timmins, Ontario. Adsorption on iron and aluminum hydroxide phases is strongly pH dependent with more extensive adsorption occurring as the pH increases (Dzombak and Morel, 1990). The progressive increase in pH observed within tailings impoundments results in an increase in the potential for the attenuation of dissolved metals as the pore water migrates along the groundwater flowpath.

**SUMMARY AND GEOPHYSICAL IMPLICATIONS**

The exposure of sulfide minerals contained in mine wastes to atmospheric oxygen results in the oxidation of these minerals. The oxidation reaction depletes the sulfide minerals from the mine waste, and releases H$^+$, SO$_4$$^{2-}$, Fe$^{(II)}$ and other metals to the water flowing through the wastes. The solid-phase products of these reactions are typically ferric oxyhydroxide or hydroxysulfate minerals. The sulfide oxidation reactions, therefore, also convert the sulfide minerals which are conductors, into...
hydroxide minerals, which are dominantly insulators. This change in electrical properties may provide an indication of the depth and extent of sulfide oxidation at inactive mine sites. In addition to changing the electrical properties of the waste materials, oxidation also affects the magnetic susceptibility of the sulfide minerals contained in the wastes, and the magnetic mineral pyrrhotite is converted to non-magnetic oxide phases such as goethite or ferrihydrite.

At many sites the acid produced by sulfide oxidation is consumed by pH-buffering reactions involving the non-sulfide gangue minerals contained in the waste pile. As these acid-neutralization reactions proceed, the pH of the pore water progressively increases, enhancing the potential for attenuation of dissolved metals by adsorption and precipitation reactions. The quality of pore water leaving mine tailings impoundments and waste rock piles is dependent on the extent of the acid-producing sulfide oxidation reactions versus the acid consuming pH-buffering reactions. Regardless of the degree of acid neutralization, the effluent water from the waste material contains increased concentrations of dissolved constituents. The increase in the concentration of total dissolved solids results in an increase in the electrical conductivity of the tailings pore water that is easily distinguishable using surface and borehole geophysical instruments. Plumes of contaminated groundwater derived from inactive tailings impoundments have been delineated using surface geophysical techniques at several sites (Pehme, 1981; DeVos, 1995). Reconnaissance surveys using surface geophysical techniques provide an excellent means of identifying locations to target for detailed hydrogeochemical studies (Bain, 1996).

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