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Review

Waste-rock hydrogeology and geochemistry

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ABSTRACT

The oxidation of sulfide minerals in waste rock has the potential to generate low-quality drainage that can present a significant challenge to mine owners, regulators, and other stakeholders. Challenges involved in managing waste rock include the large volume of waste rock produced and the difficulty in predicting the quality and quantity of leach water due to the chemical and physical heterogeneities in the waste rock, and the highly non-linear coupling of geochemical and physical processes. Many important studies have been conducted over the past decade, particularly at the field scale, that have investigated the geochemical, hydrological, microbiological, and gas and heat transport aspects of waste-rock. These studies show that although the parameters and processes that influence AMD generation and solute release are fundamentally similar between different waste-rock piles, major differences in the dominant mechanisms of water, gas and heat transport result from differences in the physical and mineralogical properties of the rock piles, and the climatic conditions, including the amount of precipitation and prevailing temperatures. Accurate prediction of the leach water quality from waste-rock requires a detailed characterization of the properties of the rock piles and the coupling of processes specific to the particular conditions. This paper provides a review of the physical and mineralogical characteristics of waste-rock piles, followed by a discussion of the principal processes related to sulfide oxidation and solute loading, and concluding with a discussion on acid mine drainage prediction and prevention techniques.

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1. Introduction

Mining activities, particularly open pit mining, can generate large volumes of waste rock that are generally stored in large unsaturated piles on the land surface at the mine site. The oxidation of sulfide minerals within waste-rock stockpiles can lead to poor-quality drainage that presents an environmental risk and financial liability to mining companies. Managing waste-rock stockpiles requires a thorough understanding of the physical, chemical, and microbial processes occurring within the waste-rock stockpiles, and an understanding of the coupling among these processes. Due to the physical and chemical characteristics of waste rock, processes within stockpiles can be dramatically different than those that occur within tailing impoundments.

Acid mine drainage (AMD) is formed through oxidation of iron-sulfide minerals, such as pyrite or pyrrhotite, and the resulting mobilization of minor and trace elements within waste rock, resulting in poor-quality leachate characterized by acidic pH and high concentrations of sulfate, iron, and metals. In many cases the geochemical reactions within waste-rock piles, or other mine wastes, do not lead to acidic conditions, but can still result in poor-quality drainage with high concentrations of sulfate, metals, and metalloids, referred to as neutral mine drainage (NMD). The generation of AMD or NMD in waste-rock piles is principally controlled by the rate of sulfide-mineral oxidation. In turn, the rate of mineral oxidation and leach-water quality is dependent on a number of processes including transport of gas and oxygen, heat, and water; acidification/neutralization reactions, and microbial activity.

The coupling of physical and geochemical processes in waste rock can be strong (Fig. 1). For example, in some waste-rock environments the generation of heat from sulfide oxidation can result in thermally driven convective gas transport, which in turn can drive oxygen transport that can further enhance oxidation rates (i.e., Lefebvre et al., 2001b). In other environments, externally driven gas transport, from wind or ambient temperature changes, can drive temperature changes within the waste rock, influencing sulfide oxidation rates (Amos et al., 2009a,b; Pham et al., 2012, 2013).

The rate and extent of specific processes in waste rock, the degree of coupling between processes, and ultimately, the quality of discharge water and solute loading rates, is a function of the geochemical and physical characteristics of the waste rock. Mineralogical characteristics that control the quality of mine drainage are predominantly sulfide-mineral content and the content of neutralizing minerals. Physical characteristics include macro-scale properties, such as the size and shape of the waste-rock stockpile, particle-size distribution within the piles, the thermal conductivity of the rock, and micro-scale properties, particularly mineral surface areas. In addition, climate factors, such as temperature and the amount of precipitation, can significantly influence AMD generation.

The characterization of waste rock is critical in predicting the extent of AMD generation and for applying effective strategies to control AMD. However, waste rock can be particularly heterogeneous in terms of both mineral content and grain-size distribution, making characterization difficult and costly. As a result, strategies are required to appropriately scale waste-rock characteristics from limited measurements made from small-scale laboratory samples to operational-scale waste-rock piles.

Several studies have been undertaken in the past decade that emphasize integrated field-scale investigations of waste-rock characterization and large-scale coupling of geochemical, hydrological, and heat and gas transport processes. This review will draw on the findings from these integrated studies to discuss issues of waste-rock characterization, geochemical and transport processes, drainage-quality prediction and AMD-prevention methods, and conclude with a review of modeling studies. The waste-rock

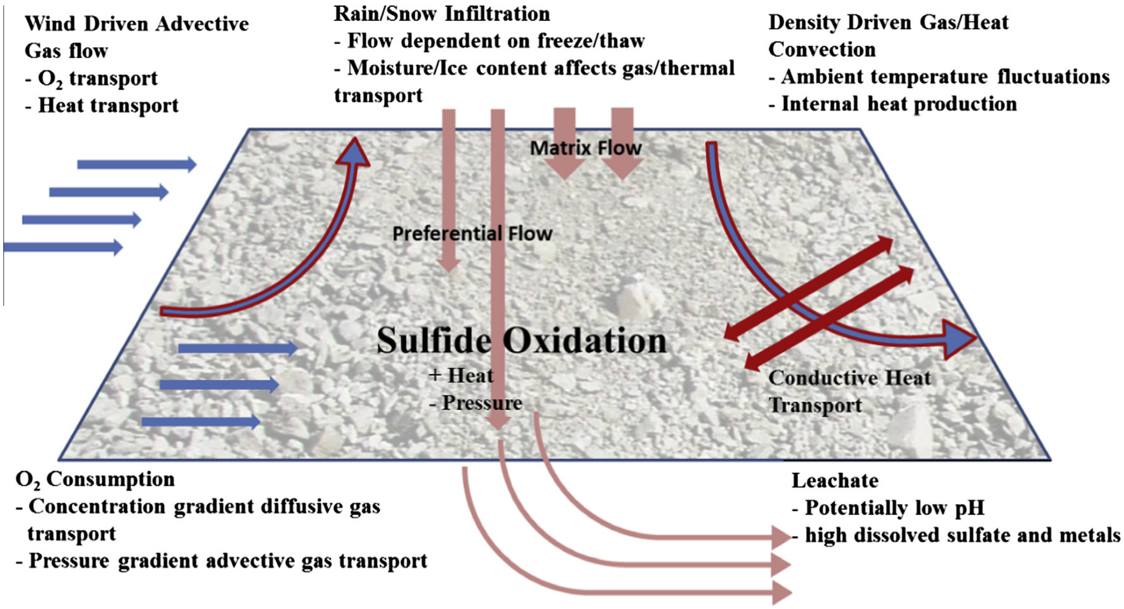

Fig. 1. Physiochemical processes occurring within waste rock. Modified after Lefebvre et al. (2001a).

characterization section reviews characteristics of waste rock and the effects of these characteristics on AMD generation. The following section discusses the range of processes encountered in waste-rock stockpiles, the implications of each process and coupling between processes. The prediction and prevention section will review scale-up methods and the effects of cover systems for reducing AMD generation through limiting water, oxygen, and gas and heat transport. The modeling section reviews efforts to model the coupling of various processes within waste-rock stockpiles.

2. Characteristics of waste-rock stockpiles

2.1. Physical characteristics

2.1.1. Internal structure and heterogeneity,

The physical and chemical heterogeneities and internal structure of a waste-rock pile affect internal chemical weathering patterns, as well as physical transport processes, including gas, water, and heat transport. Heterogeneity and internal structure are controlled by a number of factors, including the physical, mineralogical, and chemical character of the material, mine sequencing, and construction method. End- and push-dumping are common dump-construction techniques that result in significant gravity sorting. Dump construction is often carried out in several lifts, with large boulders falling to the base of the lift and finer fractions concentrating at the top. In addition, compacted surfaces develop at the top of each lift due to equipment traffic on the surface.

Stockwell et al. (2006) deconstructed a 12-m high experimental waste-rock pile consisting of hydrothermally altered quartz–chlorite–'sericite'–graphite schist regolith, located at the Key Lake mine in northern Saskatchewan, Canada. The waste-rock pile, constructed by end-dumping, contained particles ranging from clay sized to boulders larger than 1 m. Stockwell et al. (2006) observed alternating and intermixed coarse and fine lenses, approximately 1–3 m thick, dipping at the angle of repose, and a coarse rubble zone at the base of the pile. Ice lenses up to 15-cm thick were found at the base of the rubble zone, and discontinuous lenses of frozen waste rock were found above and adjacent to the rubble zone. The average annual temperature at the site was −0.4 °C, although freezing of the test pile core was facilitated by an open drain pipe installed into the base of the test pile. The study found no clear relationship between particle size and weathering patterns.

An operational waste-rock pile at the Golden Sunlight Mine in southwestern Montana, USA was investigated by Azam et al. (2007). Excavation of the East Pile, consisting of predominantly shale and latite rocks with extensive disseminated sulfide, revealed gravity sorting features resulting from the end-dumping method used to construct the piles. These features included compacted zones along traffic surfaces, a coarse rubble zone at the base of the pile, and inter-fingered beds at the angle of repose. Physical weathering processes (i.e. abrasion, particle crushing, growth of mineral and ice crystals, and slaking due to volume changes in clay minerals) and chemical weathering processes (i.e. dissolution, oxidation, hydrolysis, diffusion and precipitation) imparted an additional degree of heterogeneity in the waste-rock pile.

Fines (2006) investigated two waste-rock piles. The first pile, located in South Carolina, USA, contained relatively fine-grained material and exhibited the typical end-dumping characteristics, including dipping interbedded layers and traffic surfaces. Measured water content in this waste rock varied from 4% to 23% by volume. The second pile, near Sudbury, Ontario, Canada, was relatively coarse grained, with approximately 10% less than 100 mm. Some evidence of layering was observed in this waste rock, but no traffic surfaces had developed. Due to the coarse material with little capillarity, moisture content in the pile was not measureable in the majority of the samples collected, and assumed to be between 3% and 7% by volume.

2.1.2. Particle size

Particle size in waste rock can vary from greater than 1-m scale boulders to sub-millimeter clay-size fractions. Waste rock can generally be considered to comprise two fractions; fine fractions where capillary forces are important, and coarse fractions where capillary forces are not relevant. The geochemical and hydrogeological properties of waste rock will depend on the relative fraction of fines to coarse materials, and the grain size distribution within the fine fraction.

Smith et al. (2013c) studied the grain-size distribution of three experimental waste-rock piles (test piles) at the Diavik Diamond Mine in the Northwest Territories, Canada. The waste rock at the Diavik mine is predominantly granite with small amounts of sulfide-bearing biotite schist. Waste rock at Diavik is segregated based on the sulfide content with the low-sulfide content waste rock designated as Type I, and higher-sulfide content waste rock designated as Type III. The three test piles constructed at Diavik are designated the Type I test pile containing on average 0.035 wt.% S, the Type III test pile containing on average 0.053 wt.% S, and the Covered test pile consisting of a Type III core (0.082 wt.% S), a 1-m till layer, and a 3-m Type I thermal cover. Sieve analysis showed that the three test piles had very similar grain-size distributions (d_{50} of 11.2 mm, 6.9 mm, and 11.1 mm for the Type I test pile, Type III test piles, and Type III core of the Covered test pile, respectively), although the Type III material tended to have a larger fraction of fines (d_{10} of 0.50, 0.20, and 0.25 mm for the Type I test pile, Type III test piles, and Type III core of the Covered test pile, respectively). These d_{50} and d_{10} values for the Diavik waste rock are in the middle of the range previously reported by McKeown et al. (2000) for six metal mines. Smith et al. (2013c) suggested that the larger portion of fines in the Type III material is lithologically controlled, with

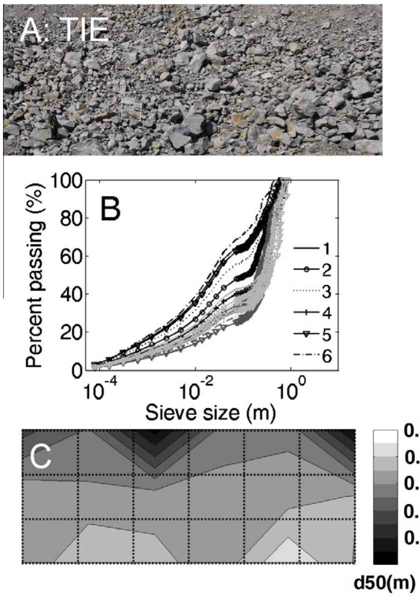

Fig. 2. (A) Photo of the east face of the Diavik Type I test pile (TIE). (B) Particle size distribution curves for TIE obtained from digital image processing particle size analysis with sieve analysis results for particle sizes <0.1 m. The individual curves are shown in black: top row, dark gray: middle row, light gray: bottom row. Line styles and symbols representing the six columns, numbered from left to right, are shown in the legend. (C) Contours of *d*50 for face TIE Contours are obtained by interpolation of *d*50 values on the center of each square defined by the dashed lines.

amount of fines related to the fraction of the less competent schist material in the waste rock.

Smith et al. (2013c) measured sulfur and carbon content of discrete particle-size fractions <50 mm of the Diavik waste rock. This analysis showed that sulfur content increased with decreasing particle size in both the Type I and Type III rock analyzed, although the Type III waste rock had higher sulfur content on average. In the Type III rock, the sulfur content was below the average of 0.053 wt.% S in the >0.62 mm fraction, and increased to greater than 0.12 wt.% S in the smallest fraction <0.08 mm. A similar trend was observed for the carbon content of the rock. These data indicate that for the Diavik waste rock there is a higher tendency for reactivity in the smallest size fractions, although these fractions will also retain greater water saturation, possibly limiting exposure to oxygen. These results are consistent with previous waste-rock studies that showed variation in mineral content, metal content, and reactivity with grain size (Munroe et al., 1999; Strömberg and Banwart, 1999; Morkeh and McLemore, 2012).

An important aspect of particle size is the correlation to surface area. Hollings et al. (2001) showed that surface area is a primary control on sulfide-oxidation rates. Chi (2011) used digital image processing (DIP) of exposed faces of the Diavik test piles, combined with traditional sieve analysis, to provide a full spectrum grain-size analysis (Fig. 2). Based on these analyses, calculations of surface area assuming spherical particles showed that particles greater than 1 mm have negligible contribution to the total surface area, suggesting that the majority of the reactivity within a pile is within the fine particles (Chi, 2011). Furthermore, the DIP analysis demonstrated a significant sorting of large particles (>0.1 m), with d_{50} values ranging from <0.1 m at the top of the 15-high test piles to >0.5 m at the base of the test pile. This analysis showed quantitatively the fine to coarse gradation from the top to bottom of the test piles, implying that reactivity will also grade from high to low vertically downward.

Yazdani et al. (2000) demonstrated that hydraulic properties of waste rock are controlled primarily by the less than 5 mm fraction, provided this fraction comprises at least 30–35% of the sample by volume. Particularly, the fine fraction will determine the shape of the soil–water characteristic curve (SWCC), air-entry pressure, and the matric suction at which residual saturation is achieved. The volumetric water content at saturation and the residual saturation are scaled by the proportion of the coarse fraction (i.e. particles greater than 5 mm).

Samples collected throughout the East Pile deconstruction at the Golden Sunlight Mine (Azam et al., 2007) were subjected to laboratory-based hydrological and physical characterization tests. Laboratory testing showed that material with 48–57% coarse sand size or finer (<4.75 mm) had soil-like matrix supported characteristics. Coarser grained samples with 40% and 30% material finer than 4.75 mm showed clast-supported rock-like characteristics. In the semi-arid climate in the region, water flow in this relatively dry pile is controlled by the soil-like material.

A large-scale particle size measurement was conducted on the Diavik Type I waste rock that showed 14.3% of the rock passing a 2.5 mm sieve (18% less than 5 mm fraction), suggesting rock-like properties (Smith et al., 2013c). However, studies by Neuner et al. (2013) and Fretz (2013) showed little evidence for macropore flow in the Diavik test piles. These studies suggest that although the Diavik waste-rock is dominated by coarse material, the limited annual precipitation (less than 150 mm per year in the study period) results in a flow regime predominantly controlled by the fine-grained matrix material. Only infrequent, high precipitation events alter this behavior.

2.1.3. Permeability

Fluid flow, and therefore chemical and heat transport processes, in waste rock are strongly controlled by the permeability of the waste-rock pile. Ritchie (1994) tabulated available waste-rock permeability measurements at that time (Table 1). These measurements were taken *in-situ* and showed a high degree of variability between various waste-rock dumps, and also within the same dump. Measurements ranged from 4×10^{-13} to 1×10^{-9} m^2 in all dumps, and from 9×10^{-13} to 1×10^{-9} m^2 in the dump with the highest observed variability (Rum Jungle). Lefebvre et al. (2001a) reported permeability measurements in the Doyon mine waste-rock dump, Quebec, Canada, determined from grain-size data, and the Norhalde, Germany waste-rock dump, estimated from the response of *in-situ* pressure measurements to barometric pressure changes (Weeks, 1979). These measurements fall within the range previously reported by Ritchie (1994; Table 1).

Within the three constructed test piles at the Diavik mine permeability balls for measuring *in-situ* permeability were installed at 3- and 6-m depths in the Type I and Type III uncovered test piles, and within the Type I and till layers of the Covered test pile (Table 1). Permeability balls are 3" diameter perforated plastic balls connected to the surface through two nylon tubes. Nitrogen gas was pumped in

Table 1
Air permeability and thermal conductivity values from various waste-rock dumps.

Minesite	Permeability (m^2)	Thermal conductivity (W m^{-1} K^{-1})	Source
Diavik, Canada – Type I Test Pile	4×10^{-10}–3×10^{-9}[a] Average: 1.8×10^{-9}	1.2–5.6[d] Average: 2.7	
Diavik, Canada – Type III Test Pile	2×10^{-10}–4×10^{-9}[b] Average: 1.8×10^{-9}	1.1–5.6 Average: 3.0[e]	
Diavik, Canada – Covered Test Pile – Type I Cover	4×10^{-10}–3×10^{-9}[b] Average: 1.4×10^{-9}	1.0–5.9 Average: 3.1[f]	
Diavik, Canada – Covered Test Pile – Till Layer	1×10^{-10}–4×10^{-10} Average: 2.3×10^{-10}[c]	1.1–3.3 Average: 2.0[g]	
Doyon, Canada	8.1×10^{-10}	2.5	Lefebvre et al. (2001a)
Norhalde, Germany	2.5×10^{-12}	1.0	Lefebvre et al. (2001a)
Aitik Mine, Sweden	2.6×10^{-11}–1.4×10^{-9}	0.71–1.63	Ritchie (1994)
Heath Steele, Canada	1.6×10^{-10}–4.7×10^{-9}	1.04–1.22	Bennett et al. (1995)
Kelian, Kalimantan	3.9×10^{-13}–9.3×10^{-10}	1.57–3.31	Tan and Ritchie (1997)
Rum Jungle, Australia	8.9×10^{-13}–1.9×10^{-9}	1.77–3.12	Kuo and Ritchie (1999)

[a] Average taken from six permeability instruments, three at 3 m depth and 3 at 6 m depth. Each instrument was sampled one to seven times between October 2006 and October 2011. A total of 38 for the Type I pile and 32 for the Type III pile.

[b] Average taken from five permeability instruments sampled one to three times between June 2007 and October 2011 for a total of 11 measurements.

[c] Average taken from three permeability instruments measure once each between June 2007 and October 2011.

[d] Average taken from measurements at 11 points ranging from 4 to 12.5 m depth between September 2006 and September 2011. Each sample point was measured from one to 13 times for a total of 89 measurements.

[e] Average taken from measurements at 11 points ranging from 4 to 10 m depth between September 2006 and September 2011. Each sample point was measured from one to nine times for a total of 41 measurements.

[f] Average taken from measurements at three points in the Type 1 cover between June 2007 and July 2011. Each sample point was measured from three to six times for a total of 16 measurements.

[g] Average taken from measurements at four points in the till cover between August 2009 and October 2010. Each sample point was measured from three to five times for a total of 16 measurements.

one tube at a known rate, while pressure in the ball was measured through the second tube. From the know gas flow rate and measured pressure, permeability of the surrounding material can be determined. Measured permeabilities range from 2×10^{-10} to 4×10^{-9} m^2, although the maximum values may have been limited by the permeability of the ball itself. Measurements show that there is no discernible difference between the Type I and Type III test piles. This similarity is not unexpected given the similar lithology and grain-size distribution observed for this rock. Similarly, there is little difference between the Type I test pile, which was constructed by end-dumping, and the Type I layer of the Covered test pile, which was free-dumped and then leveled with a dozer. The similarity in these measurements suggests that the dumping method did not significantly alter the permeability of the material; however, the permeability balls in the Type I pile were installed at a maximum depth of 6 m in a 15-m high pile, and also do not account for traffic surface effects.

Permeability has been measured in the uncovered Diavik test piles periodically in the summer months (June to October) from 2006 to 2011 (Table 1). Individual points were measured on average six times over this period. Measurements at a given point varied by factors ranging from 2 to 7.5 (average: 3), although no temporal trends were apparent. The variability may be due to differences in moisture content at the time of measurement.

Waste-rock segregation by end-dumping leads to a commonly expressed conclusion that the construction process gives rise to a high permeability zone along the base of the dump. Ritchie (2003) showed measurements of the air permeability at 1-m intervals down four locations in White's dump at Rum Jungle, Australia, and at 1-m intervals at two locations in a waste rock dump at the Aitik mine, Sweden. In all six cases, the probe holes were drilled to the base of the dump. Although the measurements indicate that the permeability can change by 2 or 3 orders of magnitude from one part of a dump to another, in only one case is there evidence that the permeability increases by a large amount towards the base of the dump.

Saturated hydraulic conductivity was measured by Neuner et al. (2013) on the <5-mm matric fraction of the Diavik waste rock using a constant head permeameter, and by Fretz (2013) on the <0.5-m fraction using a 32 m^3 (4 m × 4 m × 2 m) constant head field permeameter. Measurements of the matric fraction yielded saturated hydraulic conductivities of 2×10^{-6} to 3×10^{-5} m s^{-1} (permeability of 2×10^{-13} to 3×10^{-12} m^2). The field permeameter saturated hydraulic conductivity was determined to be 6×10^{-3} m s^{-1} (permeability of 6×10^{-10} m^2), which is comparable to the *in-situ* permeability measurements of the test piles using the gas-permeability balls. The field permeameter measurement is considered a minimum value as drain flow out of the permeameter may have been restricted by the pipe size.

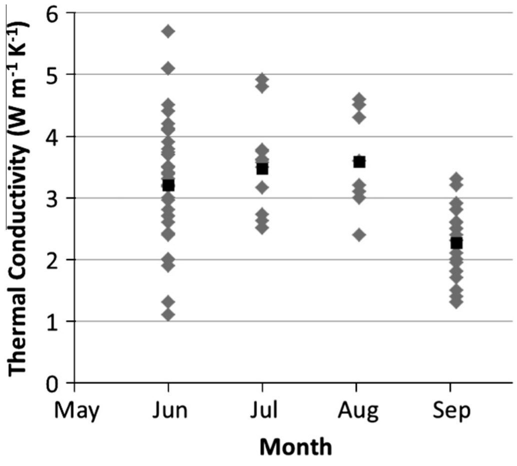

Fig. 3. Thermal conductivity measurements in uncovered Diavik test piles from 2006 to 2011. Average values for each month are shown as black squares. Individual points are shown as gray diamonds.

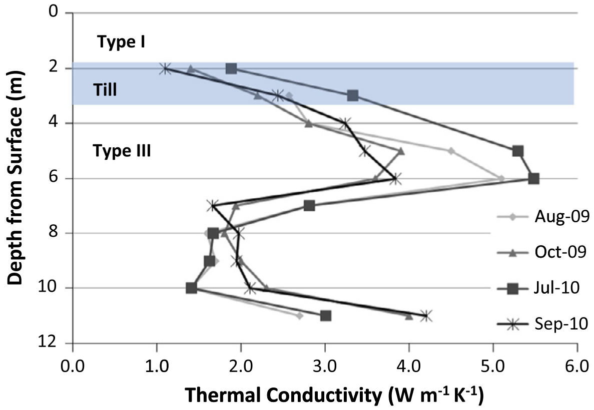

Fig. 4. Thermal conductivity values measures within a vertical drill hole in the Diavik Covered test pile from August 2009 to September 2010. The shaded area represents the thickness of the till layer.

2.1.4. Thermal conductivity

Thermal conductivity is an important parameter controlling heat transport in waste-rock piles. Thermal conduction in rock is a function of various parameters including the type of rock, the relative effectiveness of grain-to-grain paths, the pore fluid, and temperature (Robertson, 1988). In a dry waste-rock pile, heat conduction is primarily through particle to particle contact. Increased water content creates a coating of water around the contact points and enhances the heat conduction between grains (Harries and Ritchie, 1981). Ice is approximately 3.8 times more conductive than water at 0 °C, and has the potential to increase thermal conductivity (Pham et al., 2013).

Waste-rock thermal conductivity values reported in the literature range from 0.7 to 3.3 W m^{-1} K^{-1}, reflecting the range in waste-rock lithology and pile properties. Thermal conductivity has been measured at several points within the Diavik Type I and Type III test piles at multiple times between September 2006 and September 2011. Conductivity values range from 1.0 to 5.6 W m^{-1} K^{-1}, with an average of 3.0 W m^{-1} K^{-1}in the granitic material and 2.0 W m^{-1} K^{-1} in the till cover material (Table 1). These values are higher than those previously reported and potentially reflect the formation of ice within the piles. Measurements from within the uncovered Diavik test piles show some seasonal variation, with higher variability observed in June and an apparent decrease in the average value in September (Fig. 3). These variations indicate that thermal conductivity is not a static parameter and highlight the need for multiple measurements, both spatially and temporally.

Thermal conductivity was measured in two vertical drill holes 11-m deep in the Diavik Covered test pile (Fig. 4). These measurements showed both a spatial and temporal trend. Thermal conductivity values were lowest near the top of the test pile and increased nearly linearly to a maximum value at a depth of about 6 m. This increase was potentially due to an increase in moisture and ice through the test pile. The highest values were observed earlier in the summer, and decrease as the pile warms through the field season, potentially due to melting ice within the pile.

2.2. Mineralogy

The oxidation of sulfide minerals, formation of secondary minerals, and acid-neutralization reactions have been well documented for sulfide-bearing mine wastes, as previously reviewed by Jambor (2003) and Blowes et al. (2013), among others. The conceptual understanding of mineralogical reactions in sulfide-bearing mine wastes, as described in the above noted references, has been developed primarily with respect to mine tailings, and to some extent natural analogues, but has equal relevance to sulfide-bearing waste rock. The following section provides a brief review of sulfide oxidation and secondary reactions in mine waste, in general, followed by some specific examples from waste-rock studies, particularly field-scale investigations.

Jambor (2003) provided a summary of the stages of pyrite oxidation and associated mineral assemblages within mine waste. Pyrite and pyrrhotite are the most common sulfide minerals in mine waste with other sulfides such as arsenopyrite, sphalerite or chalcopyrite also being important at some sites. In cases where pyrite and pyrrhotite are both present, invariably pyrrhotite oxidation precedes that of pyrite. Alteration products including native sulfur, marcasite, and Fe-sulfates are found as alteration rims or coatings on unaltered pyrrhotite. Iron-oxyhdroxides are found peripheral to the pyrrhotite and alteration rims. Continued oxidation will result in depletion of pyrrhotite and secondary marcasite, and oxidation of pyrite with Fe-oxyhydroxides as the primary alteration product. Jarosite formation is indicative of decreasing pH, at least locally. At early stages of weathering, alteration of biotite, but not muscovite or feldspars, is observed. Late stages of oxidation are marked by near complete depletion of pyrrhotite, decreasing pH due to kinetically limited buffering effects, and goethite as the primary Fe-oxyhydroxide.

Acid neutralization in mine waste waters occurs through the dissolution of primary minerals including carbonates, (oxy)hydroxide minerals, and aluminosilicate minerals. Acid-consuming reactions in mine waste are summarized by Blowes et al. (2013). Initially, fast dissolution of carbonate minerals results in near-neutral pH conditions. Dissolution of carbonates generally follows the sequence, calcite, dolomite-ankerite, siderite, representing the decreasing solubility of these common carbonates observed in mine waste. Upon depletion of carbonate minerals, solution pH will fall until the solubility of hydroxide minerals is reached. The dissolution of aluminum hydroxides, generally considered to be amorphous Al hydroxide, gibbsite or Al hydroxysulfate phases will maintain the pH in the range 4.0–4.5. Following the depletion of Al-bearing hydroxide phases, the dissolution of Fe-oxyhydroxide minerals, such as ferrihydrite or goethite, will maintain the pH between 2.5 and 3.5. Throughout the pH range, dissolution of silicate and aluminosilicate minerals will provide further acid-neturalization capacity, although the rate of dissolution of these minerals is generally slow, so that buffering to a specific pH does not occur.

Hannam et al. (2012) and Hannam (2012) analyzed samples from the Diavik operational-scale waste-rock pile using optical microscopy, scanning electron microscopy (SEM), and micro-X-ray fluorescence (μXRF) and micro-X-ray diffraction (μXRD) synchrotron analysis. Samples were collected from drill cuttings from 30 to 40-m deep drill holes. Optical mineralogy results showed unaltered pyrite with a greater abundance of pyrrhotite, consistent with baseline reports on geochemistry (Blowes and Logsdon, 1998) and mineralogy (Jambor, 1997) at the Diavik site. Pyrrhotite showed varying degrees of alteration, in contrast to the baseline studies, which showed relatively unaltered pyrrhotite (Jambor, 1997). Elemental maps obtained from scanning electron microscope – energy dispersive X-ray (SEM-EDX) spectra indicated that iron concentrations extend through cracks and grain boundaries, although sulfur does not, possibly indicating Fe-(oxy)hydroxide formation accumulating in the voids as the pyrrhotite weathers. Elements such as silica, aluminum, and potassium tend to accumulate in the cracks, likely as a result of concurrent weathering of micaceous minerals. Several μXRD patterns along the grain edges revealed the presence of marcasite, indicative of early-stage pyrrhotite oxidation (Blowes and Jambor, 1990). The signature of early stage weathering observed and the lack of a consistent trend in weathering patterns with depth were consistent with the relatively recent placement of the waste rock.

Evans et al. (2003) performed X-ray fluorescence (XRF) and X-ray diffraction (XRD) analysis on samples retrieved from an 8-m drill-hole profile within a coal spoils heap. Jarosite was relatively abundant in the oxidized upper three meters of the heap, whereas alunite was the dominant sulfur mineral at 4 m, and pyrite was the dominant mineral below 4 m in the oxygen depleted zone. Evans et al. (2003) suggested that alunite is formed from Al derived from weathered clay minerals. The trend showed a progression of weathering from the upper portion of the dump towards the bottom.

Smuda et al. (2007) conducted a mineralogical and geochemical study of the Excelsior waste-rock dump at the Cerro de Pasco mine, Peru to determine controls on element mobility, particularly with respect to seasonal wet and dry cycles. The waste-rock pile was emplaced between 1943 and 2000. Samples were collected from the top and base of the dump. Waste rock from the polymetallic Zn–Pb–Cu mine includes 70–80% quartz-pyrite rocks from the ore body, 15–20% sericitized monzonites/tuff and approximately 5% dolomitic rocks. Quartz-pyrite rocks were relatively unaltered, although pyrite grains in close proximity to each other had varying degrees of alteration, with the smaller grains showing the highest degree of alteration. The small pyrite grain size and high porosity of the volcanic rocks lead to high degrees of alteration; pyrite grains were highly altered and large boulders were reported to have completely decomposed. Carbonate rocks consisted of dolomite and siderite. Smuda et al. (2007) suggested that whereas the dolomite has acid-neutralizing potential, the iron released from siderite dissolution also represented additional acid-generating capacity, making the dissolution of siderite neutral in terms of overall acid generating capacity. Secondary minerals observed in rock samples included hydronium-jarosite and K-jarosite solid solution, goethite and hydronium-jarosite and Pb–Fe-jarosite in Pb-rich samples. These assemblages are consistent with the high degree of alteration observed (Jambor, 2003). Samples from efflorescent salt accumulations at the top and at the base of the pile included gypsum, Mg-sulfates, and heavy metal sulfates. These observations were consistent with the mobilization of elements during the wet season followed by high evaporation in the dry season, leading to concentration of leach water and precipitation of metal salts.

Investigating the mobility of arsenic, Kocourková et al. (2011) completed mineralogical and geochemical studies of two profiles through a waste-rock pile at Dlouhá Ves, Czech Rebublic. The profiles included a 1.2-m excavation at the top of the rock pile and a 1.5-m outcrop at the base of the pile (referring to an exposed section of the waste-rock on the slope of the pile). Arsenopyrite was highly corroded and found to be the only arsenic-bearing primary mineral in the pile. Arsenic mobilization was found to be affected by the pyrite/arsenopyrite ratio. Where pyrite was abundant, low As/S ratios lead to the formation of jarosite-group minerals resulting in highly acidic pore water and mobilization of As and metals including Pb, Cu, Zn and Cd. Where arsenopyrite was the dominant sulfide, coatings of scorodite and other Fe–As phases formed, limiting further oxidation.

3. Processes related to sulfide oxidation and solute loadings

3.1. Geochemistry

The geochemistry within waste-rock and other pyritic mine waste, controlled by sulfide-oxidation reactions and the resulting acid-neutralization reactions, has been reviewed extensively by others, including a recent review by Blowes et al. (2013). This review will provide a brief summary of mine-waste geochemical reactions generally following Blowes et al. (2013; and references therein), followed by a review of recent field-scale waste-rock studies.

The oxidation of pyrrhotite and pyrite by dissolved O_2 can be described as;

$$Fe_{1-x}S_{(s)} + \left(2 - \frac{x}{2}\right)O_2 + xH_2O \Rightarrow (1-x)Fe^{2+} + SO_4^{2-} + 2xH^+ \quad (1)$$

and

$$FeS_{2(s)} + \frac{7}{2}O_2 + H_2O \Rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (2)$$

respectively, where x in $Fe_{(1-x)}$ can range from 0 to 0.125. The ferrous iron released by reactions (1) and (2) can be oxidized:

$$Fe^{2+} + \frac{1}{4}O_2 + H^+ \Rightarrow Fe^{3+} + \frac{1}{2}H_2O \quad (3)$$

potentially leading to the precipitation of ferric oxyhydroxides:

$$Fe^{3+} + 3H_2O \Rightarrow Fe(OH)_3(s) + 3H^+ \quad (4)$$

where $Fe(OH)_3$ represents (oxy)hydroxides, such as ferrihydrite. The overall reaction for pyrite:

$$FeS_{2(s)} + \frac{15}{4}O_2 + \frac{7}{2}H_2O \Rightarrow 2SO_4^{2-} + Fe(OH)_3(s) + 4H^+$$

indicates the release of 4 mol of protons (acid) for each 1 mol of pyrite oxidized, and $2 + 2x$ moles of protons are released per mole of pyrrhotite. Although, the release of acidity from pyrrhotite is stoichiometrically less than pyrite, pyrrhotite has a lower activation energy and reacts much faster than pyrite. Under acidic conditions the oxidation of sulfides may occur with ferric iron as the oxidant; for example with pyrite:

$$FeS_{2(s)} + 14Fe^{3+} + 8H_2O \Rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (5)$$

where the supply of Fe^{3+} is maintained only in the presence of dissolved oxygen as described by Eq. (3).

Acidic conditions generated through sulfide-oxidation reactions (Eqs. (1)–(5)) can promote the mobility of many metals due to the increased solubility of many minerals and decreased sorption at low pH. The dissolution of carbonate minerals, aluminum and ferric-oxyhydroxide minerals, and aluminosilicate minerals can buffer pH. The dissolution of carbonate minerals, such as calcite, dolomite, ankerite, or siderite can maintain the pH to near neutral; for example:

$$CaCO_3 + H^+ \Rightarrow Ca^{2+} + HCO_3^- \quad (6)$$

releasing alkalinity and cations such as Ca, Mg, Mn, and Fe, or other metals found as substitutions or impurities to the water. The depletion of carbonate minerals is generally followed by a decrease in pH, and potentially, an increase in Al concentrations, reflecting the dissolution of Al oxyhydroxide minerals. The dissolution of Al oxyhydroxides, such as amorphous hydroxide [$Al(OH)_3$] or the crystalline form, gibbsite, will generally maintain the pH in the range of 4.0–4.5. Following Al oxyhydroxide dissolution the next most soluble phases are Fe oxyhydroxides, such as ferrihydrite or goethite, maintaining the pH to approximately 2.5–3.5. The dissolution of aluminosilicate minerals, including chlorite, smectite, biotite, muscovite, plagioclase, and amphibole, can proceed concurrently with carbonate and oxyhydroxide mineral dissolution, but is generally kinetically limited, and the pH is not constrained to a specific value. Dissolution of aluminosilicate minerals results in the release of a range of elements including H_4SiO_4, Al, K, Ca, Mg, and Mn.

Smith et al. (2013b) reported on the initial geochemical response from the Diavik Type III test pile. Construction of the 15-m high Type III test pile, containing an average of 0.053 wt.% S, was completed in 2006. The test pile is lined with an impermeable liner which drains to two basal drains at the base of the test pile. Data collected from the basal drains during the 2007 field season (late May to the end of November) showed an initial pH near neutral in June followed by a decreasing trend through the field season, with minimum pH values of <5 recorded in August. The decrease in pH was accompanied by a decrease in alkalinity from approximately 50 mg L^{-1} $CaCO_3$ to generally <10 mg L^{-1}, with minimum values <1 mg L^{-1} observed in August. Sulfate concentrations followed an opposite trend, with initially low concentrations increasing to a maximum in excess of 2000 mg L^{-1} in August, followed by a decrease to the end of the field season, but generally remaining above 500 mg L^{-1}. The decrease in pH, depletion of alkalinity, increase in SO_4, Fe, and other metals, including Ni and Co, were indicative of pyrrhotite oxidation with rapid depletion of carbonate minerals. Increasing concentrations of Al and Fe, and geochemical equilibrium modeling suggested that the pH was neutralized by dissolution of Al (oxy)hydroxide and Fe (oxy)hydroxide phases. Release of Mn was attributed to aluminosilicate weathering and release of Zn, Cd and Cu were attributed to sphalerite and chalcopyrite oxidation. The observed trends in pH and solute concentrations were interpreted to be due to the geochemical changes superimposed by changes in internal pile temperature through the field season and possibly changes in flow-path length as the test-pile batters thawed inward through the summer.

Bailey et al. (2013) studied residuals from blasting in the Diavik test piles and 2-m-by-2-m scale active zone lysimeter experiments. Residuals include SO_4 derived from sulfide oxidation during blasting, nitrogen species, including NH_3, NO_2^-, and NO_3^- from undetonated ammonium nitrate fuel oil (ANFO) explosives, and ClO_4^- and Cl^- from the boosting agent. Bailey et al. (2013) used concentrations of total N and Cl, measured throughout the 2007–2010 field seasons, as conservative tracers to identify the first flush of water through the waste rock. Ratios of SO_4 to total N and Cl were used to distinguish between SO_4 derived from blasting and SO_4 derived from *in-situ* oxidation. Total N mass-balance calculations indicated that whereas the 2-m-by-2-m scale experiments had mostly been flushed of blasting residuals, data from the larger test-pile experiments showed only a small portion (<10%) had been flushed. Overall, the blasting agents proved to be an effective means of quantifying transport and oxidation processes within the waste rock.

A geochemical characterization of the South Dump at the Doyon Mine was presented by Sracek et al. (2004). The study included analysis of pore-water samples from suction lysimeters in three vertical boreholes; two of which were in predominantly sericite-schist lithology (Site 6 and Site 7) initially containing 7.0 wt.% S on average, and the third within a predominantly diorite lithology (Site TBT) initially containing 5.5 wt.% S on average. Samples from Site 6 and Site TBT, collected in the dry season (October 1995) and the recharge period (April 1996), showed both spatial and temporal trends. The pH at both sites was very acidic ranging from approximately pH 2–3 with an increasing trend from top to bottom of the pile. The low pH and elevated concentrations of Al and Mg are indicative of neutralization by silicate minerals, particularly chlorite and muscovite. In the dry season maximum concentrations of Al, Mg, SO_4, and Fe were observed at depths of approximately 10 m and 22 m for Site 6 and Site TBT, respectively, likely indicating zones of increased pyrite oxidation. In the recharge period, trends in these solutes showed a relatively uniform increasing trend with depth, likely as a result of flushing with fresh recharge water.

Geochemical data from three experimental waste-rock piles at the Antamina mine, Peru are presented by Bay et al. (2009). Pile 1, containing coarse grained marble hornfels with approximately 2–3 wt.% S and considered moderately reactive, was completed in January 2007 and data to October 2008 are presented. Piles 2 and 3, containing finer grained predominantly exoskarn waste with greater than 3 wt.% S and considered reactive, were constructed between June 2007 and January 2008, and data to October 2008 are presented. Despite the neutral or slightly alkaline pH for each pile (between pH 7 and 8.5 for Pile 1 and between pH 7 and 8 for Pile 2) elevated concentration of metals were observed in the effluent. For Pile 1 Zn concentration between 0.5 and 2.5 mg L^{-1} were measured, although other metals including Mo, As, Cu, and Pb were below detection. For Pile 2, elevated concentrations of Zn (up to 4.5 mg L^{-1}), Mo (up to 7 mg L^{-1}), As and Cu (>0.2 mg L^{-1}) were observed. The effluent from Pile 3 showed elevated concentrations of Zn (up to 45 mg L^{-1}) and Cu (>0.2 mg L^{-1}). Each pile showed varying concentrations and trends between the basal lysimeter (36 m × 36 m) and the sub-lysimeters (4 m × 4 m) demonstrating the geochemical heterogeneity within the piles and the variations with scale.

Peterson et al. (2012) provided a more detailed summary of the Antamina Pile 2 geochemistry, presenting data from July 2008 to July 2011 with a focus on seasonal trends related to the annual wet-dry cycle. Data from the 36 m × 36 m basal lysimeter showed seasonal variation in pH from maxima of approximately pH 7.8 in the lowest flow period (October) to pH 7 in the highest flow periods (March). Minimum values in pH were coincident with maximum concentrations of Cu and Zn, whereas elements such as Mo and As showed maximum concentrations during the first flush of each wet season (November or December) and minimum concentrations at the end of each wet season (May). In February 2011 a larger drop in pH was observed; from pH 7.7 in December to pH 6.4 in February, which was accompanied by increases in Cu from 0.1 mg L^{-1} to 67 mg L^{-1}, Zn from 5.9 mg L^{-1} to 75 mg L^{-1}, and SO_4 from 1500 mg L^{-1} to 1850 mg L^{-1}, over the same period. Minima in Mo and As were observed shortly after the maxima in Cu and Zn. The pH recovered to 6.7 at the end of the wet season; no further data are presented. Peterson et al. (2012) suggested that potential reasons for the seasonal variation in pH and solute concentrations include localized depletion of carbonate minerals in parts of the pile, seasonal flushing, and variation in residence time.

Leach water quality from waste rock storage areas at the Ekati mine, Northwest Territories Canada, are presented by Ketchum et al. (2012). Seepage water data from 2000 to 2011 from several seeps from two waste rock storage areas showed variations over time and between seeps, reflecting differences in waste-rock types within the piles. Waste-rock types included granite, biotite schist, kimberlite and diabase. Values of pH ranged from less than 5 to greater than 8. Ketchum et al. (2012) attributed the lowest pH values to interaction with the naturally acidic tundra soil. Major and trace metal chemistry reflected weathering of silicate minerals and sulfide, in addition to carbonate minerals predominantly in the kimberlite. Ratios of Mg to Ni were used to help distinguish the predominant mineralogy of the waste rock feeding the seeps.

3.2. Microbiology

The role of microorganisms in sulfide mineral oxidation has been widely described in reviews by Colmer and Hinkle (1947), Evangelou and Zhang (1995), Nordstrom (2000), Baker and Banfield (2003), Johnson and Hallberg (2003, 2005) and most recently synthesized in Blowes et al. (2013). Bacteria, including *Thiobacillus* species and the *Acidithiobacillus* species, are known to accelerate the generation of acidic drainage (Nordstrom and Southam, 1997; Blowes et al., 2013 and references therein). Microbially-mediated, sulfide-mineral oxidation can occur via contact or non-contact mechanisms (Hallberg and Johnson, 2001). Contact oxidation involves the attachment of a cell or bacterium to the sulfide mineral and the generation of an oxidizing agent (Fe^{3+}) in the interface between the cell wall and mineral surface that oxidizes the sulfide mineral (Rohwerder et al., 2003). Non-contact mechanisms involves the oxidation of dissolved Fe^{2+} to Fe^{3+} that subsequently oxidizes the sulfide mineral, thereby returning Fe^{2+} to the cycle (Rohwerder et al., 2003).

The oxidation of Fe^{2+} is known to be the rate limiting step in biotic pyrite oxidation under acidic pH conditions (Singer and Stumm, 1970). Microbially mediated pyrite oxidation by *Acidithiobacillus ferrooxidans* that catalyzes Fe^{2+} oxidation in field studies is reported to be orders of magnitude faster than abiotic laboratory rates (Kirby et al., 1999). Species responsible for microbiological oxidation have been shown to change through time during the acidification of mine wastes environments (e.g., Leduc et al., 1993; Southam and Beveridge, 1993; Blowes et al., 1995; Elberling et al., 2000; Moncur et al., 2005). Blowes et al. (1995) observed the succession of bacterial species with progressively lower pH in a sulfide-rich mill tailings impoundment at the Kidd Creek mine tailings impoundment near Timmins, Ontario, Canada, resulting in ideal conditions for *Acidithiobacillus* species that are known to catalyze sulfide mineral oxidation. At the Nickel Rim mine tailings impoundment Ontario, Canada, Benner et al. (2000) found the highest populations of S-oxidizing bacteria at recharge zones, where gaseous and dissolved oxygen entered the tailings. The highest populations of Fe-oxidizing bacteria where found in discharge zones where reduced water comes in contact with the atmosphere.

The microbial ecology of effluent from sulfidic waste-rock stockpiles is anticipated to change with the geochemistry similar to other mine wastes, from neutrophilic S- (e.g., *Thiobacillus* species) to acidophilic S- and Fe-oxidizers (e.g., *Acidithiobacillus* species) with degrading water quality (progressively lower pH and higher concentrations of SO_4, Fe, and other dissolved metals).

Bailey et al. (2012) described the succession of the microbial population in the Type III (0.53 wt% S) and Type I (0.035 wt.% S) waste-rock test piles at the Diavik Diamond Mine. The Type I waste-rock test-pile effluent was characterized with near neutral pH and low S concentrations. A population of neutrophilic S oxidizers was observed from 2008 through 2010 (maximum of 10^6 bacteria/mL in 2010) and lower numbers of acidophilic S and Fe oxidizers, at less than 10^3 bacterial/mL. The effluent from the higher S content Type III waste-rock test-pile varied in pH from near neutral in May to acidic conditions by October every year. The population of neutrophilic S oxidizers decreased as the pH declined. Increases in the populations of acidophilic S and Fe oxidizers coincided with the decrease in neutrophilic S-oxidizers. These results were similar to those observed in mill tailings impoundments (Blowes et al., 1995; Benner et al., 2000).

More recent work by Bailey (2013) focused on using deep sequencing and a temporal comparison of the bacterial phylogenies at different scales to examine the bacterial diversity in drainage from waste rock. Results indicate that the Type I test pile has the highest phylogenetic diversity whereas the acidic drainage in the Type III waste rock has a less diverse phylogeny, dominated by the *Hydrogenophilaceae* family, specifically the genus *Thiobacillus* (Bailey, 2013). In addition, the acidophilic Fe-oxidizer, *Acidithiobacillus* species, was present in drainage from the Type III active zone lysimeters where the pH decreased to 3.5 and the highest concentrations of sulfide-mineral oxidation products were observed (Bailey, 2013). The results from this study provide a baseline for the succession of the microbial community in waste rock stockpiles in the Arctic.

Dockrey (2010) examined the microbial population in waste rock piles at the Antamina mine site in the Peruvian Andes.

Drainage chemistry was neutral pH and populations of neutrophilic S oxidizers as large as 10^8 bacteria per gram were observed. Dockrey (2010) observed an exponential relationship between the sulfate loadings in discharge and microbial population, with maximum populations corresponding to maximum loadings.

Waste-rock material collected from the three waste rock piles at Antamina were examined using high resolution imaging techniques. A low abundance of bacteria was observed on samples from Piles 1 and 2 on weathered pyrite and no bacteria were found in Pile 3 (See Section 3.1 for a description of Piles 1, 2 and 3). A piece of massive sulfide composed of chalcopyrite, pyrrhotite and pyrite from a field cell had biofilms of bacteria observed within porous schwertmannite. Dockrey (2010) concluded that mixed populations of neutrophilic and acidophilic bacteria are living in acidic microenvironments surrounding acid generating mineral surfaces in otherwise circumneutral pH mine waste.

3.3. Hydrology

3.3.1. Evaporation and infiltration

The amount of water available for sulfide oxidation and leaching of oxidation products is a function of the amount of precipitation and evapotranspiration. Net infiltration into a waste-rock pile can be represented by equation:

$$\text{Net infiltration} = \text{Precipitation} - \text{Evapotranspiration} - \text{Surface Runoff} \tag{7}$$

In this context surface runoff is considered to be water that is shed from the upper surface of the dump, and therefore, does not penetrated into the dump or contribute to evaporation from the dump surface. Harries and Ritchie (1983) recorded runoff for individual rainfall events over a two consecutive wet seasons for the White's dump at the Rum Jungle mine in northern Australia. On average runoff was 15% of rainfall, and a maximum of 33%. The surface of White's dump is relatively smooth and well graded. Observations of the 600 m × 900 m Claude waste-rock pile at the Cluff Lake Mine, in northern Saskatchewan, Canada, indicated little ponding or runoff on the west portion of the pile, which was coarse grained and without a traffic surface (Bellehumeur, 2001). On the east portion of the pile, which was finer grained with a compacted traffic surface, water ponded and flowed overland to catchment areas. These catchment areas were generally local topographic lows with open porous structures that facilitated immediate infiltration into the rock pile (Bellehumeur, 2001). Other studies, including Carey et al. (2005) and Neuner et al. (2013) reported little runoff from waste-rock piles at the Key Lake mine and Diavik test piles, respectively; both of these studies are discussed below.

Carey et al. (2005) studied evaporation on the top of the Deilmann South waste-rock pile located at the Key Lake uranium mine in northern Saskatchewan, Canada over an 81-day period from June 6 to August 25, 2002. The waste rock is predominantly a sandstone waste-rock pile with a relatively uniform fine- to medium-grained sand texture. Evaporation was directly measured using eddy covariance and estimated using the Penman (1948) model corrected using the methods of Granger and Gray (1989) to estimate actual evaporation. Significant features of the waste-rock pile were a high albedo, resulting in a low ratio of net radiation to incident shortwave radiation, and lack of vegetation, resulting in relatively little daily and seasonal changes to energy fluxes. During the study period 236 mm of rainfall occurred and measured evaporation was 145 mm (61%), resulting in 91 mm of infiltration (39%). Modeled potential evaporation was 247 mm, and actual evaporation was 134 mm (57%), agreeing well with measured values.

Neuner et al. (2013) and Fretz et al. (2012) employed the FAO Penman–Montieth method, in conjunction with a bare soil coefficient to limit evaporation based on water availability (Allen et al., 1998) to estimate evaporative flux and net infiltration into the Diavik uncovered test piles. In addition, net infiltration was compared to 2-m scale active active zone lysimeter experiments located adjacent to the Diavik test piles. The experiments consisted of 1.5- to 1.7-m deep HDPE tanks, with the tops removed, filled with either Type I or Type III run-of-mine waste rock. Outflow was directed though heat-traced PVC drains into tipping bucket rain gauges to measure flow. The area surrounding the tanks is in-filled with waste rock to provide a continuous surface level with the top of the tanks. Estimates of net infiltration with the FAO model compared well with measurements of outflow from one of the active zone lysimeter experiments and flux estimates from tensiometer measurements in the Type III test pile. These comparisons, and the studies of Carey et al. (2005), suggested that Penman type estimates using local meteorological data can provide realistic predictions of evaporation from the surface of waste-rock piles provided a reasonable method of limiting actual evaporation is employed, including a reliable estimate of the evaporation depth.

The study by Fretz et al. (2012) provided important insights into the effects of the timing and magnitude of rain events on net infiltration. Fretz et al. (2012) estimated evaporation and infiltration from 2007 to 2010 at the Diavik test piles and active zone lysimeter experiments and reported fractional infiltration (infiltration as a fraction of total rainfall) ranging from 0.10 in 2009 to 0.46 in 2008 under natural rainfall conditions. The Diavik mine site is located in a relatively dry climate, and total rainfall in the study years ranged from 71 mm in 2009 to 150 mm in 2008. Mean annual precipitation is approximately 280 mm, of which approximately 60% is snow. From June to August of 2008 three rainfall events of 14, 13, and 33 mm, contributed the majority of infiltration. In these summer months, when net radiation and potential evaporation are high, only relatively large rainfall events contribute to infiltration. In late September 2008, a relatively small 16-mm rainfall event contributed significantly to net infiltration because potential evaporation was significantly less than in the summer months. In 2009, only small rainfall events occurred (<10 mm), resulting in a much reduced fraction (0.10) of the rain contributing to infiltration.

3.3.2. Unsaturated water flow

Water flow through unsaturated waste rock can be characterized as either matrix flow, where water flows under capillary forces as can be described by the Richards equation, or macropore, or non-capillary flow, where flow is more rapid and channelized. Solute mobilization, the rate of solute transport and the concentrations of solutes in waste-rock leachate will depend heavily on the flow mechanism. The degree to which each of the mechanisms is active depends on the properties of the waste rock (i.e. particle-size distribution) and the hydrological conditions, particularly the magnitude and timing of precipitation and infiltration events.

3.3.2.1. Cluff Lake constructed pile experiment. Smith and Beckie (2003) and Nichol et al. (2005) examined the hydrological behavior of a 5-m high constructed waste-rock pile, consisting of coarse grained poorly sorted rock, with particles ranging from 1.5-m boulders to clay. The constructed pile experiment, located at the Cluff Lake Mine was built upon a contiguous grid of sixteen gravity draining 2 m × 2 m pan lysimeters, giving an overall dimension of 8 m × 8 m below the core of the pile. Chloride tracer was applied to the upper surface of the pile via an artificial rainfall event. Several natural and artificial rainfall events occurred during the study period. Average annual precipitation is 455 mm, with 305 mm falling as rain.

Hydrographs from some 2 m × 2 m lysimeters show an outflow response within hours of the start of large precipitation events, indicating wetting front velocities orders of magnitude greater than the median water velocity determined from residence time estimates (Smith and Beckie, 2003). Each 2 m × 2 m lysimeter showed distinct hydrograph responses and, in addition, each lysimeter showed multiple arrivals. The variability in the hydrograph response is indicative of multiple spatially distinct flow paths within the constructed pile experiment. Composite hydrographs of 4 m × 4 m and 8 m × 8 m footprints also show multiple arrivals, suggesting that these scales are too small to average the variability in outflow in response to large rain events (Smith and Beckie, 2003; Nichol et al., 2005). Similarity in the drain down curves at fluxes lower than 2.2×10^{-9} m s^{-1} for the 2 m × 2 m lysimeters and whole pile 8 m × 8 m composite suggests that flow through the finer matrix material is relatively uniform over the 2 m × 2 m and 8 m × 8 m scales.

Nichol et al. (2005) distinguished between macropore and non-capillary flow. Macropore flow is considered to be flow in a structured porous media where water interacts with matrix water held in capillary tension. Non-capillary flow is considered flow in a structured porous media that does not significantly interact with matrix water. A chloride-tracer experiment indicated both of these preferential flow mechanisms were active within the constructed pile experiment in response to large rainfall events. Non-capillary flow was evident as distinct spikes in outflow rates and tracer concentrations, within 1.5–2 h after the start of the rainfall event, prior to the main hydrograph rise, with flow rates and concentrations returning to pre-event levels within 3–12 h. This type of response is indicative of flow and transport through highly conductive pathways, such as clast supported cobble and boulder structures, with little interaction with matrix materials. Nichol et al. (2005) estimated that this flow mechanism accounted for approximately 0.1% of total outflow volume during the study period.

Macropore flow was indicated by tracer response coincident with the main hydrograph response and persistence of tracer in the outflow from that point onward. This response reflected the exchange of water between the fast preferential flow paths and the slower matrix flow, which constituted the main component of the hydrograph response. Nichol et al. (2005) estimated that macropore flow accounts for approximately 5% of net infiltration during large rainfall events.

3.3.2.2. Diavik test piles. The Diavik mine site is in a region of continuous permafrost where the mean annual air temperature is approximately −9 °C and the mean monthly temperatures range from a low of −30 °C in January and February to a high of 12 °C in July (Pham et al., 2013). Investigations of the test-scale waste-rock piles by Neuner et al. (2013) indicated a strong coupling between thermal and hydrological processes. Neuner et al. (2013) showed that in 2007 rainfall into frozen ground, in the early spring, resulted in the propagation of a wetting front that followed the thaw front into the test piles. Fretz et al. (2011) extended the work of Neuner et al. (2013) for the period from 2007 through 2010 and similarly found that water flow through the core of the Type III test pile was predominantly controlled by the annual freeze/thaw cycle.

Snow was wind scoured from the crest of the test piles but accumulated on the batters to an estimated average depth of 1.5 m, resulting in an estimated water equivalent of approximately 400 mm. In 2007, snowmelt on the test piles occurred primarily in May when temperatures within the test piles remained below 0 °C. The maximum measured outflow from the Type III test pile occurred on July 23, three days after the maximum daily air temperature, and when the cumulative rainfall for 2007 was 29 mm (31% of 2007 total rainfall) and the thaw front had reached a depth of 3 m (Neuner et al., 2013). Fretz et al. (2011) compared the Type III test pile discharge and internal temperatures from 2006 to 2010 and observed that test pile discharge occurred before the temperature in the core of the test pile rose above 0 °C. Fretz et al. (2011) concluded that the shorter flow paths through the batters of the test pile, the earlier thaw of the test pile batters, and the increased snow accumulation on the batters results in early season flow from direct snowmelt, remobilization of water in the batters during thaw, and early precipitation events infiltrating through the test pile batters.

Neuner et al. (2013) conducted investigations of flow mechanisms and solute loading calculations and concluded that flow in both the Diavik test piles and active zone lysimeter experiments was dominated by matrix flow and not macropore or non-capillary flow despite the predicted rock-like nature of the waste rock based on the fraction of fines present. However, an applied rainfall event of 29 mm (equivalent to a 35-year recurrence interval) resulted in some indications of macropore flow to a depth of 6.8 m from the surface. Neuner et al. (2013) calculated wetting front migration rates of 0.2–0.4 m/d for common rainfall events and up to 5 m/d for intense rainfall events. Tracer test study results indicated that pore water migrated at rates of <0.01–0.03 m/d in response to common rainfall events and up to 0.70 m/d in response to intense rainfall events. Fretz (2013) determined similar wetting front velocities for the Diavik test piles, although minimum values of 0.01 m/d were determined at shallow depth (1 m) for multiple infiltration events.

3.3.2.3. Antamina experimental waste-rock piles. Blackmore et al. (2012) conducted a tracer test on two experimental waste-rock piles at the Antamina mine located in the Peruvian Andes. The mean annual air temperature in the region is 5.5–6.0 °C, with a mean annual precipitation of 1200 mm, the majority of which falls in the wet season from October to April (Bay et al., 2009). At the Antamina site five experimental waste-rock piles were constructed. The piles were 36 m × 36 m at the base and 10 m high, constructed by end-dumping. The piles were constructed on top of a basal lysimeter system consisting of a 36 m × 36 m lysimeter (Lysimeter D) with three 4 m × 4 m sub-lysimeters (Lysimeters A and B under the crest of the piles and C under the batter of the piles) within the base of the larger lysimeter. Piles 4 and 5 are the focus of the study by Blackmore et al. (2012). Pile 4 is a mixture of waste rock designated as Class B and C, which are mixtures of marble, hornfels and marble, and are relatively coarse grained. Pile 5 is a mixture of Class A and C waste rock, with Class A waste rock consisting of a finer grained skarn. Class A, B and C materials are characterized as having 23%, 6%, and 4% passing a 2 mm sieve, respectively. Tracers, including bromide (~3000 mg L^{-1}) and uranine (~10 mg L^{-1}), were applied to Piles 4 and 5 on January 23 and 24, 2010, respectively, through an artificial rainfall event equivalent to a four-year recurrence interval event.

Blackmore et al. (2012) reported that bromide breakthrough was observed in all four Pile 4 lysimeters 4 to 6 h after application. Maximum tracer concentrations reached a C/C_o value of 0.44, 1.5 days following tracer application and the majority of the tracer was flushed from the pile before the onset of the rainy season in October. The fast tracer breakthrough, high tracer concentrations, and relatively uniform response between lysimeters suggested that preferential flow was the dominant flow mechanism. Breakthrough of the uranine, known to adsorb to matrix material, was similar to bromide breakthrough, again suggesting preferential flow with little interaction with the matrix material. Breakthrough response was much different for Pile 5 (Blackmore et al., 2012). Significant continuous bromide breakthrough occurred in Lysimeters A and B within 2 days and 4 days of tracer application, respectively, and in Lysimeter D, two weeks after application. Maximum tracer concentration observed were an order of magnitude less than observed in Pile 4 lysimeters, and bromide continued to be discharged at significant concentrations through the study period.

Uranine breakthrough was negligible during the study period. Blackmore et al. (2012) suggested that the delayed tracer breakthrough and long tails to the breakthrough curves, along with strong retention of uranine, is indicative of a flow regime dominated by matrix flow.

The results of Blackmore et al. (2012) were consistent with a previous study of experimental Piles 1, 2 and 3 at the Antamina site (Bay et al., 2009). Pile 1, consisting of coarser-grained Class B rock, exhibited rapid outflow response to rainfall events, consistent with the results of Pile 4. Pile 1 showed seasonal changes in outflow in response to wet/dry season rainfall rates. In addition, sulfate loadings were primarily controlled by discharge rates, despite decreasing solute concentrations in the wet season (Bay et al., 2009). Preliminary hydrological characterization of Piles 2 and 3, containing finer-grained Class A rock, showed a delayed response to rainfall events, consistent with the tracer test results from Pile 5 (Bay et al., 2009; Blackmore et al., 2012).

The three studies summarized above, including the constructed pile experiments at Cluff Lake, the test pile and active zone lysimeter experiments at Diavik, and the constructed waste-rock piles at Antamina, demonstrate three distinct hydrological regimes dependent on waste-rock composition and prevailing meteorological conditions. Cluff Lake is in a temperate climate, with 405 mm of annual rainfall on average. Observations suggest that both preferential and matrix flow mechanisms are active depending on the magnitude of the rainfall event. At the Diavik site mean annual precipitation is approximately 280 mm, of which approximately 60% is snow. Hydrological conditions are dominated by the cold, dry environment. Flow through the test piles is strongly controlled by the thawing front and there is little evidence for preferential flow, except for a 29-mm rainfall event with a recurrence interval of 35 years. In these dry conditions, flow is restricted to the high capillarity matrix material (Neuner et al., 2013; Fretz et al., 2011). The Antamina site is characterized by moderate above freezing temperatures and high precipitation averaging 1200 mm per year. In this environment, discharge from the experimental waste-rock piles is highly influenced by the seasonal wet/dry cycle, and the flow mechanism is strongly controlled by the material properties (Bay et al., 2009; Blackmore et al., 2012).

3.4. Gas transport

Oxygen is a primary reactant for sulfide mineral oxidation, and therefore, it is often a controlling factor on sulfide-oxidation rates. As such, studies of gas transport in waste rock have typically been concerned with the transport of oxygen. However, the movement of gases can also carry a significant amount of heat, which can influence the temperature within waste rock piles. Gas transport processes in waste rock include; transport of dissolved gases in infiltrating water, diffusive transport in the gas phase, and advective transport in the gas phase. Advective transport can be driven by pressure gradients that result from gas consumption within the pile due to sulfide oxidation, thermally induced density gradients (convection), barometric pressure changes (barometric pumping), and air flow over the pile due to the wind. The dominating processes are determined by the physical and geochemical properties of the waste rock and the prevailing environmental conditions.

Generally gases, and particularly atmospheric gases such as oxygen, are very insoluble in water. As a result, the concentration of oxygen in infiltrating water is very low and generally not considered to have an important influence on sulfide-oxidation rates. Barometric pressure fluctuations can result in some enhancement to gas transport in porous media (Massmann and Farrier, 1992; Auer et al., 1996), but this process has not been well studied in waste rock.

The consumption of oxygen due to sulfide-mineral oxidation reactions can result in both pressure gradients and oxygen concentration gradients within the waste rock, and between the interior of the waste rock and the atmosphere surrounding the waste-rock pile. Typically, reaction-induced pressure gradients are not considered to be a significant transport mechanism. However, separate modeling studies by Binning et al. (2007) and Molins and Mayer (2007) demonstrated that under conditions where diffusive gas transport is dominant, reaction-induced advective transport can account for a significant fraction of total gas transport (24% in the study by Binning et al. (2007), and 10–15% in the study by Molins and Mayer (2007)). Further study is needed in this area.

Diffusion is generally considered to be the dominant gas transport mechanism in low-permeability waste-rock piles, where advective processes are inhibited. In modeling studies, Pantelis and Ritchie (1992) suggested that diffusion dominates in waste-rock piles with a permeability of 10^{-10} m^2 or less. Lefebvre et al. (2001a,b) showed that at the Norhalde mine in Germany, both diffusion and convection are important gas transport mechanisms in waste rock with a horizontal permeability of 8×10^{-11} m^2 and a vertical permeability of 8×10^{-12} m^2.

Temperature gradients within waste-rock and between the interior and exterior of a waste-rock pile result in air density gradients, and therefore, pressure gradients that drive gas flow. Lefebvre et al. (2001a,b) showed that at Mine Doyon, Canada the temperature within the waste-rock pile increased to 65 °C, driving convective gas discharge rates of 50 m day^{-1}. At the Diavik mine, seasonal temperatures vary from a monthly average of 12 °C in July to −30 °C in the January and February, resulting in freezing of the uncovered test piles in the winter and almost complete thawing in the summer. The relatively low sulfide content of the Diavik test piles does not support the rates of sulfide oxidation that would be required to significantly affect the interior temperature of the waste rock, and therefore, internal pile temperatures are controlled by air temperatures exterior to the pile. Pham et al. (2013) calculated that the maximum air discharge rates due to density driven convection were a maximum of 130 m day^{-1} at the base of the test pile in the winter months. Here significant differences in air temperature and density are a result of extreme cold winter temperatures external to the pile.

As wind blows over a structure such as a waste-rock pile, differences in air velocities around the pile will result in pressure gradients. Advective gas transport through a waste-rock pile can be induced by these gradients. Anne and Pantelis (1997) and Ritchie and Miskelly (2000) coupled computational fluid dynamics models, to simulate a steady, unidirectional wind flow over a waste-rock pile, to the two-dimensional multi-phase model FIDHELM (Pantelis, 1993) to simulate oxygen transport and reactivity within the waste-rock pile. The simulations showed that under the conditions studied wind flow could significantly affect the transport of oxygen into the waste rock, and thereby, increase the oxidation rates by up to 30%. Amos et al. (2009a,b) measured gas pressures in the Diavik Type III test pile. Pressure measurements in the test pile correlated well with wind vectors demonstrating that wind-driven gas advection was a dominant gas transport process in the Diavik test pile (Chi et al., 2013). Chi et al. (2013) also demonstrated the transient nature of the wind effects, which depend heavily on the direction and magnitude of the wind. Given the high permeability and relatively small size of the test pile, wind-induced pressure waves quickly penetrate through the test pile. The effect of the transient nature of wind-induced gas transport on oxygen and heat transport is not well understood.

Singurindy et al. (2012) measured gas concentrations, temperature, and moisture content in one of the Antamina experimental piles with a focus on the effects of pile moisture, and the pronounced wet and dry seasons, on gas transport. A spatial profile of CO_2 and O_2 concentrations in April 2010, near the end of the rainy season, did not show any correlation with moisture content. However, temporal trends clearly showed a decrease in O_2 concentrations and an increase in CO_2 concentrations with increases in moisture content through the rainy season. Furthermore, short term decrease in O_2 concentrations and an increase in CO_2 concentrations where observed in response to large rain events. The results indicated that the increase in moisture content was inhibiting gas transport, limiting the ingress of O_2, and prohibiting the egress of CO_2 released from carbonate dissolution reactions. The opposite trend was apparent in the dry season, with moisture contents decreasing, increases in O_2 concentrations, and decreases in CO_2 concentrations, as gas transport rates increased.

3.5. Heat transport

In waste-rock piles there is often a strong coupling between heat transport, gas transport, and geochemical processes. As noted above, there can also be a strong coupling between heat transport and hydrological processes in northern environments (Neuner et al., 2013; Fretz et al., 2011). The mechanism of heat transport in waste-rock piles is controlled by environmental conditions, sulfide-mineral content, and the physical properties of the rock pile. Convective/advective heat transport mechanisms, driven by air-pressure gradients, can dominate when the permeability of a waste-rock pile is high. Conductive heat transport, the transfer of heat through the bulk material driven by thermal gradients, can dominate when the permeability is low.

Lefebvre et al. (2001a,b) provided a summary of two contrasting waste-rock piles that highlight the differences in heat transport processes induced by varying waste-rock pile properties. The South Dump at the Doyon mine in Quebec, Canada is composed of mainly sericite schist with a relatively coarse texture (d_{10} and d_{50}, 2 and 40 mm, respectively) and a sulfide content averaging 7 wt.%. The Nordhalde waste-rock pile in the Ronnenburg mining district in Germany, is composed primarily of slates with a sulfide content averaging 3.1 wt.% and a relatively finer texture (d_{10} and d_{50}, 0.02 and 5.5 mm, respectively). As a result of the differences in the grain-size distribution between the two piles, the permeability is significantly different. The effective vertical air permeability of the Doyon South Dump was determined to be 8.1×10^{-10} m^2, significantly higher than that of the Nordhalde waste-rock pile, which was 2.5×10^{-12} m^2.

Measured thermal gradients and oxygen profiles (Lefebvre et al., 2001a) and numerical simulations (Lefebvre et al., 2001b) indicated that heat transport in the Doyon dump was primarily convective, driven by the high temperatures greater than 40 °C, generated in the core of the dump. The high temperatures were a result of a high rate of sulfide oxidation and a high rate of oxygen transport, facilitated by the high permeability and the temperature gradients that developed. Temperatures within the Nordhalde waste-rock pile were much lower, reaching maximums of 15–20 °C; although, significantly above the mean surface temperature of 9 °C (Lefebvre et al., 2001a). Numerical simulations indicated that these temperatures cannot be achieved without some degree of convective gas transport, required to provide sufficient oxygen supply to continually drive sulfide oxidation and heat production. However, due to the low permeability, the degree of thermally driven gas transport was limited.

In both the Doyon and Nordhalde waste-rock piles the thermal regime was primarily controlled by the generation of heat through sulfide-mineral oxidation. The enhanced oxygen transport induced through convective heat transport resulted in higher rates of sulfide oxidation, and therefore a feedback to the thermal regime. At the Diavik site, heat transport was in response to ambient air temperatures, and sulfide oxidation rates responded to temperature changes (Pham et al., 2010, 2011, 2012, 2013), in contrast to driving temperature changes, as at the Nordhalde and Doyon mine sites.

Cold and freezing temperatures in northern environments can slow the rate of sulfide oxidation and limit the flow of water though waste-rock piles. Thus the management of waste rock in cold climates can potentially take advantage of these thermal effects, provided they are well understood. Based on an estimated oxidation rate within the Diavik Type III test pile, Pham et al. (2013) calculated the potential heat release from sulfide oxidation, and showed it to be insignificant at this site. This is presumably due to the low sulfide content (average of 0.053 wt.% S) of the Type III test pile. Despite the lack of heat generated through sulfide oxidation, thermally driven air convection was induced through changes in ambient temperatures external to the pile. Predicted air velocities bases on measured thermal gradients indicated that in the winter the buoyancy of the warmer, lighter air within the test pile interior drove vertical air flow to the surface of the pile and drew colder air horizontally inward through the sides of the piles. The opposite occurred in the summer, when the colder, denser air within the test pile core seeped horizontally outward, drawing in warmer air vertically from the upper surface. Calculated air velocities from density-driven convection indicated that the air velocities were greater in the winter months, indicating greater heat transfer in the winter and an overall cooling effect (Pham et al., 2013).

Pham et al. (2013) calculated monthly heat flux of the Diavik Type III test pile based on conductive and convective heat-transfer mechanisms. Conductive heat transport for 2007 and 2008 was calculated based on measured temperature gradients and measured properties of the waste rock. Convective heat transfer was calculated based on average air velocities determined from measured air pressure gradients (Amos et al., 2009a) and temperature gradients between the exterior and interior of the test pile. Observed air pressure gradients will have components of wind-induced, density-induced, and barometric pressure effect; however, in the Type III test pile, wind effects appeared to have been dominant (Amos et al., 2009a,b; Chi et al., 2013). Based on these calculations, the Type III test piles lost heat from September to April or May and gained heat in the summer months, approximately June to August. On an annual basis, there was a net loss of heat from the test pile, indicating a general cooling of the pile. A small zone of permafrost appeared to be developing in the core of the Type III test pile, below a depth of 12 m, in the early stages of the experiment (Pham et al., 2012).

The study of Pham et al. (2013) of the Diavik Type III test pile showed that the active layer thickness (the depth of thaw) exceeded 12 m. Although this study only included the early progression of the thermal regime of the test pile, it appears that enhanced convective air flow and heat transport due to wind effects increases the depth of the active layer. It is expected that this effect is amplified in the test pile, which is a batter dominated system, i.e. the footprint of the test piles is relatively small, and therefore affected more by processes on the batters of the test pile. Pham et al. (2012) studied the thermal regime within three drill holes in the operational waste-rock pile at Diavik. The drill holes ranged from 32 to 40 m deep and were clustered together (approximately 10 m apart) in the centre portion of the dump (greater than 100 m from any edge). Measured temperature profiles in the drill holes in the first year after installation (July 2010) showed an active layer depth of approximately 10 m. A one-dimensional analytical equation fitted to the observed data indicated that conductive heat transport was the dominant mechanism in the central portion of the operational dump. One-dimensional conductive heat-transport modeling predicted an active zone greater than 10 m initially, consistent with field measurements, then a rapid decrease in the active layer to less than 4 m by 2014 due to cooling of the pile under ambient conditions (Pham et al., 2012).

Phillip et al. (2009) provided a summary of findings from an investigation into air flow in a waste-rock dump at the Sullivan mine near Kimberly, British Columbia, Canada. The study was undertaken as a result of four fatalities that occurred in a monitoring station connected to a 400-mm drain pipe emanating from the toe of the dump. The investigation showed that changes in ambient air temperature induced temperature and air density gradients between the pile interior and exterior. With warm exterior temperatures, the colder more dense air within the pile interior sank, exiting the drain pipe and bringing oxygen deficient air from within the pile into the monitoring station. Phillip et al. (2009) showed that the movement of air into and out of the pile was very dynamic with changes in direction occurring several times within a two-week period in May 2007.

4. Prediction and prevention

4.1. Scaling sulfide oxidation and metal leaching rates from the laboratory to the field

The prediction of drainage quality from waste-rock piles is an important aspect of mine planning and permitting. A common approach is to use scale-up factors to predict field-scale water quality and solute loading from small-scale laboratory tests. Kempton (2012) provided a review of the scaling factor approach commonly employed in scaling estimates. The prediction of full-scale water quality using the scaling factor approach uses laboratory derived leach rates corrected for factors thought to relate the leach rate with scale. Scale factors typically considered include pH, moisture content, fragment size, temperature, water–rock contact, oxygen concentration, surface area, and mineral content (Malmstrom et al., 2000; Kempton, 2012).

Laboratory leach rates are often derived from humidity cell tests (e.g. ASTM, 2009). These tests are principally rate experiments, providing rates of geochemical reactions, particularly sulfide-oxidation rates, but do not provide meaningful concentration estimates given inherent differences in the hydrological and geochemical systems at the laboratory and field scales. For example, Evans et al. (2006) showed that at larger scales, low water–rock ratios and longer residence times promote equilibrium controls on solute concentrations; thus, making scaling of kinetic surface-controlled rates from small scale laboratory experiments problematic.

Scaling factors are often empirical and those ascribed to be 'mechanistic' are often not well constrained and the effect of the mechanism has not been rigorously tested. For example, Kempton (2012) cited 'water contact' as a potential scale effect, noting the differences in flow mechanism observed in waste rock. The assertion by Kempton (2012) was that the flow is either in the coarse or fine fractions; however, it is clear from the available studies (as noted above) that flow in various fractions of a pile varies with hydrological conditions, which in turn vary seasonally and inter-annually. Likewise, Malmstrom et al. (2000) used a field-derived hydrological factor, implying that only 65% of the water in the waste rock was mobile (Eriksson et al., 1997), to scale laboratory to field-scale leaching rates. However, this scaling factor was determined during a tracer test at a relatively constant flow rate (Eriksson et al., 1997), thus not taking into account the variability in flow regimes that would likely be active under varying hydrological conditions. Furthermore, the studies by Kempton (2012) and Malmstrom et al. (2000) used surface-area effects as additional scaling factors. Surface-area effects assume that the sulfide oxidation rate is proportional to surface area, and would predict very little generation of sulfide oxidation products in coarse fractions. It is not clear, therefore, if the lack of flushing of these coarse fractions needs to be accounted for again with the water contact scale factor, or if the effect of these two factors is cumulative. Nevertheless, Malmstrom et al. (2000) were able to show that mineral weathering rates in the waste-rock dump at the Aitik mine in northern Sweden could be scaled from laboratory experiments using reasonable scaling factors to within one order of magnitude to field results.

A primary goal of the Diavik waste rock project is to investigate scaling effects and provide a more robust conceptual model for predicting field-scale water quality from laboratory derived leach rates (Smith et al., 2013a). The project has involved a set of 36 humidity cell experiments with varying rock type, with duplicates at room temperature and in a cold room at 4 °C (18 at room temperature, 18 in the cold room), four 2-m scale active zone lysimeters as described above, and three 15-m scale test piles. Geochemical, heat, hydrological, and gas transport processes are studied at each scale to mechanistically describe the processes that control sulfide oxidation rates. Humidity-cell experiments have been run for over 5 years, and indicate that the geochemistry continues to evolve over time (Smith et al., 2013a; Langman et al., 2014). Stanton et al. (2012) showed using reactive transport simulations that leach water quality from each humidity cell can be described using a single oxidation rate and varying only measured surface area, measured sulfide content, and temperature. These results suggest an intrinsic oxidation rate dependent on temperature and observed rates dependent on the surface area of sulfide minerals (assuming that the surface area of the sulfide minerals is proportional to the sulfide content). Amos et al. (2011) showed that the Diavik humidity cells leach rates can be reasonably scaled to the 2-m scale active zone lysimeter experiments, using only measured surface area and sulfide content as scaling parameters. The lack of reactivity in large boulders (which have negligible surface area compared to fine materials) is accounted for by taking into account the difference in surface area. The active zone lysimeter experiments include large boulders up to 2 m in diameter, reflecting the general heterogeneity observed in waste rock but generally do not experience preferential flow except for the largest rain events (Neuner et al., 2013). Ongoing studies at the Diavik site will continue to the larger test piles to continue the investigation of geochemical, thermal, and hydrological mechanisms that affect leaching and water quality in a systematic manner.

4.2. Covers

Soil covers can provide effective mitigation of AMD, typically by limiting the ingress of oxygen and water into a waste-rock pile. Covers can generally be categorized as resistive barriers, capillary barriers, or store and release barriers. Resistive barriers employ a low conductivity highly saturated layer to limit water and oxygen transport. Capillary barriers promote high saturation and inhibit water transport through a contrast in hydraulic conductivities induced by layering coarse and fine materials. Store and release barriers provide temporary water storage near the surface and promote evapotranspiration to inhibit downward water movement into the underlying waste rock.

Adu-Wusu and Yanful (2006) monitored the performance of three test cover systems overlying a 6-m acid generating waste-rock layer over a three year period and compared results to uncovered waste-rock at the Whistle mine, Ontario, Canada. The cover systems consisted of a 0.9-m pit-run gravelly sand overlying a barrier layer, which consisted of either a 0.46 m sand and bentonite mixture (92% and 8%, respectively), a 0.60 m sandy silt layer with approximately 5% clay, or a 0.008 m geosynthetic clay liner. Percolation through the cover systems over the three year period was 7%, 20%, and 59% of precipitation for the geosynthetic clay liner, sandy silt, and sand and bentonite layers, respectively, compared to 56.4% for the uncovered waste-rock. The effectiveness of the covers as an oxygen barrier could not be assessed due to the experimental design, however, in all cases the effluent of the barrier systems was improved over that of the uncovered waste-rock. Adu-Wusu and Yanful (2007) reported on post-monitoring excavation of the test cover installations. They concluded that defects in the barriers caused by improper installation coupled with freeze–thaw effects resulted in higher than expected percolation through the barrier layers. The sandy silt barrier was deemed ineffective due to its coarse particle content, lack of clay content, and poor cohesion.

O'Kane et al. (1998) and Weeks and Wilson (2005) studied a soil cover consisting of a 50-cm compacted till layer overlain by a 30-cm non-compacted till layer covering a waste-rock dump at the Equity Silver Mine, British Columbia, Canada. Compaction of the lower till layer resulted in a three order of magnitude reduction in hydraulic conductivity allowing the layer to maintain greater than 90% saturation over the ten-year period of the study. The upper, non-compacted layer, with a vegetated surface, had lower levels of saturation ranging from 50% to 85%, with upward hydraulic gradients in dry periods, suggesting that the layer was performing as a store-and-release system. Oxygen concentrations measured within the waste rock below the cover show a clear decreasing trend, indicating the ability of the saturated cover to limit oxygen ingress.

Bussière et al. (2007) constructed four experimental cells to test the performance of low plasticity silty materials, including natural silt and non-acid-generating tailings, in covers with capillary barrier effects. The capillary barrier effects induced by the layering of the silty materials with coarser grained sand effectively retained sufficient moisture within the silt layer to substantially reduce oxygen ingress. Furthermore, the geotechnical properties of the silty materials were such that the hydrological properties remained effectively unchanged over the four-year duration of the tests. Lab experiments using a inclined box and numerical studies based on the LTA tailings dump located at Malartic, Quebec, Canada showed that the moisture content within inclined capillary barriers is influenced by the slope of the barrier, which may result in lower moisture content, and reduced effectiveness as an oxygen barrier, in the upper portion of the slope (Bussière et al., 2003).

A modeling study by Kim and Benson (2004) considered advective and diffusive oxygen transport in the gas and aqueous phase through a multiplayer composite cap. Results of the simulations indicated that oxygen transport through the seven-layer cap, including a geomembrane and clay barrier, was predominantly (greater than 99%) through gas-phase diffusion. Analysis of similar caps without the geomembrane liner yielded similar results.

The sulfidic waste-rock dumps at the Rum Jungle uranium mine, Australia, were covered in 1984–1985 (Taylor et al., 2003). The cover system was designed to limit infiltration to less than 5% of rainfall using a low permeability clayey layer to resist infiltration, a store and release layer to provide moisture to vegetation and prevent desiccation of the underlying low-permeability layer, and an upper layer to prevent erosion and support plant growth. Through an extensive study including excavation of the covers in several locations, Taylor et al. (2003) found that the cover system performed to design specification within the first decade but concluded that after 18 years it was likely that infiltration through the covers was greater than 5% of rainfall. Excavation of the cover revealed that the thickness of the layers was less than the design criteria, highlighting the need for good construction practices and quality assurance. The increased infiltration was attributed to areas of high permeability that were likely caused by a combination of factors; including termite and ant activity, root growth, and shrinkage/desiccation cracks.

The cover systems discussed above where aimed at reducing water and oxygen transport into the waste rock. In northern environments, covers have the potential to create a thermal barrier and promote freezing within the core of a waste-rock pile. Pham et al. (2011) studied the thermal effects of a cover system on the Diavik covered test pile. The cover included a 1.5 m low permeability till layer overlain by a 3 m layer of low sulfide (Type I) run-of-mine waste rock. The low-permeability cover sufficiently inhibited advective gas and heat transport mechanisms such that heat transport was limited to conduction and the annual freeze–thaw layer was restricted to the low-sulfide cover material. In contrast, the uncovered Diavik test piles thaw to a depth of 12 m each summer (Pham et al., 2013). Maintaining a frozen core within the waste rock has the potential to limit the ingress of water and significantly slow the rate of sulfide oxidation. Pham et al. (2012) simulated the thermal regime of the Diavik operational-scale waste-rock pile and showed that a cover system similar to that on the covered test pile would limit the annual freeze–thaw layer to a minimum depth of 3.0 m, in contrast to 3.7 m for an uncovered pile. After 100 years under a climate warming scenario the simulated cover scenario predicted an active layer of 3.9 m, compared to 7.0 m for an uncovered pile. The results indicated that the cover system has the potential to maintain the higher sulfide Type III rock below the cover in a permanently frozen state.

4.3. Numerical simulations

The coupling of complex processes within waste-rock piles can often make the interpretation of observed data difficult and non-intuitive. Numerical models provide a means of quantifying the effects of physical and geochemical processes on the thermal, hydrological, and geochemical parameters observed. This quantification of processes allows for conceptual models to be more rigorously tested and provides the potential for predicting long-term behavior of waste-rock piles under various closure scenarios. Challenges involved with modeling sulfide oxidation within waste-rock piles stem from the highly heterogeneous nature of the waste rock, both from a physical and geochemical point of view, and the coupling of physical and geochemical processes.

Significant processes in waste rock that affect sulfide-oxidation rates and leach-water quality include water flow in matrix and preferential flow paths, conductive and advective heat transport, diffusive and advective oxygen transport, spatially and temporally variable sulfide-oxidation rates, and secondary geochemical reactions. Available models simulate a subset of these processes in an attempt to represent the dominant processes at a given site. The examples below provide an overview of the available model capabilities.

Fala et al. (2005) simulated hypothetical waste-rock piles using the two-dimensional unsaturated flow model HYDRUS (Simunek et al., 1999). The simulations included homogeneous sand or gravel and gravel with layers of sand to simulate capillary breaks. The transient simulations of homogenous and heterogeneous materials demonstrated the differences in wetting front migration, flow paths, and soil moisture profiles that could be expected as a result of the difference in the soil properties and pile configuration (i.e., the distribution of the fine materials). The simulation described flow using a form of the Richards (1931) equation and therefore did not include macropore flow. This simplification was not considered significant given the objectives of the study. Javadi et al. (2012) used a similar approach to simulate water flow and solute transport through one of the experimental waste-rock piles at the Antamina site using the reactive transport model MIN3P (Mayer et al., 2002). The simulated pile was relatively fine grained and homogeneous. Recharge was simulated as a fraction of measured precipitation and the upper surface of the pile was assumed to have a lower hydraulic conductivity than the rest of the pile. The simulation reasonably reproduced the timing and magnitude of the observed pile discharge, but did not reproduce the early arrival of the applied bromide tracer. The inability of the model to reproduce the tracer breakthrough is an indication of the occurrence of preferential flow. Eriksson and Destouni (1997) used a probabilistic Lagrangian approach to simulate the distribution of travel times, representing preferential flow paths, within the waste-rock heaps at the Aitik mine, Sweden. The simulations showed that the flow heterogeneity was a possible explanation for the observed variability in copper concentrations in the waste-rock leachate.

Molson et al. (2005) coupled one of the heterogeneous flow models of Fala et al. (2005) to the reactive transport model POLYMIN (Molson et al., 2004). The simulations coupled the complexities of flow with mineral dissolution kinetics governed by the shrinking core model (Levenspiel, 1972), changes in oxygen diffusion rates as a result of changes in saturation, equilibrium controlled mineral dissolution/precipitation, and pH. Whereas the results of the modeling were somewhat scenario specific, they demonstrates the coupling of processes and the non-intuitive nature of the interactions. For example, although the fine-grained layers in the simulation retained high moisture content, thus reducing oxygen diffusion, oxidation rates were high in these layers due to the high reactive surface area of the fine grained material.

The approach of Molson et al. (2005) employed a relatively sophisticated geochemical representation of pyrite oxidation and secondary reactions. In contrast, Lefebvre et al. (2001b) used a simpler geochemical description with a more rigorous representation of the physical system, including coupling between the oxygen dependent and exothermic sulfide oxidation reactions and heat and air/oxygen transport, using the TOUGH/AMD code. The model was used to simulate the Nordhalde waste-rock pile in the Ronnenburg mining district, Germany, and the South Dump of the Mine Doyon, Canada, as described above. Similarly, Pantelis et al. (2002) presented a basic set of mathematical equations to describe sulfide oxidation and water, gas, and heat transport in waste rock, which are the basis of the FIDHELM code (Pantelis, 1993).

A version of the MIN3P code (Molins and Mayer, 2007) couples kinetic and multicomponent gas diffusion and advection with a full range of kinetically and equilibrium controlled geochemical reactions. Multicomponent gas diffusion is described on the basis of the dusty gas model, which accounts for all relevant gas diffusion mechanisms. This model does not include thermal mechanisms. The base version of the MIN3P code (Mayer et al., 2002) has been applied to waste rock as described above (Javadi et al., 2012), although the extended version has not.

More complete representations of sulfide oxidation in waste rock were presented by Linklater et al. (2005) using the SULFIDOX code (Brown et al., 2001), and da Silva et al. (2009) using the THERMOX code. SULFIDOX and THERMOX include descriptions of heat transport, diffusive and convective air transport, spatially and temporally dependent pyrite oxidation rates, and secondary geochemical reactions. Neither code includes the effects of preferential flow. THERMOX was used to simulate the Doyon waste-rock pile (da Silva et al., 2009). Results were equivalent to those previously obtained by Lefebvre et al. (2001b) with respect to oxygen concentrations, gas fluxes and temperature, and also included simulation of geochemical parameters including sulfate and pH. Sulfate concentrations were underestimated in the simulations compared to maximum observed values whereas the pH was overestimated. da Silva et al. (2009) suggested that the discrepancy was due to an underestimation of the pyrite-oxidation rate as a result of the friability of the host rock, or seasonal changes in recharge, that were not accounted for in the model. SULFIDOX was used to simulate weathering of the Aitik waste-rock dump. The two-dimensional transient simulations reasonably reproduced oxygen concentrations, internal pile temperatures, and effluent geochemistry including pH and Cu, Fe, SO_4, Al, Ca, Si, K, Na, and Mg concentrations (Linklater et al., 2005).

5. Conclusions and future outlook

Research over the past two decades has focused on the study of integrated processes within waste rock and understanding the fundamental processes that govern the rate and extend of sulfide oxidation and the release of metals. Whereas most studies are consistent with respect to the parameters and mechanisms that influence AMD generation and solute release, the most striking aspect, when looking at the studies as a whole, is the relative importance of various mechanisms at different sites, owing to the variability in waste-rock properties and climatic conditions. This observation highlights the importance of site-specific waste-rock characterization and understanding of the fundamental mechanisms controlling thermal, hydrological, and geochemical processes, and particularly the coupling of processes. Prediction of leach-water quality from waste-rock piles will require further understanding of scale effects, and particularly quantitative mechanistic descriptions of process effects at various scales. Numerical models will provide a valuable tool to incorporating greater complexity and mechanistic process description into leach water quality predictions.

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