UNSATURATED HYDROLOGY, EVAPORATION, AND GEOCHEMISTRY OF NEUTRAL AND ACID ROCK DRAINAGE IN HIGHLY HETEROGENEOUS MINE WASTE ROCK AT THE ANTAMINA MINE, PERU

by

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Abstract

Physical and geochemical heterogeneities in mine waste rock complicate the prediction and assessment of waste rock effluent water quantity and quality. The objective of this research is to provide a holistic conceptual understanding of the hydrological and geochemical processes that control effluent water quantity and quality, and the complex interactions among processes at the field scale. To this end, a prodigious dataset from three experimental waste-rock piles at the Antamina Cu-Zn-Mo skarn-deposit mine was compiled and analyzed. Analyses included solid-phase mineralogy and physical characteristics; effluent and pore-water hydrology and geochemistry; and an aqueous tracer study.

The instrumented piles (36 m x 36 m x 10 m) are each composed of a single rock type and are exposed to almost identical atmospheric conditions, isolating the effect of rock type on hydrological regimes. Physical waste rock heterogeneities result in highly variable hydrology that is strongly dependent on material particle size distributions and especially the presence of large boulders. The hydrological regimes include wide ranges of velocities for matrix flow (<2-12 cm/day), preferential flow (40-2000 cm/day), and pressure-induced wetting fronts (7-105 cm/day), all of which are strongly influenced by antecedent water content and precipitation patterns resulting from a two-season (wet/dry) climate. Evaporation is also highly variable among waste rock types on annual (24%-75% of precipitation) and multi-year timescales (28%-59% of precipitation).

Mineralogical heterogeneities result in material-specific, temporally and spatially variable circum-neutral to acidic geochemical conditions (pH 4.6-8.5). Other geochemical controls

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on solute concentrations include precipitation and dilution of secondary minerals, sorption, and pH effects from CO₂ degassing. Furthermore, hydrology strongly influences effluent aqueous geochemistry, leading to solute concentrations and loadings that can fluctuate by several orders of magnitude between wet and dry seasons (e.g., Pile 2 Cu loadings: August-2010, 1.8×10^{-7} mg/(kg·wk); February-2011, 1.6×10^{-1} mg/(kg·wk)). Hydrological controls on aqueous geochemistry include seasonal solute accumulation; solute flushing through matrix flow paths of variable velocities; mixing and dilution at the pile base; and seasonal changes in moisture content that control internal CO₂ concentrations. The results highlight the need to account for unsaturated hydrology during the prediction and assessment of aqueous geochemistry from waste rock.

Preface

This research is presented in four body chapters, one of which has been published (Chapter 4), and three of which are more detailed compilations that will be divided into several publications and submitted for peer review in the near future (Chapters 2, 3, and 5).

A version of Chapter 4 entitled *Rapid seasonal transition from neutral to acidic drainage in a waste rock test pile at the Antamina Mine, Peru* was co-authored by Roger Beckie, Bevin Harrison, K. Ulrich Mayer, and Leslie Smith, underwent peer review, and was published in 2012 in the Proceedings of the 9th International Conference on Acid Rock Drainage. (Peterson et al., 2012).

This research is part of a collaboration among researchers at The University of British Columbia (UBC), Teck Metals Limited's Applied Research and Technology Group, The University of Alberta, and Compañia Minera Antamina S.A. I was largely responsible in the design, construction, and instrumentation of several of the experimental piles and field barrels, including those upon which the research herein is based. I processed and analyzed all data and results presented here unless otherwise noted, including 2007-2008 precipitation and Pile 1 effluent flow data compiled by Bay (2009); saturated hydraulic conductivity measurements performed by Blackmore and Urrutia (2009); soil water characteristic curves generated by Speidel (2011); concentration and loadings plot templates by Matt Lindsay; and joint 2012-2013 flow data post-processing with Mehrnoush Javadi. Daniel Bay and Nathan Fretz provided spreadsheets which I modified for Penman-Monteith evaporation analysis (Chapter 3). Laura Laurenzi compiled the database employed for PHREEQC modeling presented in Chapter 5, as well as the initial input files, which I modified. Sharon Blackmore and I, with the help of Michael Gupton and the Antamina Mine staff and with the advice from our research supervisors Roger Beckie, K. Ulrich Mayer, and Leslie Smith, designed and implemented the tracer study described in Chapter 2. My research supervisors and research colleagues provided feedback on the methodologies I developed for this dissertation, as well as on scientific interpretation.

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Chapter 1: Introduction and project description

1.1 Introduction

Surface mining operations such as strip mining, open-pit mining and mountaintop removal have greatly increased the production of mine waste rock from mining operations in recent decades. This, in turn, has led to environmental, societal and regulatory challenges because contaminated waters from mine waste, commonly in the form of acid rock drainage (ARD) or neutral rock drainage (NRD), can significantly harm local and regional ecosystems and communities (e.g., Duhigg, 2009; Solomon 1995; Thornton, 1996; York, 2010). For example, approximately 2,000 abandoned mine sites on United State National Forest Service lands 'present significant environmental or human health problems due to a release, or threat of a release, of a hazardous substance, pollutant, or contaminant' and will cost approximately \$2.1 billion USD to mitigate (USDA, 2014).

In order to reclaim areas that have been impacted by mine waste effluent waters and more importantly to ensure that negative environmental impacts are minimized in the future, a greater understanding between the hydrological and geochemical waste rock processes must be established. This includes hydrological processes such as flow and evaporation, which control the timing and quantity of flow from waste rock dumps; the geochemical processes that produce and neutralize acidity, mobilize metals into aqueous forms, and attenuate aqueous solutes through solid phase precipitation and sorption; and the relationships between those hydrological and geochemical processes.

The Antamina Mine in Ancash, Peru is the world's third-largest open-pit Cu-Zn-Mo mine (Figure 1.1). The waste rock dumps are currently hundreds of meters tall by hundreds of meters wide and growing. By proposed mine closure in 2029, the mine is expected to produce 2.2 billion tonnes of waste rock (Harrison et al., 2012). The quartz-monzonite porphyry intrusion at Antamina led to a skarn ore body hosted in carbonate limestone, marble, and hornfels (Escalante et al., 2010; Lipten and Smith, 2004; Love et al., 2004; Redwood, 1999). These host rocks have high neutralization potential and effluent water from the waste dumps is predicted to be net neutral producing with a possibility of net acid generation from certain types of waste rock after 30-40 years (Golder 2004). This study is part of collaboration between the Compañia Minera Antamina S.A., Teck Metals Limited's Applied Research and Technology Group, The University of British Columbia (UBC), and The University of Alberta that characterizes hydrological, geochemical, and microbiological properties of waste rock at Antamina.

The Antamina research program has developed one of the most thorough experimental set-ups available for the characterization, linkage, and scaling of flow, evaporation, and geochemical processes in waste rock. The multi-scale project includes several one-dimensional laboratory column studies; forty-three 1 m tall, 300-kg field barrel experiments; five 36 m x 36 m x 10 m, ~20,000-tonne experimental waste-rock piles; and five 15 m x 15 m experimental cover study cells. This study focuses specifically on the hydrology and geochemistry of three of the five experimental waste-rock piles and associated field barrels, all of which are located at the mine and are exposed to the distinct wet and dry seasons of the high Peruvian Andes.

The overall objective of this study is to increase our understanding of the relationships between physical waste rock properties, meteorology, hydrological processes, and geochemical processes that are applicable not only to Antamina but also in a variety of mine settings. To this end, universal waste rock processes such as matrix and preferential flow, evaporation, and metal mobilization and attenuation will be evaluated (Section 1.3). A greater understanding of these

processes will decrease uncertainty in water quantity and quality predictions, in turn helping mine planners worldwide develop robust water management, storage, and treatment facilities in a timely, cost-effective manner. The findings comprise a comprehensive data set that can also be used to guide regulatory policy and to develop dumping and mine closure strategies, in turn minimizing potentially negative environmental impacts of waste pile discharge for mines around the world.

1.2 Literature review

Waste rock physical and mineralogical heterogeneity can lead to highly variable hydrological and geochemical conditions in waste rock effluent, and the large-scale nature of waste-rock dumps (i.e., up to hundreds of vertical meters) can complicate assessment of those conditions. Therefore, research to gain a better understanding of the processes controlling the characteristics of flow through waste rock has been the subject of recent investigation. This research is motivated by the need to expand the conceptual understanding of complex unsaturated flow systems found in waste rock in the manner of Pruess (1999), who described thick, fractured, unsaturated zones that could be considered analogous to some waste rock systems, and Nichol et al. (2005), who investigated complex unsaturated flow regimes in a similar experimental wasterock pile under different atmospheric conditions.

Large-scale (i.e., tens of meters to hundreds of meters) field investigations of flow through waste rock are needed in order to represent the heterogeneous properties of waste rock, such as highly variable waste rock mineralogy (e.g., Parbhakar et al., 2009), broad particle size distributions (e.g., Stromberg and Banwart, 1999), and large-scale internal physical features that are common in many waste rock dumps (e.g., Smith and Beckie, 2003). These characteristics are sensitive to experimental scale and are not accounted for in experiments commonly undertaken in laboratoryscale studies (e.g., decimeter-scale humidity cells).

Only recently are large-scale studies being conducted to characterize the physical and geochemical nature of flow through waste rock. These studies have assessed large-scale flow through waste rock by deconstructing existing waste-rock piles (e.g., Newman et al., 1997; Stockwell et al., 2006), conducting in-situ borehole and drainage sampling of existing waste-rock piles (Lefebvre et al., 2001; Linklater et al., 2005; Sracek et al., 2004), or constructing large-scale, instrumented, experimental waste-rock piles (e.g., Andrina et al., 2007, Neuner et al., 2009; Neuner et al., 2013; Nichol, 2002; Marcoline, 2008; Miller et al., 2007; Smith et al., 2009; Smith et al., 2013 a,b). This research is based on instrumented large-scale (i.e., 10 m) experimental waste-rock piles, and builds upon the current dataset for waste rock hydrological and geochemical properties in addition to addressing some of the processes controlling the hydrology and geochemistry of waste rock that are currently not fully represented in the literature.

The sections that follow discuss the current understandings in unsaturated flow, evaporation, acid rock drainage, and neutral rock drainage as they apply to mine waste settings. A final section provides background linking hydrology and geochemistry.

1.2.1 Unsaturated flow through mine waste

Research on water flow through mine waste to date has primarily focused on mine tailings, which are comparatively physically homogeneous (e.g., Al et al., 1997 and 2000), are often largely saturated, and lend themselves to more straightforward characterization of hydraulic properties than physically heterogeneous and predominantly unsaturated waste rock systems.

Pore water velocities through tailings can be similar to natural saturated sand-silt-clay unconsolidated systems under comparable gradients. At the abandoned Ni-Cu Nickel Rim Mine in Sudbury, ON, Canada for example, horizontal flow velocities were measured to be about 1 cm/day to 2 cm/day (Johnson et al., 2000). Tailings hydrology research also includes vertical velocities of acid water fronts, neutralization fronts, and sulfide weathering fronts (Blowes and Jambor, 1990); oxygen diffusion vertically down through tailings (Moldrup et al., 2003); and the development of hardpan iron oxide layers that impact vertical water and oxygen flow (Moncur et al., 2005). Hydrological (e.g., Al and Blowes, 1999) and reactive transport (e.g., Brookfield et al., 2006) modeling studies have successfully modeled saturated and unsaturated flow through tailings. Advances to the understanding of flow systems in tailings such as these have contributed to improvements in operational procedures such as thickened tailings (e.g., Barbour et al., 1993; Fawell et al., 2009; Fourie, 2009) and cover systems (e.g., Yanful et al., 1993, 2006; O'Kane et al., 1998) which can reduce environmental risks associated with tailings impoundments. While studies conducted in tailings environments provide beneficial information on characteristics of water flow through mine waste, characterizing flow through waste rock remains complex and not well understood.

Waste rock is inherently physically heterogeneous (e.g., Eriksson et al., 1997), complicating laboratory- and field-scale research. Particle sizes of waste rock often span from clays to boulders, with highly variable particle size distributions (e.g., Stromberg and Banwart, 1999). Some coarse-grained waste rock types tend to be clast-supported and exhibit "rock-like" flow behavior, while others with finer particle size distributions will be matrix-supported and exhibit "soil-like" flow behavior (Smith et al., 1995; Smith and Beckie, 2003). The Antamina Mine contains a broad range of waste rock lithologies (e.g., Love et al., 2004), including marble and

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hornfels, which are generally massive and less friable and have coarse particle size distributions that fall into the "rock-like" category, and skarns and intrusive which are more friable and have finer particle size distributions that could exhibit either "rock-like" or "soil-like" behavior. Additionally, waste rock is often disposed of using an end-dumping method, which can create coarse basal "rubble zones" and fining-upward layers that dip at the angle of repose, ~37° (Figure 1.2; Fala et al., 2005; Smith and Beckie, 2003; Stockwell et al., 2006). The broad particle size distributions and internal structures such as sloped layers of waste-rock piles create complex internal hydrological and gaseous flow regimes that are as yet not well understood.

Two types of flow that comprise flow regimes in waste rock are matrix flow and preferential flow. Matrix flow, or capillary flow through finer-grained portions of waste rock, is generally slower flow (velocities of meters per year) compared to preferential flow (velocities as high as meters per hour; e.g., Neuner, 2009; Nichol et al., 2005). Matrix flow tends to occur in the <5 mm size fraction, as capillary effects are not as prevalent in the coarser materials (Tokunaga et al., 2002; Yazdani et al, 2000). Matrix flow generally adheres to the assumptions valid in the Richards (1931) equation, which models unsaturated flow through porous media. Preferential flow can be triggered by large precipitation events and unstable flow (Ritsema et al., 1998), and can result from a variety of mechanisms that are particle size-dependent. For example, preferential flow can result from 'macropores', which are traditionally described in agricultural methods as conduits created by biological process by-products such as root structures and insect or animal burrows (Chen, et al., 1992; Ahuja, et al., 1995). Other types of preferential flow include finger-flow (Gerke, 2006; Lu, et al., 1994; Ritsema, et al., 1994; Ritsema, et al., 1998; Wang, et al., 2003), unstable flow (Dekker, et al., 1994; Glass, et al., 1989; Ritsema, et al., 1994; Ritsema, et al., 1998), funnel flow including capillary breaks (Abdul, et al., 1989; Gerla, et

al., 1996; Gillham, 1984; Pruess, 1999; Silliman, et al., 2002), and film flow through fractures (Tokunaga & Wan, 1997; Tokunaga & Wan, 2001). Observed or inferred preferential flow mechanisms in waste rock identified in previous research include: flow along capillary breaks (e.g., Heilig et al., 2003); macropore flow through coarser-grained waste rock and non-capillary flow (Nichol et al., 2005); flow over boulders (Eriksson et al, 1997); and concentrated and faster flow in finer-grained materials due to low air-entry pressures in the coarser-grained materials and increased unsaturated hydraulic conductivity at higher moisture content in the finer materials (Newman et al., 1997). The mechanisms that cause preferential flow in waste rock are still under investigation, and the relative proportions of matrix and preferential flow have been identified as an important control in numerical modeling of preferential flow in waste rock (e.g., Broda et al., 2013; Javadi et al., 2012).

Field-based mechanistic studies similar to this research have improved the understanding of pore water velocities and wetting front velocities, the latter of which are pressure induced and travel ahead of the water from a precipitation event. Nichol et al. (2005) found through analysis of a waste rock tracer study conducted at the Cluff Lake Mine in Saskatchewan, Canada that a broad range of water velocities and residence times exists in coarse, granular waste rock, and that residence times are controlled by matrix and preferential flow paths. Furthermore, they found that rapid increases in flow rates may indicate the arrival of a wetting front as opposed to preferential flow, and that wetting fronts can travel approximately three to four orders of magnitude faster than the mean velocity of water travelling through waste rock. Bay et al. (2014), on the other hand, found that wetting fronts in a coarse waste-rock pile at the Antamina Mine in Peru only traveled approximately one order of magnitude faster than pore water velocities. The results of Nichol et al. (2005) and Bay et al., (2014) demonstrate that waste rock

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pore water velocities and wetting fronts vary between different waste rock types and meteorological settings. However, at present studies reporting the relationship between wetting front velocities and pore water velocities in several different waste rock types under identical meteorological conditions are limited.

During the deconstruction of an experimental waste-rock pile at the Key Lake Mine in Saskatchewan, Stockwell et al. (2006) were able to discern alternating fine and thin layers dipping at the angle of repose and a void-filled rubble zone at the base of the pile. They also found that it was not possible to determine a field-based soil water characteristic curve from insitu particle size and moisture content measurements. Marcoline (2008) reported the effect of surface conditions on unsaturated flow regimes in a coarser-grained experimental waste-rock pile at the Cluff Lake Mine, and used a deuterium tracer study to determine matrix flow velocities of approximately 1.5 m/yr and preferential flow velocities as high as 5 m/day in that waste rock. Average pore water velocities in matrix-dominated experimental test piles at the Diavik Mine in northern Canada under permafrost conditions were estimated to be 1 m/yr to 5 m/yr (Neuner et al., 2009).

In addition to the more mechanistic studies described above, modeling studies pertaining to both the liquid (Fala et al. 2003; Fala et al., 2005; Savci and Williamson, 2002) and gas (Amos et al. 2009; Lefebvre et al., 2001a,b; Wels et al., 2003) phases within waste rock dumps are increasing, including advances in reactive transport modeling in waste rock settings (e.g., Lefebvre et al., 2001a,b; Linklater et al., 2005; Linklater et al., 2006; Molson et al., 2005). Extensive sets of both hydrological and geochemical parameters are required for this type of modeling and are limited in current waste rock literature.

While the understanding of water velocities and wetting front velocities, hydraulic conductivities, and matrix and preferential flow regimes in large-scale waste rock systems is increasing, the number of studies reporting those hydrological properties is still relatively limited.

1.2.2 Evaporation from mine waste

Evaporation is another hydrological process that greatly impacts waste rock dump effluent flow, and like unsaturated flow it is well studied in many disciplines but is less understood in largescale, field-based bare waste rock settings.

Extensive research has been conducted concerning atmospheric-based analytical techniques for estimating evaporation under a variety of settings, especially in agricultural settings for irrigation purposes. One early-developed and still widely-used example is the Penman (1948) method, which uses meteorological data to determine potential evaporation. The Penman-Monteith (Monteith, 1965) approach expands on that to include the effect of transpiration. The Food and Agricultural Organization of the United Nations developed a modification of the Penman-Monteith method in an attempt to standardize estimation of evapotranspiration using atmospheric, crop, and soil parameters (FAO-PM; Allen et al., 1998). Other widely-used approaches include a variety of pan evaporation methods (e.g., Allen et al., 1998; Sumner and Jacobs, 2005); the Hargreaves equation (e.g., Hargreaves et al., 1985; Hargreaves and Allen, 2003), and the Blaney-Criddle approach (e.g., Blaney and Criddle, 1950; Allen and Pruitt 1986).

Research on evaporation estimation for mine settings is more limited, and much of the current literature focuses on mine tailings (i.e., Barbour et al., 1993; Fujiyasu et al., 2000; Newson and Fahey, 2003; Seneviratne et al., 1996; and Simms et al. 2007). For example, Barbour et

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al. (1993) used measured evaporation fluxes of about 2.5 mm/day and up-ward seepage analysis to determine that tailings tended to remain saturated even at maximum rates of potential evaporation. Simms et al. (2007) used extensive laboratory and field evaporation data and was able to accurately simulate evaporation from tailings using the SOILCOVER (Wilson et al., 2004, 2007) model until the accumulation of secondary minerals began to affect evaporation rates.

Research on evaporation from mine waste cover systems has also increased since the idea of using an evaporation layer to limit ingress of water into mine waste was introduced by Rasmuson and Eriksson in 1987 (from Simms and Yanful 1999). Subsequent cover study research that considered the effect of evaporation include laboratory (e.g., Yanful et al., 1999), field (e.g., O'Kane et al., 1998; Simms and Yanful 1999; and Yanful et al., 1993), and modeling studies (e.g., Choo and Yanful, 2000; Swanson et al., 2003; and Yanful et al., 2006).

Evaporation from bare waste rock surfaces is much less understood, but is important in water balance planning during operational periods and post-closure when engineered cover systems are not constructed. Neuner (2009) calculated evaporation using a water balance for 10-day, one-year, and 1.5-year periods for two experimental waste-rock piles at the Diavik Mine in the Northwest Territories, Canada. Estimates of evaporation ranged from 51% of precipitation (Type 3 pile over a 1.5-year period) to 102% of precipitation (Type 1 pile over a one-year period). Bay (2009) estimated evaporation from a coarse-grained waste-rock pile at the Antamina Mine at 59% of precipitation using a water balance evaporation calculation based on one year of data. This research, through an experimental set-up that allows for observed evaporation from three waste rock types under the same meteorological conditions for three- to four-year study periods, will augment the relatively small available dataset of evaporation from

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bare waste rock, and will attempt to determine possible mechanisms that account for the broad range of observed evaporation from waste rock.

As for modeling evaporation from waste rock, Carey et al., (2005) used the eddy covariance method to measure evaporation from a mine waste-rock pile near Key Lake, Saskatchewan, Canada, and found that measured results matched well with modeled estimates using the Granger and Gray (1989) modified Penman method. Fretz et al. (2012) compared water balance evaporation estimates and tensiometer-based flux estimates from the flat lower-permeability upper surface of an experimental waste-rock pile at the Diavik Mine with a modified FAO-PM method considering influence of the cold climate. They found that the FAO-PM method was suitable for the upper surfaces of waste-rock piles and calibrated the depth of the surface layer which is susceptible to evaporation to 0.05 m. While the evaporation from the flat upper surface of waste-rock piles was modeled successfully in those two studies, pile slopes pose several challenges to the applicability of evaporation between the upper flat surfaces and slopes of waste-rock piles and to determine the suitability of the FAO-PM method for three types of waste rock.

1.2.3 Acid rock drainage (ARD) and neutral rock drainage (NRD)

The geochemical mechanisms of acid rock drainage are well-researched, for example sulfide oxidation processes (e.g., Evangelou and Zhang, 1995; Evangelou, 1998) and the importance of primary and secondary mineralogical assemblages of mine waste (e.g., Al et al., 1997; Moncur et al., 2005; Sracek et al., 2004). The importance of bacteria as catalysts to sulfide oxidation is an on-going research topic (e.g., Baker and Banfield, 2003; Nordstrom, 2000; Stromberg and

Banwart, 1994). It has been shown that fines with diameters <0.25 mm are significantly more reactive than coarser size fractions, contributing to 80% of sulfide oxidation and silicate dissolution due to the increased surface area and mineral exposure (Strömberg and Banwart, 1999). Reviews on ARD processes are available (e.g., Akcil, 2006; Blowes et al., 2003; Morin and Hutt, 1997; Nordstrom and Alpers, 1999) and are still being produced and updated (e.g., INAP, 2009).

Neutral rock drainage has also been researched but to a lesser extent. Neutral rock drainage is produced in waste-rock piles when acidic waters, usually generated by sulfide oxidation, are buffered to a neutral pH by carbonates and, to a lesser extent, silicates (e.g., Blowes et al., 1998; Moncur et al., 2005; Sherlock et al., 1995; Sracek et al, 2004). Sulfide oxidation releases metals from the solid phase into solution and creates acidity, and most metals, such as Fe, Cu, and Ni precipitate out of solution to form secondary minerals when the pH of the water increases to circum-neutral as a result of acid buffering by carbonates. Under neutral conditions several metals and metalloids such as Zn, Se, Mo, Cd, As, and Sb remain soluble (Price, 2003) and can be transported away from the source zone. Solutes of interest at Antamina – e.g., As, Cu, Mn, Mo, and Zn – fall into both categories.

Most of the research mentioned above concerns acid and/or neutral conditions in mine tailings, and much less research focuses on the geochemistry of waste rock. An example of a waste rock system where acid production is greater than neutralization potential, resulting in ARD, is the experimental waste-rock pile at Key Lake, Saskatchewan, Canada (Stockwell et al., 2006). The average pyrite content at the site is 0.67 wt%, and the average carbonate content, found in the form of dolomite, is 2.1 wt%. Conversely, at the Agnico-Eagle site in Quebec, Canada, NRD results from a higher neutralization potential than acid production potential (Blowes et al., 1998).

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The quantities of sulfide and carbonate minerals in waste rock at the Agnico-Eagle site are 5 wt% and 30 wt%, respectively.

Waste rock mineralogy and solid phase elemental composition are the driving factors of effluent water quality, and solid-phase characteristics are highly variable among and within each lithological waste rock type at Antamina and at other mines. This research provides in-depth solid-phase characterization of waste rock with broad ranges in neutralization and acid production potentials that may result in both acidic and neutral drainage. That characterization and the ability to observe the transition from neutral to acidic conditions at the 10-m scale are two unique aspects of this research that will improve our understanding of water quality from waste-rock piles.

1.2.4 Linking hydrology and geochemistry in mine waste

As mentioned above, the hydrology and geochemistry of mine tailings are both well understood in comparison to the hydrology and geochemistry of waste rock. Similarly, hydrological controls on geochemical processes are better understood in tailings settings than for waste rock, and drainage chemistry of homogeneous mine tailings can be and has been predicted from the detailed characterization and linking of water flow, gas flow, and solid- and aqueous-phase geochemistry for multiple data sets (e.g., Blowes and Jambor, 1990; Moncur et al., 2005). One of the most important hydrological controls on tailings geochemistry is moisture content in unsaturated tailings and its relationship to sulfide oxidation rates: the diffusion coefficient for oxygen transport into tailings decreases as moisture content increases (Wunderly et al., 1996), which can be the rate-limiting step in sulfide oxidation (e.g., Moldrup et al., 2003; Wunderly et al., 1996). The development of hardpan iron oxide layers can also impact vertical water and oxygen flow (Moncur et al., 2005), which directly affect sulfide oxidation rates and solute accumulation. Water residence time – which is directly related to water and wetting-front velocities – is important in kinetically controlled dissolution reactions, for which water must be in contact with a mineral for a certain amount of time in order for a reaction to progress such that significant solute concentrations accumulate (Maher, 2010; Nordstrom 2011). Additionally, water residence time is also important for kinetically controlled secondary mineral precipitation (Nordstrom 2011). Therefore, knowledge of velocities of tailings pore water, acid water fronts, neutralization fronts, and sulfide weathering fronts are critical in predicting pore water pH, and solute accumulation and transport (Blowes and Jambor, 1990).

Some of the mechanisms that link hydrology and geochemistry that are well-understood in tailings environments, such as residence time and oxygen availability at the sulfide grain are, in principle, applicable to waste rock systems. Waste rock is much more physically and mineralogically heterogeneous, though, so the processes are more complex and are still not well understood. For example, oxygen transport in fine-grained homogeneous tailings will likely be limited to diffusion when tailings become saturated, whereas the coarse grained, unsaturated nature of waste rock may allow for oxygen transport through advection, possibly providing an unlimited supply of oxygen for sulfide oxidation (Ritchie, 1994). In more extreme cases, internal heat from sulfide oxidation may create thermal convection cells, not only providing an unlimited oxygen supply but also creating a 'chimney' effect that can increases sulfide oxidation rates (e.g., Sracek et al., 2004; Wels et al., 2003). While research on oxygen transport and sulfide oxidation in waste rock is increasing, the impact of CO₂ degassing (as a function of waste rock moisture content) on aqueous geochemistry is currently not prevalent in the literature and is expanded upon herein.

Broad particle size distributions and spatially and temporally variable flow patterns in waste rock result in very broad ranges of water velocities, for example differing by several orders of magnitude within a few meters (Nichol et al., 2005). This, in turn will result in a broader range of residence times and more complicated aqueous geochemistry. Also, the physical location of dominant flow paths in relation to different minerals such as sulfides and carbonates impacts acidification and neutralization – and the subsequent aqueous chemistry – of pore water (e.g., Andrina, 2009; Nordstrom 2011; Stockwell et al., 2006). In other words, whereas sulfide weathering and carbonate buffering occurs relatively evenly in tailings (Blowes and Jambor, 1990), it is more difficult to determine relationships between flow paths and mineral reactions in waste rock (Stockwell et al., 2006). Furthermore, dilution and mixing of spatially variable water types that flow through different paths at the base of a waste-rock pile are not well-represented in current literature despite the likely impacts of those processes on solute concentrations and loadings (i.e., mass of solute per mass of waste rock per unit time; e.g., mg/(kg·wk)) as well as mineral solubility and precipitation/dissolution reactions.

When hydrologically driven temporal variations are observed in full-scale waste dump effluent chemistry such as at the Antamina mine (Golder, 2010), it is critical to understand and be able to predict the timing of peak concentrations and/or dissolved loads at the base of the dump on a seasonal basis for water management purposes. In addition to flow mechanisms, it is important to understand how seasonal meteorological hydrology also controls flow rates through waste rock, and in turn affects solute concentrations and loadings. Bay (2009) found that for one rock type in the two-season climate of the Antamina Mine, Zn concentrations increased and loadings decreased during the low-flow dry season compared to the high-flow rainy season. For waste rock in a cold arctic climate, Wagner (2004) also found that during periods of low flow (in this

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case the winter when waste-rock piles freeze) SO_4 concentrations increased and loadings decreased. This research expands on the relationship between flow, concentrations, and loadings on seasonal and long-term trends for multiple solutes and multiple rock types which are all exposed to the same meteorological conditions, and will attempt to determine some of the hydrological mechanisms that may account for differences in seasonal patterns observed among waste rock types.

Several researchers have begun using reactive transport modeling to simulate the linked hydrological and geochemical processes in mine waste rock (e.g., Da Silva et al., 2007; Demers et al., 2013; Fala et al., 2013; Gerke et al., 1998; Gerke et al., 2001; Lefebvre et al., 2001; Linklater et al., 2005; Molson et al., 2005; Stromberg and Banwart, 1994). This research will attempt to illuminate some of the important coupled hydrological and geochemical mechanisms that pertain to those models, and to augment the current database of parameters used as model inputs.

1.3 Organization, objectives, and hypotheses

This dissertation is presented as four body chapters addressing key areas of research currently underrepresented in the literature regarding hydrology, evaporation, and aqueous geochemistry of waste rock. The key topics addressed in the chapters are as follows:

1.3.1 Chapter 2: Conceptual model development and parameterization of unsaturated flow regimes in three experimental waste-rock piles

In order to assess and understand unsaturated flow through waste rock, datasets collected from real-world, large-scale (i.e., tens of meters to hundreds of meters) experiments are needed.

Research on unsaturated flow in waste rock in different material types and under different meteorological conditions is growing. However, to date research of unsaturated flow through multiple material types under the same meteorological conditions has not been conducted at the large-scale. This research is needed in order to isolate the effects of material type on flow regimes, particularly the characteristics influencing matrix flow and preferential flow. The unsaturated flow regime influences pore-water velocities and wetting fronts through waste rock material and at present this research in multiple material types is lacking. Two resulting objectives of this study for three waste rock types under similar meteorological conditions are:

- to determine, present, and analyze hydrological parameters such as hydraulic conductivities and matrix flow, preferential flow, and wetting front velocities, and
- to develop conceptual models of flow regimes for three waste rock types, including relative proportions of matrix and preferential flow and the relationships between porewater velocities and wetting-front velocities.

One hypothesis of this dissertation is that coarse particle size fractions (i.e., gravel, cobbles, and boulders) can strongly influence waste rock flow regimes, and this chapter will attempt to address the question of whether or not it is possible to attribute flow mechanisms, velocity ranges, and matrix and preferential flow patterns to particular size fractions.

1.3.2 Chapter 3: Comparative analysis of evaporation from three experimental wasterock piles using water balance and Penman-Monteith methods

Evaporation from bare waste rock has been calculated by water balance or measured by eddy covariance in a few other waste rock studies, but the ranges in evaporation are highly variable and the dataset is not robust enough to make confident estimations based on analogous studies.

Additionally, modified Penman (Granger and Gray, 1989) and Penman-Monteith (Allen et al., 1998) methods have successfully modeled observed evaporation from to the upper surfaces of waste-rock piles, but the applicability of those analytical methods has not been determined for the loose waste-rock pile slopes. Three objectives proposed to address those gaps are:

- to calculate the evaporation component of the water balance for three types of waste rock, including flat and sloped surfaces;
- to compare the water-balance results with evaporation estimates from the United Nations Food and Agricultural Organization's modified Penman-Monteith method (FAO-PM; Allen et al., 1998) using base-case laboratory- and software-derived or recommended soil parameter values; and
- to calibrate the FAO-PM model to water-balance evaporation calculations and evaluate conditions and parameters in waste-rock settings for which the FAO-PM method may and may not be applicable.

It is hypothesized that more evaporation should occur on the pile slopes than on the flat upper surfaces as a result of increased air circulation on the slopes; that, because of higher moisture contents and greater upward capillary force, finer-grained waste rock should have higher evaporation than coarser-grained waste rock; that the FAO-PM method will be most applicable for waste rock materials that are most similar to the agricultural soils for which the method was developed; and that the FAO-PM method may be less applicable to waste rock and waste-rock piles with certain physical properties. Research questions pertaining to this topic include how the water balance calculations differ between the outer slope and upper surface; how internal flow regimes could impact water availability at the surface; how particle size distributions affect evaporation; and how might we improve the applicability of the FAO-PM method in waste rock settings.

1.3.3 Chapter 4: Rapid seasonal transition from neutral to acidic drainage in a wasterock test pile at the Antamina Mine, Peru

The ability to observe a clear transition from neutral to acidic drainage through extensive solidphase mineralogical and internal and effluent aqueous geochemistry datasets at the 'mixed' 10-m and 'un-mixed' 1-m scales is unique to this study. Objectives pertaining to the documentation and evaluation of this pH transition include:

- to quantitatively describe the changes in aqueous geochemistry that occurred when Pile 2 effluent water transitioned sharply from circum-neutral pH to slightly more acidic pH in February 2011;
- to compare solid phase and aqueous geochemistry for different material types within Pile 2 and determine the material type(s) that most strongly affect whole pile water quality; and
- to determine the solid phase elemental and physical characteristics of a bright blue precipitate that began to form at Pile 2 effluent release points during the transition.

Two hypotheses regarding the transition from neutral to acidic drainage are that, considering the broad mineralogy present within each waste rock type, water passing through certain materials will transition to acidic conditions earlier than others, and that water from those areas may impact the overall drainage water quality from a larger volume of waste rock. In order to test

these hypotheses, research questions such as how the mineralogy and aqueous effluent from the 10-m scale 'mixed' and 1-m scale 'non-mixed' studies compare will be addressed.

1.3.4 Chapter 5: Linking the hydrological and geochemical processes that control mine waste rock effluent water quality

There are very few large-scale studies (i.e., tens to hundreds of meters) that include analysis of primary and secondary mineralogy; extensive internal and effluent hydrological datasets; extensive internal, effluent, and associated smaller-sale (i.e., one-meter) aqueous geochemistry; internal pore gas measurements; and the ability to observe and analyze those datasets for three material types, under both acidic and neutral conditions, and under similar meteorological conditions. This study provides a unique opportunity to illuminate the effect of hydrological processes on waste rock effluent water quality, and to that end, some objectives to be pursued are:

- to determine, present, and analyze seasonal loading patterns, concentration patterns, and correlations for select solutes for three waste rock types;
- to determine the dominant hydrological and mineralogical controls on those seasonal patterns; and
- to provide a detailed interpretation of flow, transport and reaction processes that affect drainage water composition.

One hypothesis regarding hydrological controls on geochemistry is that the flow regimes to be outlined in Chapter 2, including variable seasonal pore water velocities and the relative proportions of preferential and matrix flow velocities, will contribute to unique seasonal solute concentrations and loading patterns for each type of waste rock. Research questions that will address this hypothesis include what patterns can be qualitatively observed between flow regimes and geochemistry, and what additional hydrological mechanisms including mixing, secondary mineral precipitation, and changes in internal moisture content may be affecting water quality on seasonal and longer-term bases.

1.4 Description of experimental piles and field barrels

Most of the data used for this project comes from three 36 m x 36 m x 10 m experimental wasterock piles containing instrumentation to measure and sample in-situ and effluent water and gas (Figure 1.3). Additionally, data originate from some of the 1-m tall field barrels that were constructed concurrently with and are composed of the same material as the experimental piles (Figure 1.4). The piles and associated field barrels were constructed in 2006 (Pile 1), 2007-2008 (Piles 2 & 3), and 2008-2009 (Piles 4 & 5. All of the piles are composed of run-of-mine waste rock and constructed according to the methods in Corazao Gallegos (2007) and Bay (2009), which are described briefly below. Bay (2009) and Aranda (2009) conducted interpretation of data from Pile 1 and its associated field barrels, respectively; this research expands on their interpretations and analyzes the hydrology and geochemistry of Piles 1-3; and Blackmore (in progress) is interpreting the data from Piles 4 and 5.

1.4.1 Experimental piles: Construction details, instrumentation, and sampling

The base of each experimental pile is covered with an impermeable geomembrane. This 36 m x 36 m Lysimeter D and three smaller (4 m x 4 m) interior Sub-lysimeters A, B, and C, capture all pile recharge (Figure 1.5). Sub-lysimeters A and B are located under the traffic-compacted 'crowns' of the piles, Sub-lysimeter C is located underneath the outer slope of the pile, and Lysimeter D is under both the crowns and the slopes of the piles. The lysimeters are named by

pile designation followed by the lysimeter designation, e.g., P2D is the Pile 2 large D lysimeter and P3B is the Pile 3 smaller interior B sub-lysimeter. Just above the geomembrane are two instrumentation lines L5 and L6. Protecting L5 and L6 and the geomembrane are layers of sieved waste rock. The lower layer is 30 cm thick, and contains particles smaller than ~5 cm, and the second layer is 1.2 m thick, contains particles smaller than ~10 cm, and ensures that large boulders, sometimes >1m in diameter, that are end-dumped from a 10-meter height do not penetrate into the lower protective layer or damage instrumentation.

Above the protective layers are sloped panels of waste rock housing four instrumentation lines (L1-L4). The piles are built progressively out with run-of-mine waste rock discharged from ~280-tonne CAT 797 haul trucks from a height of 10-12 meters in three separate dumping sessions (Tipping Phases I, II, and III), creating the internal fining upwards particle gradation and basal rubble zones that can be associated with full-scale waste-rock piles (e.g., Smith and Beckie, 2003; Stockwell et al., 2006). The approximate total masses of Piles 1, 2, and 3 are 19,560 tonnes, 21,780 tonnes, and 17,560 tonnes of waste rock, respectively.

Instrumentation lines L1-L6 each host dozens of sensors and samplers that allow for in-situ water and gas sampling, and for continual measurement of soil moisture content, electrical conductivity (EC), temperature, and gas pressure (Figure 1.6 to Figure 1.8; Table 1.1). Instrument names are designated by the pile number (P1, P2, or P3), followed by the instrumentation line (L1-L6), then by the instrument type (G - gas port; SWSS - soil water solution sampler; T- thermistor; TDR time domain reflectometry probe; TE - ECH₂O probe), and finally by the location on the instrumentation line. The lowest numbers start at the bottom of the pile (Lines 1-4), South or left side of the pile (Line 5), and East or back side of the pile (Line 6). For example, P2L1TE3 (Pile 2, Line 1, ECH₂O Probe 3) is the third ECH₂O probe from the bottom of Line 1 in Pile 2. The cables and tubing associated with the sensors are protected by flexible 2" corrugated plastic tubes that run from the sampling port to the instrumentation hut, where all data is recorded using Campbell Scientific CR1000 dataloggers and associated multiplexers. Effluent water from the four lysimeters is carried to the instrumentation hut through a system of high-density polyethylene (HDPE) tubing. There, effluent temperature and electrical conductivity are recorded at 30-minute intervals and the flow volume and rate are continuously measured using tipping bucket flow meters. Samples are taken weekly or bi-weekly for chemical analysis by an external laboratory (2007-2009: Envirolab S.A, Lima Peru; 2010: SGS Del Per, S.A.C) and are measured in the field for pH, temperature-corrected EC or specific conductance (SC), temperature, and dissolved oxygen.

1.4.2 Field barrels: Construction details and sampling

Field barrels were constructed in conjunction with the experimental piles for each of the two protective layers and each of the tipping phases. The field barrels are designated first by their pile number (1, 2, or 3), followed by their location in the pile (0 for the protective layer, 1 for the first or rear tipping phase, 2 for the second or center tipping phase, and 3 for the third or outer tipping phase), and then by a designation for duplicates (A or B). There are two exceptions in the nomenclature:

1) Field Barrels 2-1A and 2-1B are not duplicates. They are composed of intrusive material from two different pit locations. Both materials are present in the Tipping Phase II of Pile 2.

2) Field Barrel 3-4A represents material located in the outermost part of the third (outer) tipping phase (Tipping Phase III) of Pile 3. It is from a different location in the pit than the material in the inner part of Tipping Phase III, which is represented by Field Barrel 3-3A. The construction

of Pile 3 was suspended during the discharging of material 3-3A due to the abundance of very large boulders, which created hazardous construction conditions. The material represented by Field Barrel 3-4A was used to complete construction of Tipping Phase III.

The field barrels were all constructed according to the methods in (Aranda, 2009). A field barrel is a waste rock-filled 205-liter plastic drum that is open to the atmosphere at the top with an outflow spout to allow effluent to drain freely into a 20-L collection bucket (Figure 1.4). For the selection of waste rock placed in each field barrel, approximately 16 tonnes of waste rock was separated prior to discharge on the experimental pile and was then mixed and separated into 4tonne piles. From one of those, 1200 kilograms were coned and quartered twice, the components larger than 10 cm were removed, and approximately 300 kilograms were separated out for use in a field barrel with the remainder used for other analyses. The ~300 kilograms of <10 cm waste rock were placed in the barrel atop a 15-cm layer of # 50-#60 mesh silica sand drainage material and a filter fabric. Several duplicate field barrels were constructed to assess reproducibility and material heterogeneity. Samples were taken from the collection bucket on a weekly or bi-weekly basis, except during the dry season, when there was no recharge through the field barrels and no samples could be taken. Samples were measured in the field for specific conductance, pH, temperature, and dissolved oxygen, and analyzed for dissolved solutes and total metals at an external laboratory (2007-2009: Envirolab S.A, Lima Peru; 2010: SGS Del Per, S.A.C.).

1.4.3 Experimental piles and field barrels: Waste rock characteristics

The waste rock in Piles 1-3 represent three waste rock types from the Antamina skarn deposit, including the carbonate rich gangue rock (Pile 1), rock from the intrusion (Pile 2), and skarn rock from the contact interface between the gangue and the intrusion (Pile 3).

1.4.3.1 Antamina waste rock classification

The mine's classification scheme is currently based on solid phase content of Zn (weight %), As (weight %), sulfides (visual estimate %), and oxides (visual estimate %, only applicable to waste rock used in tailings dam construction). Based on the solid phase concentrations, the waste rock is grouped into three classes: highly reactive Class A, slightly reactive Class B, and non-reactive Class C (Table 1.2, Aranda, 2009). Pile 1 contains slightly reactive Class B marble, marble diopside, and hornfels gangue rock; Pile 2 is composed of reactive Class A igneous quartz monzonite intrusive rock; and Pile 3 is composed of reactive Class A skarn rock, which is predominantly exoskarn (from the outer area of the alteration) with minor amounts of endoskarn (from the inner area of the alteration).

While each pile represents a specific type of waste rock (i.e., marble/hornfels, intrusive, or skarn), it is important to note that each of the piles were built in four phases, and the waste rock for each phase originated from a different location in the mine. Therefore, even though each pile is composed of one specific waste rock 'type', there are distinct mineralogical signatures in the waste rock from each construction phase (see Chapter 5, Table 5.3-5.5 for details). The placement of the distinct waste rock types above Sub-lysimeters A, B, and C as well as the construction of a field barrel associated with each tipping phase allows for the investigation of heterogeneity not only among but also within waste rock types.

1.4.3.2 Particle size distribution

The highly variable particle size distributions of Antamina waste rock have the potential to significantly impact waste rock hydrology and geochemical reactivity. Pile 1 is by far the coarsest-grained pile, dominated by boulders, cobbles and gravel (Figure 1.9). Pile 3 also

contains some boulders, which have the potential to contribute to preferential flow, and has a relatively broad range of finer-grained particle size distributions among tipping phases. Pile 2 contains no boulders and has relatively narrow range of finer-grained particle size distributions. Much higher hydraulic conductivities and lower moisture contents can be expected from a coarser particle size distribution (Pile 1) and lower hydraulic conductivities and higher moisture contents can be expected from the finer particle size distributions (Pile 2 and 3).

Regarding the geochemical impact of particle sizes on reactivity, individual discharges in Pile 1 have as few as 2% particles with diameters <0.25 mm (Appendix B; Figure B.2) which have higher-surface area and are therefore more highly reactive (Strömberg and Banwart, 1999). Conversely, Pile 2 individual discharges have up to 22% of particles of the more reactive <0.25 mm size fraction, and Pile 3 individual discharges have up to16% of particles of that size fraction (Appendix B; Figure B.3 and Figure B.4).

1.4.4 Mineralogical and elemental analyses of waste rock

Significant work has previously been completed by others at UBC, the University of Western Ontario, and Teck's Applied Research and Technology (ART) facility to characterize the solid phase properties of several of the materials that comprise Piles 1-3. Aranda (2009) and Blaskovich (2013) compiled information from analyses at UBC and ART detailing the mineralogical, elemental, and mineral availability based on mineral liberation analysis (MLA) for all of the tipping phases in Pile 1. Haupt (in progress) performed sequential leach tests on Class B material to assist in the creation of a modified classification methodology. Provost (2010) also performed sequential leach tests on four samples from Piles 2 and 3, and obtained elemental compositions of the same samples from whole rock digestion performed by ALS Environmental laboratory (Vancouver, BC). Blaskovich (2013) analyzed some of the sequential leach samples from Piles 2 and 3 at ART to detail the mineral liberation availability using MLA. Dockrey (2010) performed x-ray diffraction (XRD) and scanning electron microscopy (SEM) for some of the materials from Piles 2 and 3. Blackmore (in progress) obtained additional mineralogical and elemental information on the same samples and others from fusion and pressed pellet x-ray fluorescence performed at the University of Western Ontario. To determine particle surface areas, BET analyses have been carried out on all of the Pile 1 materials (Aranda, 2009) and on several of the Piles 2 and 3 materials (Blackmore, in progress).

To complement the existing work, additional solid phase mineralogical and elemental analyses were completed at UBC and in commercial laboratories to better characterize the solid-phase composition of waste rock pertaining to this research, and are presented in Chapter 5. The following analyses were performed by ALS Labs in Lima, Peru: solid phase major ion and trace metal concentrations using whole rock digestion and inductively-coupled plasma mass spectrometry (ICP-MS); acid-base accounting (ABA), including maximum potential acidity (AP) and neutralization potential (NP) using the unmodified Sobek et al. (1978) method without siderite correction; and solid phase S and C by Leco. Pile 2 blue precipitate samples (Chapter 4) were analyzed for trace metal concentrations using whole rock digestion and ICP-MS and solid phase S and C using Leco by ALS Labs in North Vancouver, BC, or Acme Labs in Vancouver, BC. Pile 2 and 3 solid phase and precipitate samples were also examined using a Philips XI-30 Scanning electron microscope (SEM) fitted with a Princeton Gamma-Tech Energy-dispersive Xray spectroscopy (EDS) system in the Department of Earth and Ocean Sciences at the UBC. Identification of mineral phases was performed by powder X-ray diffraction (XRD) on a Siemens D8000 Diffractometer. Qualitative identification of phases was carried out using EVA

software, and quantitative analyses – i.e., the relative proportions of the minerals present – were completed using Rietveld (1967, 1969) refinement with Topas v.3.0 software.

1.5 Tracer study

Three tracers were applied at the top of all of the experimental waste-rock piles in January 2010. The purpose was to determine precise flow velocities and examine the relationships between particle size distributions, waste rock internal structure, and preferential and matrix flow mechanisms. The first tracer, the ion bromide applied as lithium bromide, acted as the conservative tracer and was the only tracer analyzed for this study. It is well-documented that bromide travels at about the same velocity of water in porous media, exhibiting very little sorption and retardation in most rock types (e.g., Mackay et al., 1986; LeBlanc et al., 1991). Laboratory experiments carried out at UBC in the fall of 2009 confirmed that bromide acts conservatively and does not sorb to the waste rock types in the experimental piles at Antamina.

The other two tracers applied during the tracer study were the fluorescent tracer sodium fluorescein and deuterium oxide (D_2O), or heavy water. Sodium fluorescein sorbed strongly to pile materials, and was therefore only useful in detecting a tracer peak in Pile 1 with an in-line Turner Designs Cyclops fluorimeter during a period of no sampling (Chapter 2). Samples were taken for the analysis of D_2O for the possibility of analysis in a separate study.

1.5.1 Application

The three tracers were applied together as individual rain events for each of the piles (Table 1.3). The tracers were added to a large cistern of water and mixed thoroughly before being sprinkled on top of each pile using a water distribution and sprinkling system that was designed at UBC and tested on-site at the mine (Figure 1.10). The system was designed to achieve uniform water distribution over the top of each pile with no water application on the slopes of the piles. The Pile 1 tracer application occurred on January 19, 2010, as 25.5mm of precipitation applied over three hours at a rate of 8.5mm/hr and corresponds approximately to a 7-8 year rain event (i.e., every 7-8 years a rain event occurs with a similar intensity and duration as the applied rain event). The Pile 2 tracer was applied on January 20, 2010, as 26.9 mm of rain applied over 4.5 hours at a rate of 6.0 mm/hr which corresponds approximately to a 5 year rain event. The Pile 3 tracer application occurred on January 22, 2010, as 27.5mm of rain applied over three hours and 40 minutes at a rate of 7.5 mm/hr, which corresponding approximately to a 6-7 year rain event. Collection cups were placed at regular intervals on the surface of the piles and the sprinkler system was adjusted as needed throughout the application process to assure uniform distribution. The largest source of non-uniform distribution was variable wind direction/velocity and gusting. See Appendix A for tracer intensity-duration-frequency graphs and distribution plots.

1.6 Research contributions and practical applications

The primary purpose of this dissertation is the synthesis and analysis of prodigious multi-scalar, multi-parameter hydrologic and geochemical data from end member waste rock types producing acidic and neutral drainage in a distinct two-season wet/dry climate. This study builds on the methods and findings of previous studies to develop a comprehensive platform of parameters to be used directly by Antamina and in future reactive transport modeling to more accurately predict waste dump effluent water quality. Standing alone or combined, the following factors make this study unique:

- the abundance and variety of data available from in-situ and effluent sensors and sampling for the experimental waste-rock piles;
- the separation of intrusive, skarn, marble, and hornfels waste rock as end-member materials;
- the controlled experimental set-up that allows for accurate calculation of the evaporation component of the water balance for specific types of waste rock at the field scale;
- the neutralization capacity and presence of neutral-soluble metals in the waste rock;
- the ability to interpret waste rock drainage quality and quantity at relatively large scales;
- and the distinct wet and dry seasons that create yearly cycles of moisture contents reaching close to both saturation and field capacity.

The findings are especially applicable to mines with similar carbonate-hosted skarn ore bodies and/or exposed to similar climatic conditions. The waste rock flow and geochemical mechanisms and parameters presented and analyzed in this dissertation contribute to a comprehensive data set that will be used to reduce uncertainty long-term predictions of water quality, guide regulatory policy, and develop dumping and mine closure strategies. The findings can eventually contribute to the development of efficient dumping techniques in order to inhibit sulfide oxidation, metal dissolution, and transport, in turn minimizing potentially negative environmental impacts and water treatment requirements.

1.7 Tables

Instrument	Parameters Measured / Use	Make	Location	Model	Quantity		
					Pile		
					1	2	3
TDR Probe	Soil moisture	In-house (UBC)	Vancouver, BC		22	5	5
Single Point Thermistor	Temperature	RST Instruments	Coquitlam, BC	SPT 2252 ohm, 0.1 Degree C	44	16	16
EC Probe	Electrical conductivity (EC)	In-house (UBC)	Vancouver, BC		4	4	4
ECH ₂ O Probe	Soil moisture, temperature, EC	Decagon Devices	Pullman, WA	ECH ₂ O	0	22	22
Soil Water Solution Sampler	Collect in-situ water samples	Soil Moisture Equipment Corp.	Santa Barbara, CA	1920F1 Pressure- Vacuum SWS	20	20	20
Gas Samplers	Collect in-situ gas samples	In-house (UBC)	Vancouver, BC		64	64	64
Tipping Bucket	Effluent flow	PlasticSmith Fabricating	Vancouver, BC		4	4	4

Table 1.1. Instrumentation summary for Piles 1, 2, and 3.

Table 1.2. Antamina waste rock classification system (from Aranda, 2009).

Class	Reactivity	Lithology	Zinc (%)	Arsenic (%)	Sulfides (%)	Oxides (%)
A	Reactive	Hornfels Limestone Marble Skarn Intrusive	>0.15	>0.04	>3	>10
В	Slightly Reactive	Hornfels Limestone Marble	0.07-0.15	<0.04	2-3	<10
С	Non-reactive	Hornfels Limestone Marble	<0.07	<0.04	<2	Minimal

Pile	Application date	Area, top of pile (m²)	Applied water volume [†] (L)	Area- normalized applied water (mm)	Duration (min)	Intensity (mm/hr)	Approximate storm frequency (years) [‡]
1	19-Jan-10	231	5890	25.5	180	8.5	7-8
2	20-Jan-10	242	6515	26.9	270	6.0	5
3	22-Jan-10	220	6050	27.5	220	7.5	6-7

 Table 1.3. Tracer application details for Piles 1, 2, and 3.

[†] Volume includes water discharged from cistern and water from natural rainfall [‡] Event frequency is based on IDF graphs for the region provided by Antamina

1.8 Figures



Figure 1.1. Location of the Antamina mine in Ancash, Peru. (Map: Creative Commons Attribution-Share Alike 3.0 Unported License. Based on work at nmun-regensburg.de & Traveldudes.org adapted by Peterson).



Figure 1.2. Rubble zone (solid oval) and highly-heterogeneous but generally fining-upward sequence (dashed lines) created at various scales by the end-dumping method at (a) an experimental waste-rock pile at the Antamina Mine, Peru, and (b) a disassembled waste-rock pile at Key Lake, Saskatchewan, Canada (adapted after Stockwell et al., 2006).



Figure 1.3. Schematic drawing of the experimental waste-rock piles, showing the locations of the four lysimeters Lys A to Lys D, and the six instrumentation lines L1 to L6.



Figure 1.4. One-meter tall field barrels containing approximately 300 kilograms of waste rock exposed to the atmosphere and draining freely into collection buckets for volume measurement and chemistry sampling.


Figure 1.5. Photograph of one of the experimental waste-rock piles at Antamina showing a side view of smaller Sub-lysimeters A to C and large Lysimeter D; instrumentation lines L1, L2, L3, and L4; and tipping phases TP1, TP2, and TP3.



Figure 1.6. Pile 1 instrumentation schematic.



Figure 1.7. Pile 2 instrumentation schematic.



Figure 1.8. Pile 3 instrumentation schematic.



Figure 1.9. Particle size distribution curves (PSDs) for Piles 1 to 3. Average curves (left) are averages of all of the materials in the pile, i.e., from each tipping phase. The ranges (right) are the upper and lower bounds from all of the tipping phases for each size fraction. PSDs from the individual tipping phases are located in Appendix B.



Figure 1.10. Testing of the tracer water distribution system (left) and tracer application on Pile 2 (right).

Chapter 2: Conceptual model development and parameterization of unsaturated flow regimes in three experimental waste-rock piles

2.1 Introduction

Prediction of the quantity and quality of water that is discharged from mine waste rock dumps is critical to mine planners through all phases of mine development and closure. Waste dump effluent water quantity – i.e., the volume and timing of water that recharges to the base of the dump and is released at discharge points, or seeps – is important in water management during mining operation and closure if and when any of the following processes are necessary: water quality treatment; transfer of water among internal mine water storage facilities; and controlled discharge of mine water to the environment. The quality of mine waste effluent – i.e., the types and amounts of dissolved and total metals, metalloids, and salts present in the water – is a crucial factor in the design and operation of water treatment facilities and discharge to the environment through all stages of the life of mine, as well as technical re-use of effluent water during mine operation. The accurate prediction of mine waste effluent water quantity and quality are key components of the management processes that insure the physical integrity of water storage and transfer facilities such as dammed reservoirs, wetlands, holding tanks, and pumping systems, and the short- and long-term aqueous geochemistry of water that is discharged to the environment.

Effluent water quantity and quality are both highly dependent on the fluid flow regimes of waste rock dumps. These flow regimes include surface runoff; infiltration and evaporation; fast and slow matrix flow through soil-like waste rock; fast preferential flow, possibly through low-resistance flow paths in coarser-grained waste-rock or as water flowing over surfaces of and through voids associated with boulders; spatially and temporally variable unsaturated hydraulic

conductivities; and pressure-induced wetting fronts. The flow regimes inherently control the timing and volume of water discharged at the base of a dump, but they also have a major impact on water quality for several reasons (Section 1.2.4; Chapters 4 and 5).

In order to more accurately predict waste dump effluent water quantity and quality, then, conceptual models of complex waste rock systems should include potential combinations of flow types and velocities, and the physical properties of the waste rock and atmospheric conditions that determine those flow regimes. Unsaturated flow through any material is complex because of three-phase interactions, but the broad particle size distributions and structural qualities of wasterock piles make the characterization of fluid flow even more difficult.

Unsaturated flow is well-researched in many disciplines, from soil science for agricultural purposes to hazardous waste disposal and mine tailings. Unsaturated flow through the porous matrix is expected to follow the Richards (1931) equation, and many of the complexities that cause divergence from the Richards equation are also well documented. For example, literature describing the causes and effects of preferential flow based on film flow through fractures, fingering, macropore flow, and unstable flow at both field and laboratory scales is abundant (e.g., Dekker et al., 1994; Ritsema et al., 1998; Tokunaga & Wan, 1997 and 2001; Section 1.2.1).

The body of research devoted to unsaturated flow specifically through waste rock is also growing, including field-based mechanistic studies similar to this research (e.g., Bay et al., 2013; Marcoline, 2008; Neuner et al., 2009; Nichol et al., 2005; Savci and Williamson, 2002; Stockwell et al., 2006; Section 1.2.1). Additionally, waste rock modeling studies include advances in reactive transport (e.g., Lefebvre et al., 2001a,b; Linklater et al., 2005; Linklater et al., 2006; Molson et al., 2005) for which extensive sets of both hydrological and geochemical parameters are required. The augmentation of field-based ranges of those parameters is an additional motivation for this research.

In this study, precipitation data and waste rock physical properties are observed in conjunction with effluent and internal flow patterns and a tracer study for Piles 1, 2, and 3, which are described in Chapter 1. The objectives of the study are to synthesize, evaluate, and analyze different types of flows that are observed in each of the piles in order to determine and present hydrological parameters and develop conceptual models and for the three single-type waste rock systems at the Antamina mine. The conceptual models can later be used for water quantity and quality prediction from each type of waste rock at Antamina; for integrating the single type parameters into predictions of full-scale, mixed waste-rock piles; and as guides for conceptual models at mines that have similar waste rock types and/or atmospheric conditions as the Antamina mine.

2.2 Conceptual model formulation

An overview of the numerous flow components comprising the unsaturated flow regimes is given below. Detailed descriptions of the complexities of unsaturated flow in waste rock are outlined in the literature (e.g., Bay, 2009; Nichol et al., 2005; Smith et al., 1995; Smith and Beckie, 2003), and this study increases our understanding of those complexities and presents parameter ranges for components of unsaturated flow. Many of the flow components have variable definitions and multiple uses in current literature, so a description of the terms used in this hydrological study are included for clarity.

In this study, matrix flow is defined as capillary flow through the granular matrix that adheres to the Richards (1931) equation and has pore water velocities on the order of millimeters to

centimeters per day. Matrix flow tends to occur in the <5 mm size fraction, as capillary effects are not as prevalent in the coarser materials (Tokunaga et al., 2002; Yazdani et al, 2000). Each material type has a range of matrix flow velocities, including faster flow through coarser or more saturated material, and slower flow through finer or less saturated material. 'Pistoning', or pressure-induced downward displacement of antecedent water from pore spaces by a wetting front, is a component of matrix flow.

Preferential flow has many definitions depending on the discipline. The definition adopted for this study is 'the observation of water or solute movement faster than expected by an experimental observer or the concentration of flow into spatially localized areas' (Nichol et al., 2005). Preferential flow can result from 'macropores', finger-flow (Gerke, 2006; Lu, et al., 1994; Ritsema, et al., 1994; Ritsema, et al., 1998; Wang, et al., 2003), unstable flow (Dekker, et al., 1994; Glass, et al., 1989; Ritsema, et al., 1994; Ritsema, et al., 1998), funnel flow including capillary breaks (Abdul, et al., 1989; Gerla, et al., 1996; Gillham, 1984; Pruess, 1999; Silliman, et al., 2002), and film flow through fractures (Tokunaga & Wan, 1997; Tokunaga & Wan, 2001).

Many of the preferential flow studies listed above focus on agricultural or waste disposal settings, but macropore flow, funnel flow, and film flow may also be applicable to waste rock settings. In agricultural settings, macropores refer to large conduits at the soil surface which are created by the growth and eventual degradation of plant roots, animal burrows, or cracks formed by shrinking/swelling and freezing/thawing (e.g., Ahuja, et al., 1995; Chen and Wagenet, 1992) that can lead to 'bypass flow' which minimally interacts with the matrix (Booltink et al., 1993). For this study in mine waste rock, macropores refer to large pores in coarse gravel- and cobbledominated waste rock that can serve as high-velocity saturated or unsaturated preferential flow paths. Bypass flow has also been observed in waste rock settings, both as faster flow around the

matrix via macropores as discussed above, and as very slow flow in very fine-grained areas that store large amounts of water and have minimal solute exchange with the matrix (Nichol et al 2005). Velocities of water flowing along the walls of fractures as film flow are reported to be three orders of magnitude faster than saturated pore water velocities, at 2 m/day to 40 m/day (Tokunaga & Wan, 1997). The mechanisms of film flow (and surface zone flow, Tokunaga & Wan, 2001) in fractures may be similar to water flowing over the surfaces of boulders. Indeed the presence of boulders has been hypothesized to be the main cause of preferential flow in a waste rock dump (Eriksson et al., 1997). Capillary breaks, which are a type of funnel flow and are observed along internal sloping surfaces resulting from the end-dumping technique (Figure 1.2), have been observed in waste rock dumps similar to those at Antamina (Andrina, 2009; Fala et al., 2005; Neuner, 2009; Stockwell et al., 2006). Andrina (2009) found that flow through the finer-grained and coarser-grained sloping layers resulting from the end-dump method depended on rainfall intensity, with more evenly-distributed vertical-downward flow under higher rainfall intensities. For this study, unless a hypothesis is specified, preferential flow could be a result of any of the mechanisms described above.

In this study, 'velocity' is defined as the velocity of a molecule of water through the waste rock, and can be estimated from large-scale measurements in a variety of ways, e.g. from flux measurements or tracer signals. 'Velocity' applies to molecules of water moving through matrix flow paths (matrix velocity), preferential flow paths (preferential flow velocity), or a combination and/or average of both matrix and preferential flow paths (combination flow velocity). 'Wetting-front velocity' is the velocity of a wetting front that moves through porous media because a mass of water is displaced downward due to gravity and/or increased hydraulic pressure from above (Smith et al., 1995). Wetting-front velocities, then, are not always

representative of water molecule velocities, and may be orders of magnitude faster than measured matrix velocities (e.g., Bay, 2009; Nichol et al., 2005).

Saturated hydraulic conductivity (K_{sat}) is the hydraulic conductivity under saturated conditions, and is the maximum hydraulic conductivity. Unsaturated hydraulic conductivity (K_{unsat} or $K(\theta)$) is the hydraulic conductivity as a function of water content (θ). Unsaturated hydraulic conductivity increases with increasing water content to reach maximum conductivity at saturation (K_{sat}). Unless specified, all saturated and unsaturated hydraulic conductivities discussed here are in the vertical downward (K_z) direction.

The parameters described above along with evaporation and storage (Chapter 3) characterize unsaturated flow in waste rock. The synthesis of the parameters results in increased conceptual understanding of the mechanisms controlling waste rock dump effluent water quality and quantity.

2.3 Methods

The reader is referred to Chapter 1 for detailed methods of experimental pile construction; tipping phase, lysimeter, instrumentation names and locations; and additional details of the tracer study methods described briefly below.

2.3.1 Precipitation and effluent flow rates

Precipitation was measured continuously at the location of the experimental piles with an 8" Rainwise rain gauge, which has a reported accuracy of +/- 1% (www.rainwise.com), and recorded with a CR1000 datalogger (Campbell Scientific). Rain data were not available from the experimental piles rain gauge from February to June 2008 due to a faulty electronic connection, and were estimated over this time period from nearby weather stations by Bay (2009).

There is no runoff leaving the experimental piles, so all precipitation evaporates, is stored within the pile, or infiltrates to the collection lysimeters at the bases of the piles (Section 3.2.1). The water that is collected in the lysimeters is directed through a system of HDPE and PVC pipes to an instrumentation hut, where flow rates are measured using acrylic tipping bucket flow meters. Tipping buckets were designed at UBC according to the methods in Corazao Gallegos (2007) and constructed at PlasticSmith Fabricating in Vancouver, Canada.

The four-lysimeter design of the experimental piles (Figure 1.3) allows for the examination of flow patterns for the entire pile (D lysimeters) and for isolated areas within the pile (A, B, and C sub-lysimeters). D lysimeter flow represents flow through all of the material sub-types found in each pile and includes infiltration from the flat, compacted surface, or crown, of the pile as well as all of the slopes. A and B sub-lysimeter flow consists of flow through material from two tipping phases, and represents flow only infiltrating through the crown of the pile. Only in the case of extreme non-vertical flow paths would infiltration from the slopes of the piles reach the A and B sub-lysimeters. The outer C sub-lysimeters have only one material type above them, and represent infiltration through the slopes of the piles. Within this chapter, 'pile flow' refers to flow from the D lysimeters – which comprises 96.3% of the pile footprint and a similar percentage of total pile flow volume and is therefore a good proxy for whole-pile flow – unless otherwise noted. Lysimeter D is considered to be slope-dominated because of the high slope-tocrown ratio of the piles (i.e., 4.6:1 in plan view, and 11.8:1 in total surface area). In general, volumetric measurements such as effluent flow, precipitation, and tracer application have been normalized to the lysimeter catchment areas and are reported in mm for comparative purposes.

2.3.2 Tracer study

In January 2010, a tracer study was conducted on all three experimental piles in order to better understand flow regimes on a 10-m scale (Figure 1.10). The tracers were applied as discrete artificial precipitation events on January 19, 21, and 22, 2010, for Piles 1, 2, and 3, respectively. The study period is from tracer application through August 17, 2011.

2.3.2.1 Tracer application and sampling

The tracers were applied to the crowns of the piles, above Lysimeters A, B, and D, and tracers were not applied to the slopes of the piles, above Sub-lysimeter C. Under the assumption of only vertical flow, Sub-lysimeters A and B will collect only tracer water, Sub-lysimeter C will collect only non-tracer water, and Lysimeter D will collect both tracer and non-tracer water in proportion to the crown vs. batter.

A sprinkler system constructed of a water tank truck, fire hoses, pressure gauges, garden hoses, and garden sprinklers was used to apply the solution only on the top area of the pile. Distribution was determined using measuring cups placed on the soil surface, and sprinklers were adjusted throughout the application period to obtain maximum uniformity (Appendix A). Over periods of several hours, 5891 to 6516 liters of water was artificially applied on the top surface of each pile (Table 2.1). The tracer applications corresponded to area-normalized heights of 25.5 mm to 27.5 mm of water and approximately 5- to 8-year storm events, and contained known concentrations of the tracers bromide (as lithium bromide) and sodium fluorescein. Except for one occurrence about twelve hours after Pile 1 tracer application, sodium fluorescein was not seen in effluent waters of any of the three piles and was assumed to have sorbed onto pile materials, so only bromide tracer data are described here.

Discrete samples from each lysimeter were collected at high (15- 180 minute) intervals for the first 24 hours after tracer application with the exception of Pile 1, for which samples were inadvertently not taken during the night following tracer application. Samples were then taken several times a day for two weeks after tracer application, and twice daily through February 2010. As an unfortunate result of miscommunication with mine staff, no samples were taken between February 27, 2010 and April 9, 2010. Linear interpolation between known sample concentrations was used to estimate daily concentration values, which were then used to calculate mass released during that time period. If major deviations in bromide concentrations from the linearly interpolated estimates occurred during the data gap, the estimates may over- or underestimate the actual bromide mass released during that time.

During tracer application, a Turner Designs Cyclops In-line Fluorimeter was continuously measured for sodium fluorescein after tracer application. This data from the fluorimeter was only used in the detection of a tracer spike during the night following the Pile 1 application, during which no bromide sampling occurred.

2.3.2.2 Laboratory analysis of bromide

A Metrohm 861 Ion Chromatograph (IC) analyzer in the Department of Land and Food Science at UBC was used to determine bromide concentrations of the initial tracer applied and tracer concentrations from piles effluent water samples. Standard solutions were created to match effluent water matrices, and were verified using SPEX CertiPrep brand certified standards and the method of standard additions. The total number of samples analyzed for all three piles was 1,092, approximately 5% of which were duplicate samples and provided quality assurance for the precision of the IC method.

2.3.2.3 Tracer study interpretation with "flow-corrected time"

Bromide concentration results were interpreted using a 'flow-corrected time' method as outlined in Eriksson et al. (1997). The method uses flow-normalized time intervals to look at tracer breakthrough in situations such as Antamina where periods of high and low flow are observed. In the method, the units τ are analogous to days, and are the time period over which the same amount of flow occurs, essentially condensing periods of low flow and elongating periods of high flow. The details of the flow-corrected time analysis are outlined in Appendix A.

2.3.3 Internal moisture content, electrical conductivity, and temperature

Six instrumentation lines (Figure 1.6; Corazao Gallegos (2007); Bay (2009)) contain 22 Zegelin 3-rod time domain reflectometry (TDR) probes for measurement of volumetric moisture content in Pile 1. The TDR probes were designed and constructed at the University of British Columbia (UBC) according to the methods described in Nichol et al. (2002, 2003) and were used with a Moisture Point MP-917 soil moisture measurement instrument and Campbell Scientific CR1000 datalogger. TDR measurements were taken at 30-minute intervals, and are reported to have an approximate error of +/-2% volumetric moisture content (VMC) in the 0%-15% VMC range (Nichol, 2002). Temperature measurements at each TDR probe in Pile 1 were also taken at 30-minute intervals with 32 single-point thermistors (RST Instruments; TH0002 2252 ohm; +/- 0.1 °C; www.rstinstruments.com), and were used to correct raw TDR measurements for temperature according to the methods in Bay (2009). Piles 2 and 3 each contain five TDR probes and thermistors along Instrumentation Line 4, but TDR measurements of were taken sporadically and the data is not included as part of this study. Piles 2 and 3 each contain 22 multi-purpose ECH₂O probes (Decagon Devices, Inc.) along all six instrumentation lines (Figure 1.7 and Figure 1.8).

ECH₂O probes measured volumetric moisture content (+/- 3% VMC), electrical conductivity (+/- 10% EC), and temperature (+/- 1°C) at 30-minute intervals.

The arrival of wetting fronts, as indicated by increases in VMC, was determined for five probes along each instrumentation line. The probes have approximately 1.75 m of vertical separation as well as a component of horizontal separation. Wetting-front velocities were calculated as the vertical distance between the probes divided by the difference in arrival time between the probes.

2.3.4 Particle size distributions

Particle size distribution (PSD) analyses were performed for samples from each of the tipping phases and the two protective layers for all three experimental waste-rock piles. Analyses were conducted by Golder Associates during the construction process according to method ASTM D 5519, and are described in Chapter 1 and Aranda (2009).

Pile 1 is composed of coarser-grained marble and hornfels waste rock (Figure 1.9). Pile 2 is finer-grained intrusive waste rock that is relatively homogeneous with a narrow range of PSD curves among material sub-types. Pile 3 skarn waste rock has a similarly fine-grained particle size distribution as Pile 2, but is more heterogeneous with a broader range of PSDs among tipping phases, including a significant amount of large (>1m) boulders in the outer tipping phase of the pile. Details on the dominant size fractions and implications for flow are discussed in Section 2.4.5.1, and PSDs of individual tipping phases and related soil parameters such as the coefficient of curvature are outlined in Appendix B.

2.3.5 Saturated hydraulic conductivity

Eight to ten single ring infiltrometer (area = $2.68m^2$) saturated hydraulic conductivity tests were performed by Blackmore and Urrutia (unpublished data) on the upper traffic surface of all three experimental piles in March and April of 2009. Tests locations were chosen to have maximum and uniform spatial distribution on the top of the piles. Test location maps are located in Appendix C.

2.3.6 Soil water characteristic curves

Soil-water characteristic curves (SWCC) were generated as part of a separate study (Speidel, 2011) with SoilVision software (Fredlund, 1996). The software generates SWCCs by using particle size distributions and three of four volume mass parameters: water content, wet density, specific gravity, and porosity (Fredlund, 1996; Fredlund et al., 2002; Fredlund and Xing, 1994). All parameters were determined on-site at Antamina by Golder Associates with the exception of Pile 1 porosity, which was measured in the laboratory at UBC (Speidel, 2011; Appendix D).

2.4 Results and discussion

Effluent flow patterns from the catchment lysimeters are described in light of meteorological conditions below, followed by the presentation and analyses of tracer study results. Observations regarding internal wetting front propagation and velocities are then discussed. Finally, soil and hydrological properties which can be estimated, calculated, and/or determined through laboratory and field experiments, including detailed differences in PSDs among material types, are then presented in light of the previously discussed observed hydrological behaviors they partially control.

2.4.1 Effluent flow patterns: Three-stage seasonal flow

For this study, a "water year" is considered to be July 1 through June 30. This timing ensures that for each flow year all precipitation from the wet season is included and that pile flow has slowed to a comparable rate at the end of each water year.

Annual precipitation recorded at the study site was 1281, 1535, 1290, and 1274 mm for the 2007-08, 2008-09, 2009-10, and 2010-11 water years, respectively (Figure 2.1, Table 2.2). The 2008-09 wet season had more rainfall than average years. The wet season started slightly later in 2010-2011, which is relevant because the flow stages were consequently delayed during that water year as compared with other years, affecting effluent water volume and quality.

There are three distinct stages of effluent flow throughout the water year (Figure 2.2).

- Stage I is the annual wet-up stage at the beginning of each wet season which usually occurs in October through December. During this stage, precipitation is greater than effluent flow.
- Stage II encompasses the peak of the wet season, usually from January through mid-April. During this stage there is a relatively constant ratio of precipitation and effluent flow.
- 3) Stage III is the draindown stage that occurs at the end of the wet season and through the dry season from late April through September. During this stage, effluent flow from the piles is greater than precipitation.

The flow stages affect mineral dissolution and precipitation, sorption, solute and CO_2 accumulation, and dilution, and as a result, seasonal effluent water quality. Details of three-stage flow in the experimental piles are outlined below, and the impact on solute mobility is discussed in Chapter 5.

2.4.1.1 Stage I

During Stage I, effluent flow rates increase from dry season rates but are generally still quite low (1 mm/day to 5 mm/day, depending on the material type and the year). During Stage I, effluent flow generally only increases in the C and D lysimeters, which incorporate the higherconductivity pile slopes, and which also have shorter flow paths than the A and B sub-lysimeters below the crowns. Stage I is when infiltration enters the finer-grained matrix and wets-up the waste rock, creating a seasonal increase in storage that varies from pile to pile depending on the material properties.

Piles 1 and 3 exhibited Stage I flow every year in the C and D lysimeters at fluxes of about 1-5 mm/day (Figure 2.3). Stage I flow was only observed in P1A and P1B during the highprecipitation 2008-2009 water year, and was never observed in P3A and P3B. Evidence from effluent SC measurements shows that Stage I flow in Pile 1 is generally a combination of matrix and preferential flow paths, and that high precipitation events can trigger very fast (>10m/day) event flow velocities (Figure 2.4). Piles 1 and 3 tend to have the fastest responses to the onset of the wet season, with flow increasing as early as September or October.

Pile 2 exhibited comparatively low, delayed, and muted flow in the D Lysimeter during Stage I. Flow increased during Stage I in P2C during the 2009-2010 water year, but in general Pile 2 sublysimeter flow increases more or less at the same time, at the beginning of Stage II in late

November, December, or early January, indicating dominant matrix flow with a relatively narrow range of flow velocities, even below the pile slopes.

2.4.1.2 Stage II

During Stage II, peak flow rates are observed from all lysimeters in all piles. Stage II flow rates can increase very sharply as rapid responses to intense individual rain events, sometimes resulting from fast preferential flow. Flow rates can also increase in a more muted and delayed manner after precipitation events, representing a range of velocities of matrix flow and pressureinduced wetting fronts. After initial annual wet-up through the beginning of draindown, there are low net changes in storage during Stage II.

Piles 1 and 3 have 'flashy' flow during Stage II, with sharp increases in flow following precipitation events and equally sharp decreases in flow after short periods with little precipitation (Figure 2.3). Comparison among the D lysimeters of the three piles shows that Pile 3 has the fastest and sharpest increases and decreases in effluent flow during Stage II. P1C and to a lesser extent P1D exhibit similar flashy flows, and the other Pile 1 sub-lysimeters generally have similar but lower overall flow and slightly less dramatic increases and decreases in flow rates in response to precipitation.

Pile 2 flow from all lysimeters is sustained at relatively high flows throughout Stage II. The increases and decreases in flow in response to precipitation events are muted and delayed in Pile 2 when compared to the 'flashy' flow in Piles 1 and 3.

2.4.1.3 Stage III

Effluent flow rates decrease quasi-exponentially during Stage III, with lower air-entry pressure materials exhibiting steeper draindown curves and higher air-entry pressure materials exhibiting more gradual draindown curves (Section 2.4.5.2). Stage III corresponds to a seasonal decrease in storage, as most mobile moisture is released from the piles by gravity drainage and evaporation.

Pile 1 has the steepest draindown curve of the three piles during Stage III (Figure 2.3). Flow generally decreases very rapidly following the final precipitation event(s) of the wet season. Piles 2 and 3 have long, sustained flows throughout Stage III as represented by more gradual draindown curves. This results from the finer-grained matrix of those piles and the resulting higher air-entry pressures and the ability to retain moisture after precipitation ceases at the beginning of the dry season (Section 2.4.5.2).

During Stage III, Piles 1 and 3 sometimes have spikes in effluent flow in response to rain events at the end of the wet season. These effluent flow increases are usually in response to consecutive days of moderate rain in May or June, and are more pronounced in Pile 1 than in Pile 3.

2.4.2 Tracer study breakthrough curves

Tracer tests applied to the piles were also used to obtain insights about the dominant flow patterns in the different waste rock types. A standard technique is to analyze the concentration breakthrough curves at sampling locations (in this case, at the bottom of the pile), which can be expressed as the normalized sample concentration (C/C_0) over time, where

$\frac{C}{C_0} = \frac{Sample \ bromide \ concentration}{Initial \ bromide \ concentration}$

Eq. 2.1.

Sharp spikes in bromide concentrations in the breakthrough curves for the D Lysimeters suggest that Piles 1 and 3 have components of preferential flow and fast and slow matrix flow, while the well-defined breakthrough curves of Pile 2 flow suggest almost exclusively matrix flow with a comparatively narrow range of pore water velocities (Figure 2.5).

Not all tracer had reported to the bottom of the piles by the end of the study period, so the timing of peak concentration releases – as opposed to mean tracer mass arrival times – were used to calculate a range of preferential and matrix flow velocities (v, Table 2.3) using the equation

$$v = \frac{\text{Height of pile}}{\text{Time for peak Br concentrations to reach lysimeter}}$$

Eq. 2.2.

The cumulative mass of bromide removed from each pile throughout the study period is expressed as M/M_0 , where

$\frac{M}{M_0} = \frac{Cumulative mass released}{Initial mass applied to pile}$

Eq. 2.3.

 M/M_0 values for Piles 1, 2, and 3 at the end of the study period are 0.41, 0.61, and 0.44, respectively (Figure 2.6). Total mass released is highly controlled by seasonal volume of

effluent water as opposed to tracer concentrations - i.e., most bromide mass is removed during the wet season, even in the case of low concentrations.

2.4.2.1 Pile 1 breakthrough curves

Pile 1 has a large component of fast flow recorded in Lysimeters A, B, and D as exhibited by very rapid, sharp increases in bromide concentrations soon after tracer application, and a continuum of faster and slower matrix flow velocities as exhibited by smoother bromide concentration peaks throughout the study period (Figure 2.7).

Fast preferential flow is observed in P1D as concentration spikes on the night of January 19, 2010 (velocity ~20 m/day) as evidenced by a voltage increase from the in-line fluorimeter (Figure 2.8) and again on January 25, 2010 (velocity = 1.7 m/day). These very rapid flows are then followed by more gradual releases of bromide observed as smoother breakthrough curves which represent matrix flow. Two bromide peaks are observed on April 23, 2010 and July 21, 2010, corresponding to matrix flow velocities of 11 cm/day and 6 cm/day.

The P1A breakthrough curve shows evidence of fast flow, likely from both preferential flow paths and matrix flow paths. The fastest P1 A flow is evidenced by a spike of bromide on February 13, 2010, corresponding to a velocity of 40 cm/day. Two subsequent peaks representing the continuum of faster and slower matrix velocities occur on May 26, 2010 and December 20, 2012, corresponding to velocities of 8 cm/day and 3 cm/day, respectively. The P1B breakthrough curve is also bimodal, with peaks representing faster and slower matrix flows. The first peak, which occurred on April 10, 2010, was the first data point after the missing data gap, and concentrations may have peaked earlier than that date. The second peak occurred on

December 20, 2010. The corresponding faster and slower matrix flow velocities are approximately 12 cm/day and 3 cm/day.

The Pile 1 A, B, and D lysimeters sustained relatively constant tracer concentrations through the dry season, which was not the case for the other two piles. The sharp decrease in bromide concentrations at the onset of the 2011 wet season is good evidence of higher dilution in Pile 1, i.e., basal mixing of lower-velocity, higher-concentration antecedent water and higher-velocity, lower-concentration event water traveling through preferential flow paths and through the non-tracer shorter flow paths under the slopes. The concurrent sharp increases in Sub-lysimeter A and B bromide concentrations are evidence of pistoning of antecedent water under the pile crown. Nevertheless, low flows from Sub-lysimeters A and B in Pile 1 resulted in very low mass recovery by the end of the study period in August 2011 (Figure 2.9).

2.4.2.2 Pile 2 breakthrough curves

Pile 2 Lysimeter D bromide concentrations were slightly higher in April 2010 than February 2010, between which dates no samples were taken. Bromide concentrations then remained relatively steady through the 2010 dry season and climbed during the 2010-2011 wet season, peaking toward the end of the wet season on June 16, 2011, or 512 days after tracer application, corresponding to an average velocity of 2 cm/day.

Pile 2 tracer breakthrough curves exhibit typical matrix-dominated flow in all lysimeters (Figure 2.7). The P2A and P2B breakthrough curves reach maximum concentrations of 86 mg/L and 63 mg/L bromide on April 11, 2011 and February 6, 2011, respectively corresponding to 486 days and 382 days. This corresponds to matrix flow velocities of 2.4 cm/day and 2.6 cm/day for P2A and P2B, respectively.

The differences between the Sub-lysimeter P2A/P2B bromide breakthrough curves and the P2D breakthrough curve are most likely a result of the continuum of velocities in the pile. The flow paths above P2A and P2B appear to be well defined by a single average velocity and dispersivity, exhibited by very well-defined breakthrough curves. P2D breakthrough occurs over an extended time, including sustained concentrations through the low flow of the 2010 dry season, resulting from a range of faster and slower pathways above that lysimeter and less dilution from non-tracer flow paths on the slopes during the dry season than the wet season. Distinct decreases in bromide concentrations throughout the 2011 wet season could be evidence of infiltration of fresh non-tracer water through the shorter flow paths under the pile slopes mixing with tracer water at the base of the pile.

2.4.2.3 Pile 3 breakthrough curves

Pile 3 breakthrough curves suggest both matrix and preferential flow, with a slightly wider range of matrix velocities than observed in Pile 2 (Figure 2.7). Pile 3 Lysimeter D exhibits evidence of fast preferential flow from an early high bromide concentration spike of 57 mg/L, on February 7, 2010, corresponding to a preferential flow velocity of 63 cm/day. Lower bromide concentrations were sustained for the duration of the study period with a small concentration peak on October 28, 2010, corresponding to an average matrix velocity of 3.6 cm/day.

Maximum bromide concentrations of less than 1mg/L in the middle interior Sub-lysimeter P3A were observed in the 2011 wet season. This amounts to less than 0.1% mass removed, meaning that the tracer had not reported to the sub-lysimeter by the end of the study period and that the matrix velocity above that sub-lysimeter is less than 10 m/537 days, or less than 2 cm/day. The rear interior Sub-lysimeter P3B exhibits a clear matrix-dominated breakthrough of bromide

peaking on June 30, 2011 with a maximum concentration of 22 mg/L. However, most of the bromide was released from P3B during the dry season, resulting in only 3% of mass removed by the end of the study period. This means that, if the peak from the available dataset is used, matrix velocities can be estimated as 2 cm/day, but it is more likely that additional mass was released after the end of the study period during the 2011-2012 wet season, and that the velocity is indeed lower than the estimate from the available dataset.

2.4.2.4 Sub-lysimeter C breakthrough curves and non-vertical flow

Observation of mass released for each pile reveals comparable amounts of bromide mass reporting to Sub-lysimeters A, B, and C in Piles 1 and 3 (Figure 2.9). In Pile 2, however, much less total bromide mass reports to the C sub-lysimeter as compared with the A and B sublysimeters. Since no bromide was applied directly above the C sub-lysimeters for any of the piles, this is evidence of a component of non-vertical flow in Piles 1 and 3, and specifically a tendency for water to be diverted toward the outer slope of those piles. While the comparatively low proportion of bromide reporting to Sub-lysimeter C in Pile 2 does not exclude the possibility of non-vertical flow in that pile, it is reasonable to assume that the proportion of non-vertical flow in that pile is less than in Piles 1 and 3.

It is hypothesized that the higher percentage of boulders in the outer tipping phases of Piles 1 and 3 (Section 2.4.5.1) may cause water to flow preferentially in those areas, possibly as flow over the surface of boulders and through large voids associated with boulders. Additionally, any funnel flow that occurs will tend to follow capillary breaks along tipping boundaries toward the outer slope of the pile rather than straight vertically downward. These mechanisms that promote flow towards and within pile slopes have implications for evaporation (Chapter 3) and for geotechnical and geochemical aspects of waste rock dump design.

2.4.2.5 Cumulative mass released

The low amount of cumulative mass released from the piles as of the end of the study period (i.e., 41%, 61%, and 44% of the total mass applied for Piles 1, 2, and 3, respectively) is a combined result of 1) mass still inside the pile travelling through slower flow paths and 2) mass unaccounted for during the period of missing data (February 27, 2010 to April 9, 2010), for which linearly interpolated concentrations were assumed. The masses released from the D lysimeters during the period for which concentrations were estimated correspond to 21%, 8%, and 27% of mass released by the end of the study period and 10%, 5%, and 13% of total mass applied for Piles 1, 2, and 3, respectively. This signifies that deviations from the estimated concentrations have a greater impact on error in the cases of Piles 1 and 3 than in the case of Pile 2.

The higher total mass released from Pile 2 is unexpected, since materials with faster flow and a tendency for preferential flow (in this case, Piles 1 and 3) should release more mass sooner in the study period (e.g., Nichol et al., 2005). This suggests that for both Piles 1 and 3, mass released during the period of missing data may have exceeded mass accounted for by the linearly interpolated estimations. This is likely most relevant for Pile 1. For Pile 3, which has a strong component of slower matrix flow, it appears that the tracer center of mass had not yet arrived to Sub-lysimeters A and B at the end of the study period and it is likely that there is also a significant amount of mass remaining in that pile. Considering the lack of evidence for fast preferential flow in the beginning of the tracer study and the gradual tails of sub-lysimeter

breakthrough curves, it is hypothesized that the remaining mass (39%) was still in Pile 2 as of August 2011 at the end of the study period, and that the linear interpolation was adequate in the estimation of mass released over the sampling gap. Although the data gap may have an impact on the overall mass balance, in particular for Pile 1, the results of the tracer tests are valuable in the calculation of matrix and preferential flow velocities and in highlighting the distinctly different flow regimes in the three experimental piles.

2.4.3 Tracer study: "Flow-corrected time"

Tracer results were additionally analyzed using steady-state representation of transient flow according to 'flow-corrected time' methods outlined in Eriksson et al. (1997; Appendix A). The methods use flow-normalized time, with each time unit τ representing a uniform flow volume. Breakthrough curves using flow-corrected time follow the same patterns as the traditional breakthrough curves, except that periods of high flow are stretched out and periods of low flow are compressed compared to traditional breakthrough curves (Figure 2.10).

The temporal analysis completed according to the Eriksson et al. (1997) method to provided the arrival of the center of mass and spreading around the center of mass. The moments are apparent moments because the analysis can only account for mass that had been released at the end of the study period, at which point all of the mass had not yet been released from the piles. The number of days for the mean center of mass arrival are 143 days, 400 days, and 197 days for P1D, P2D, and P3D, respectively (Table 2.4). Corresponding combination flow velocities (i.e., combination of matrix and preferential flow velocities) of the slope-dominated Lysimeter D of the three piles are 7.0 cm/day, 2.5 cm/day, and 5.1 cm/day for Piles 1, 2, and 3, respectively.

Combination flow velocities calculated for internal Sub-lysimeters A and B are 3.6-4.1 cm/day, 2.3-2.6 cm/day, and 2.0-2.2 cm/day for Piles 1, 2, and 3, respectively. For Piles 1 and 3, for which the D lysimeters are likely strongly influenced by preferential flow near the slope, the center of mass arrival is much later for the internal sub-lysimeters than for the D lysimeters. Pile 2 exhibits similar mean mass arrival times among all three lysimeters.

Eriksson et al. (1997) propose that the relative amount of 'preferential' flow in a system can be characterized as the ratio of measured soil moisture content to apparent mobile moisture content, with a ratio closer to one indicating less preferential flow and a ratio closer to zero indicating more preferential flow. They define preferential flow as 'channelized flow' and as flow of the higher-velocity 'mobile' water in a system. Therefore 'preferential' flow according to their method is likely analogous to a combination of both fast matrix and fast preferential flow as defined in this study, and 'preferential' is used in quotes here when referring to the Eriksson et al. (1997) definition of higher-velocity water. The results of the method suggest much higher 'preferential' flow in Piles 1 and 3 than in Pile 2 (Table 2.4), which is in agreement with multiple lines of evidence for the flow patterns described above. The calculation suggests that, for the D lysimeters approximately 63%, 7%, and 62% of water flows 'preferentially' in Piles 1, 2, and 3, respectively.

Temporal moment analysis reports greater normalized spreading around the center of mass, CV_{τ} , for P1D and P3D than for all other lysimeters studied (Table 2.4). This can be confirmed visually by the high temporal variability observed in the P1D and P3D breakthrough curves compared to the well-defined Pile 2 breakthrough curves (Figure 2.7).

2.4.4 Internal wetting front patterns and velocities

Internal wetting-front velocities can be calculated using data from internal volumetric moisture content (VMC) probes, and are highly variable depending on material type, location within pile, and antecedent moisture content. During Stage I when internal moisture contents – and therefore unsaturated hydraulic conductivities – are at their lowest, wetting-front velocities are also at their lowest. Wetting fronts during Stage II have higher velocities resulting from higher moisture contents and higher unsaturated hydraulic conductivities.

Among the twelve vertical instrumentation lines total (Lines 1-4 in each of the three piles) only four lines experience wetting fronts that begin at the top of the pile and travel consecutively downward through the pile. In these cases, wetting fronts first reach the uppermost probe (TDR5 for Pile 1 and TE5 for Piles 2 & 3) followed by the next lower probes (TDR/TE4, then TDR/TE3, then TDR/TE 2) in succession until reaching the bottom-most probe (TDR/TE 1). Under the assumption of a uniform vertical-downward flow field in the area above the probes, which have a horizontal as well as vertical offset (Figure 1.6 to Figure 1.8), these probes can then be used to calculate wetting front velocities at different stages during the year.

Pile 1 is Line 3 exhibits this downward wetting front arrival through consecutive probes at the beginning of the wet season. During the initial wet-up of 2008, TDR probes in this line reflect an internal wetting-front velocity of 15 cm/day (Table 2.5, Figure 2.11). In Figure 2.11 B and Figure 2.11 C, one can see that wetting fronts consistently reach upper probes first and travel sequentially downward through Pile 2 at both Lines 1 and 2 at the beginning of most wet seasons. Pile 2 Line 1 average initial internal wetting-front velocities are 10 cm/day, 15 cm/day, and 11 cm/day for 2008, 2009, and 2010, respectively. Pile 2 Line 2 velocities average

7 cm/day, 14 cm/day, and 8 cm/day for 2008, 2009, and 2010, respectively. In Pile 3, Line 1 exhibits consecutive downward wetting fronts at the beginning of all wet seasons, with an average wetting-front velocity of 7 cm/day, 16 cm/day, and 10 cm/day, for 2008, 2009, and 2010, respectively (Figure 2.11 D). The higher velocities observed at the beginning of the 2009 wet season are consistent with the higher moisture contents and hydraulic conductivities resulting from the previous year's high precipitation (see Chapter 3 for a discussion on annual changes in storage).

The instrumentation lines described above have similar wetting front patterns during the peak of the wet season in Stage II. Example wetting-front velocities from those lines from the final major wetting front of the wet season in April, 2009 are 105 cm/day (Pile 1, Line 3), 88 cm/day (Pile 2, Line 1), and 44 cm/day (Pile 3, Line 1) (Figure 2.12). These results highlight the variability of velocities depending on antecedent moisture content, material type, and location within the pile. The values are comparable with wetting-front velocities of 50 cm/day calculated by Bay (2009) for Pile 1. The wetting front velocities are faster than matrix and combination velocities estimated from the tracer study (~2 cm/day to ~12 cm/day, Section 2.4.2) by factors of about ten to forty, which is lower than observations by Nichol et al. (2005). In that study, wetting front velocities through waste rock were observed to be three to four orders of magnitude faster than median advective velocities.

Figure 2.13 reveals that in the interior lines of all piles during Stage III, wetting fronts reach the uppermost probes but dissipate before reaching deeper probes, about three meters below the surface. For the exterior Line 4 and to a lesser extent Line 3 in each of the piles, wetting fronts often reach the lower probes of the instrumentation lines. Line 4 follows the outermost slope of each pile, and therefore each sensor is approximately 1-1.5 m below the surface of the outer

slope (Figure 1.6 to Figure 1.8). Line 3 is similar, although the interior probes 2, 3, and 4 are buried deeper in the pile than the corresponding probes in Line 4.

Because internal wetting fronts dissipate within meters of the surface during Stage III, it can be expected that effluent pulses will be less frequent and more muted in the full-scale piles during that stage than in the other stages. This is relevant for the conceptual model because it implies that high, flashy flows of effluent water are not as likely to occur during Stage III as they are during Stages I and II. When they do occur, as seen rarely in Piles 1 and 3 (Section 2.4.1.3), flashy Stage III effluent flow rates can be attributed to flow through the slopes of the piles as opposed to the crowns.

For many of the other instrumentation lines not listed above, wetting fronts show annual consistency but do not travel consecutively downward in the pile starting at the top. That is, wetting fronts reach moisture probes that are lower in the pile before reaching moisture probes that are higher in the pile. These cases are examples of the wide spatial variability in wetting front velocities in the areas above probes, which have some horizontal offset. Similar spatial variability in waste rock flow velocities was also observed at the Cluff Lake Mine (Nichol et al., 2005) where flow velocities were observed to vary by orders of magnitude within a few horizontal meters.

Figure 2.14 provides some examples of fast flow reaching the bottom of the pile first followed by the arrival of wetting fronts to probes higher in the pile, such as in Pile 2 Line 3, Pile 3 Line 2, and Pile 3 Line 3 for the initial wet-up of the wet seasons in 2008, 2009, and 2010. In all of these cases, wetting fronts are observed to first reach the uppermost ECH₂O probe (TE5), followed by the lowermost probe TE1, followed sequentially upward through the pile to TE2,

TE3, and TE4. In these cases water appears to circumvent the matrix material in which the middle probes are found, reaching the bottom of the pile before the center of the pile. This phenomenon is likely the result of a combination of by-pass flow and variable-velocity flow paths.

A second example that shows consistent evidence of fast flow reaching bottom probes before reaching upper probes is Pile 1, Line 2 (Figure 2.15). Each year during Stage I, the uppermost TDR5 was always first to report a wetting front, followed by the lowermost TDR1, followed by a downward progression of TDR4, TDR3, and TDR2. This flow pattern of fast preferential flow coupled with typical matrix flow is consistent with the tracer study results discussed above.

2.4.5 Physical and hydrological properties of waste rock

Many of the observed flow regimes discussed above can be explained through measured and laboratory-tested soil and hydrologic parameters. Of particular importance are the particle size distributions of the waste rock including the abundance of boulders, cobbles, and gravel contributing to macropore flow and fast flow over the surfaces of boulders and cobbles.

2.4.5.1 Particle size distributions

Pile 1 is significantly coarser grained than Piles 2 and 3 across almost all size fractions (Figure 1.9). Based on the modified Wentworth (1922) scale, Pile 1 is comprised dominantly of material equal to or larger than medium gravel, including high percentages of coarse gravel (faster matrix and macropore flow), cobbles (macropore and surface flow), and boulders (surface flow), and less than 10% fine gravel, sand, silts and clays (slower matrix flow). Piles 2 and 3 are consistently finer-grained than Pile 1. Pile 2 is finer than Pile 3 across most size fractions, and

Pile 3 has a broader range of PSDs among tipping phases, including a significant amount of boulders in the outer slope (Tipping Phase III).

The effective grain size, or 'D₁₀', is a typical reference value to describe the PSD: 10% of all particles in a sample are smaller than the D₁₀ particle diameter, and 90% of all particles in a sample are larger than the D₁₀ particle diameter. The effective grain size is important because the diameter of the finer particles controls the matrix flow component. The Piles 1, 2, and 3 average curve D₁₀ particle diameters are 11.58mm, 0.12mm and 0.36mm, respectively (Table 2.6). The <4.75 mm size fraction is important in capillary matrix flow regimes, since it has been observed that there is little retention and capillary flow in the materials >4.75 mm (Yazdani et al., 2000). The percentages of material passing the 4.75 mm sieve are 6.8%, 28.0%, and 27.2% for Piles 1, 2, and 3 average curves, respectively. Similarly, the percentage of sand (<2 mm) is lower in Pile 1 than in Piles 2 and 3 (3.4%, 19.5%, and 11.7%, respectively), as is the percentage of silt and clay (<0.075 mm; 2.1%, 8.5%, and 4.1%, for Piles 1, 2, and 3, respectively).

The differences in particle sizes among the three piles are hypothesized to be the driving factors for the observed variability in flow regimes, including the relative proportions of matrix and preferential flow and the wide range of evaporation patterns (Chapter 3). Specifically, the boulders present in Piles 1 and 3 are hypothesized to be a major cause of preferential flow, possibly as flow over the surfaces of the boulders, or through the voids that they create. Large boulders (>1m) are present throughout Pile 1, but are almost exclusively present in Tipping Phase III, on the outer slope, of Pile 3. This coincides with where effluent flow patterns and tracer study results indicate that preferential flow is prevalent in those piles (i.e., all of Pile 1 and on the outer slope of Pile 3). Additionally, Pile 1 has a high percentage of smaller boulders, cobbles, and gravel, which can lead to preferential macropore flow, and matrix flow velocities

that are up to six times higher than matrix velocities observed in Piles 2 and 3. Conversely, the majority of waste rock in Piles 2 and 3 is relatively finer-grained, resulting in the slower matrix flow velocities observed in those piles. Finally, the narrow-ranged, finer-grained Pile 2 PSD represents a comparatively homogeneous, soil-like material that lacks a strong tendency for the development of preferential flow paths, neither as surface flow over boulders and cobbles nor as macropore flow through gravel and cobbles. This is supported by smooth, uniform tracer breakthrough curves (Section 2.4.2) with no high spikes in tracer concentrations that represent preferential flow. In general, then, the higher percentage of boulders in Piles 1 and 3 and cobbles and gravel in Pile 1 make it more likely that large precipitation events may trigger preferential flow paths that bypass the matrix in those piles, whereas even large precipitation events are routed through the relatively homogeneous, finer-grained matrix of Pile 2.

2.4.5.2 Soil water characteristic curves

Soil water characteristic curves (SWCCs) were developed by Speidel (2011) using SoilVision software (Fredlund, 1996). Average air-entry pressures, based on averaging particle size values before importing into SoilVision software, are 0.05 kPa, 0.40 kPa, and 1.36 kPa for Piles 1, 2, and 3 (Table 2.7, Figure 2.16). The SWCCs from individual tipping phases reveal a narrow range of air-entry pressures for Pile 1 waste rock, from 0.04 kPa to 0.06 kPa (Figure 2.17). Piles 2 and 3 have much broader ranges of air entry pressures, at 0.03 kPa - 2.00 kPa and 0.40 kPa-2.00 kPa, respectively. The air-entry pressures represent the ability for a soil to retain water – i.e., not be replaced by air – and are therefore important not only regarding the residual moisture content of soils (which in turn controls dry season water storage, wet season flushing, and evaporation), but also the draindown rates during the dry season. For example, the lower air-entry pressure for Pile 1 is the main control on the very steep draindown curve (i.e., rapid

desaturation) of that pile, where the higher air-entry pressures control the more gradual draindown (i.e., slower desaturation) observed in Piles 2 and 3 (Section 2.4.1.3).

Residual water content was also calculated using the SoilVision software, and also exhibits narrow ranges for the materials in Pile 1 and broader variability for the materials in Piles 2 and 3. The values are lower than observed in most internal moisture probes in the piles, and the discrepancy is likely because laboratory/SoilVision derived values are based on a coarser grained portion of soils (<10 cm) than the material in which the moisture probes are placed (<0.5 cm). The coarser-grained materials used in the Speidel (2011) report are more representative of soil properties throughout the experimental piles.

2.4.5.3 Saturated hydraulic conductivities

The saturated hydraulic conductivities for eight positions on the top of Pile 1 range from 3.7×10^{-6} to 1.2×10^{-4} m/s (Appendix C). The Pile 2 range is 5.1×10^{-8} m/s to 4.8×10^{-5} m/s, and the Pile 3 range is 2.0×10^{-7} m/s to 1.3×10^{-5} m/s (Table 2.8, Appendix C). Arithmetic mean saturated hydraulic conductivities, which are biased toward the higher values, are 2.7×10^{-5} m/s, 1.3×10^{-5} m/s, and 5.7×10^{-6} m/s for Piles 1, 2, and 3 respectively. Geometric mean saturated hydraulic conductivities, which are not biased toward the higher or lower values, are 1.5×10^{-5} m/s, 4.8×10^{-6} m/s, and 3.7×10^{-6} m/s for Piles 1, 2, and 3, respectively. These values are representative of the faster matrix flow observed in Pile 1, and the slower matrix flows observed in Piles 2 and 3.

These values represent hydraulic conductivity on the finer-grained, compacted traffic surfaces on the crowns of each of the piles. However, average saturated hydraulic conductivities of the whole piles, including the loose slopes, are likely higher. For example, Javadi et al. (2012)
obtained a very good match of Pile 2 unsaturated flow with MIN3P (Mayer et al., 2002) by calibrating to a whole-pile saturated hydraulic conductivity of 6.7×10^{-4} m/s, an order of magnitude higher than measured values for the crown.

2.4.5.4 Pore-water velocity calculated with internal moisture content and areanormalized flux

Pore-water velocity (v, mm/day) is defined as

$$v = \frac{q}{\theta}$$

Eq. 2.4

where q (mm/day) is the specific discharge and θ (dimensionless) is volumetric moisture content. Lysimeter D temporally-averaged flux and temporally- and spatially-averaged TDR/ECH₂O probe moisture contents from February and August were used to estimate average pore-water velocities for the wet and dry seasons, respectively.

Average moisture contents based on TDR probes (Pile 1) and ECH₂O probes (Piles 2 and 3) from the dry to wet seasons range from about 17% to 20% in Pile 1, 19% to 26% in Pile 2, and 19% to 30% in Pile 3 (Table 2.8). It is important to note that the sensors are all located in very fine-grained (<0.5 cm) material, which may result in reported moisture contents that are higher than those in the majority of the pile, which consists of much coarser particles. Nevertheless, the timing of the wetting front arrivals and drainage is well captured.

Average volumetric fluxes (Q, L/day) for the D lysimeters in the wet and dry seasons were converted to area-normalized fluxes (q, mm/day) by dividing by the collection area of the D lysimeters (1248 m²). The respective wet and dry season averages are 3.2 mm/day and 0.2 mm/day (Pile 1); 5.3 mm/day and 0.6 mm/day (Pile 2); and 6.5 mm/day and 0.5 mm/day (Pile 3).

The corresponding wet and dry season average pore water velocities are then calculated according to Equation 2.4 as 1.6 cm/day and 0.1 cm/day (Pile 1); 2.0 cm/day and 0.3 cm/day (Pile 2); and 2.2 cm/day and 0.2 cm/day (Pile 3, Table 2.7). The wet season velocity estimates are similar to matrix velocities interpreted from the tracer study (Section 2.4.2) for Piles 2 and 3, but are much lower for Pile 1. It is hypothesized that Pile 1 calculations here underestimate the average pore water velocity, possibly because the technique is based on average flux and moisture content measurements, which are highly variable on short temporal scales.

2.4.5.5 Estimation of unsaturated hydraulic conductivity

Under the assumption of gravity drainage (consistent with near-constant volumetric moisture content with depth), unsaturated hydraulic conductivity at the prevailing moisture content is proportional to effluent flux from the piles. Using the average wet season (February) and dry season (August) values described above and listed in Table 2.8, the corresponding wet and dry season average unsaturated hydraulic conductivities are estimated as 3×10^{-8} m/s and 2×10^{-9} m/s (Pile 1); 6×10^{-8} m/s and 6×10^{-9} m/s (Pile 2); and 7×10^{-8} m/s and 5×10^{-9} m/s (Pile 3, Table 2.8).

The unsaturated hydraulic conductivities calculated here are rough estimates and are three to four orders of magnitude lower, even in the wet season under near-saturated conditions, than saturated hydraulic conductivities measured with ring infiltrometers on the compacted pile surface. The ranges of unsaturated hydraulic conductivities in the piles are likely much broader

than the estimates given here, partly because, based on internal moisture probe measurements, the assumption of near-constant volumetric moisture content with depth is often not valid (see, e.g., Figure 2.11 to Figure 2.15). The flux-based unsaturated hydraulic conductivities calculated here are very similar from material to material, and do not necessarily reflect the differences in flow among the material types that are observed in effluent flow patterns, tracer results, and saturated hydraulic conductivities measured with ring infiltrometers. That is, the lower fluxbased unsaturated hydraulic conductivity in coarser-grained material (Pile 1) may reflect the lower moisture content of that material during the calculation period despite a higher measured hydraulic conductivity in under saturated conditions.

2.5 Conclusions

The goals of this chapter were to develop conceptual models of the flow regimes of three types of waste rock at the Antamina Mine, and to determine and present hydrological parameters for the different types of flow that comprise the flow regimes. To this end, a detailed synthesis, evaluation, and analysis of the large dataset available from experimental waste-rock piles 1, 2, and 3 was completed, and hypotheses are proposed regarding the most important features controlling unsaturated flow. In particular, waste rock particle sizes play a very significant role in the relative proportions of fast and slow matrix flow and fast preferential flow. It is hypothesized that the boulder and cobble size fractions increase the occurrences of fast preferential flow activated by large precipitation events, likely through an increased proportion and connectivity of voids and macropores and as fast flow over the surfaces of large clasts. The gravel, sand, silt, and clay fractions influence the ranges of matrix flow velocities, with matrix velocities in cobble- and gravel-dominated materials up to six times higher than matrix velocities as in gravel- and sand-dominated materials. The fine fractions most strongly influence air entry

pressures, controlling the volume and rate of draindown during the dry season and seasonal and long-term water storage within the waste-rock piles. Finally, meteorology at Antamina, combined with the waste rock hydrological properties, dictates a three-stage effluent flow pattern.

Bromide breakthrough curves provide valuable insight into the flow regimes of each material type, for example the calculations of preferential flow velocities through the arrival of bromide concentration spikes and matrix flow velocities through well-defined center-of-mass arrival curves. Low cumulative mass recovery is most likely a result of significant mass remaining in Piles 2 and 3 at the end of the study period, and mass unaccounted for during a period of linearly-interpolated concentration estimates during a period of no sampling for Piles 1 and 3.

Saturated hydraulic conductivities measured on the compacted pile crowns with ring infiltrometers accurately reflect observed differences in flow regimes among material types in Piles 1, 2, and 3. Saturated hydraulic conductivities for the materials on the non-compacted slopes are likely higher than those measured on the crown. Unsaturated hydraulic conductivities and pore-water velocities based on flux and moisture content data do not reflect the observed differences in material type, possibly because estimates are based on temporally and spatially averaged flux and moisture content measurements and/or because the assumption of constant moisture content with depth is invalid.

The conceptual models and field-based hydrological parameters increase our understanding of flow regimes within waste rock. The results summarized above – ranges of matrix and preferential flow velocities, hydraulic conductivities, spatially uniform or variable internal flow regimes – are all important for appropriate model selection and accurate parameter input for

water quality and quantity predictive modeling. The results can be used in mine water management programs for flow estimations at larger scales, and as a link between full-scale waste rock dumps and laboratory-scale experiments. Finally, the hydrological flow regimes discussed here have crucial impacts on waste rock aqueous geochemistry, and the relationships between the two are further explored in Chapters 4 and 5.

2.6 Tables

Table 2.1. Details of tracer application for Piles 1, 2, and 3.

	Pile 1	Pile 2	Pile 3
Tracer application date	19-Jan-10	20-Jan-10	22-Jan-10
Tracer application duration (hr)	3.0	4.5	3.7
Tracer application footprint area (m ²)	231	242	220
Applied bromide concentration (mg/L)	1807	1895	3497
Volume of application (L)	5891	6516	6050
Applied bromide mass (kg)	10.64	12.35	21.15

 Table 2.2. Annual precipitation based on a July 1- June 30 water year.

Water year (July1 - June 30)	Cumulative annual precipitation (mm)
2007-2008	1281
2008-2009	1535
2009-2010	1290
2010-2011	1274

 Table 2.3. Matrix and preferential flow velocities determined from bromide concentration breakthrough curve peaks.

Test	Matrix flow velocities	Preferential flow velocities
	cm/day	cm/day
P1A	3.0-7.9	40
P1B	3.0-12.4	-
P1D	5.0-10.6	170-2000
P2A	2.4	-
P2B	2.6	-
P2D	2.0	-
P3A	<1.7	-
P3B	1.9	-
P3D	3.6	60-250

Test	Steady -state water flow	Tracer Mass Recover y	Mean flow- corrected arrival time	Mean velocity	Apparent mobile water content	Spreading around mean arrival	Normalized spreading around mean arrival	Indication of 'preferential' flow ¹
	Q		Ť	V	θ [*] m	σ_{τ}	CV _τ	θ/θ [*] m
	(L/day)	(%)	(days)	(m/day)	(-)	(days)	(-)	(-)
P1A	12	8	276	0.036	0.022	116	0.42	0.36
P1B	7	3	243	0.041	0.011	109	0.45	0.18
P1D	1960	46	143	0.070	0.022	120	0.84	0.37
P2A	28	59	437	0.023	0.076	70	0.16	0.84
P2B	34	55	383	0.026	0.080	86	0.23	0.89
P2D	2611	61	400	0.025	0.084	135	0.34	0.93
P3A	18	0.1	448	0.022	0.051	70	0.16	0.37
P3B	21	3	512	0.020	0.067	41	0.08	0.48
P3D	3380	47	197	0.051	0.053	164	0.83	0.38

Table 2.4. Steady-state flow analysis from the tracer study, based on the methods in Eriksson et al. (1997).

 1 A θ/θ^{*}_{m} ratio closer to 0 indicates more 'preferential' flow, which, by the definition of Eriksson et al. (1997), is likely analogous to a combination of fast preferential flow and fast matrix flow. A θ/θ^{*}_{m} ratio closer to 1 indicates less 'preferential' flow.

Table 2.5.	Wetting-front	velocities calculated	from interna	l moisture conte	nt probes.

	Wetting-front velocities					
	cm/day					
	Pile 1 Pile 2 Pile 3					
Stage I	15	7 - 15	7 – 16			
Stage II	105 88 44					
Stage II	Wetting fronts dissipate in upper 3 meters of pile					

Table 2.6. Particle size minimum, maximum, and average D_{10} values for Piles 1, 2, and 3.

	D ₁₀ (mm)
Pile 1 Minimum	7.63
Pile 1 Maximum	17.70
Pile 1 Average	11.58
Pile 2 Minimum	0.03
Pile 2 Maximum	2.19
Pile 2 Average	0.12
Pile 3 Minimum	0.13
Pile 3 Maximum	2.74
Pile 3 Average	0.36

Table 2.7. Soil water characteristics as determined from soil water characteristic curves (from Speidel, 2011).

Pile	Air Entry Pressure (kPa)	Residual Water Saturation (-)
1	0.05	0.06
2	0.4	0.09
3	1.36	0.14

Table 2.8. Field-based, calculated and measured hydrological properties for Piles 1-3.

	Pile 1	Pile 2	Pile 3
Volumetric internal moisture content (θ , m ³ /m ³)			
¹ Wet season average θ	0.20	0.26	0.30
¹ Dry season average θ	0.17	0.19	0.26
Area-normalized flux (q, mm/day)			
² Wet season average <i>q</i>	3.2	5.3	6.5
² Dry season average <i>q</i>	0.2	0.6	0.5
Saturated hydraulic conductivity (K _{sat} , m/s)			
³ Minimum K _{sat}	3.7 x 10 ⁻⁶	5.1 x 10 ⁻⁸	2.0 x 10 ⁻⁷
³ Maximum K _{sat}	1.2 x 10 ⁻⁴	4.8 x 10 ⁻⁵	1.3 x 10 ^{-₅}
³ Arithmatic mean K _{sat}	2.7 x 10 ⁻⁵	1.3 x 10 ⁻⁵	5.7 x 10 ⁻⁶
³ Geometric mean K _{sat}	1.5 x 10 ⁻⁵	4.8 x 10 ⁻⁶	3.7 x 10 ⁻⁶
⁴ Modeled K _{sat}		6.4 x 10 ⁻⁴	
Unsaturated hydraulic conductivity (K _{unsat} , m/s)			
⁵ Wet season average <i>K</i> _{unsat}	4 x 10 ⁻⁸	6 x 10 ⁻⁸	8 x 10 ⁻⁸
⁵ Dry season average K _{unsat}	2 x 10 ⁻⁹	6 x 10 ⁻⁹	6 x 10 ⁻⁹
Pore water velocity (<i>v</i> , cm/day)			
⁶ Wet season average <i>v</i>	1.6	2.0	2.2
⁶ Dry season average <i>v</i>	0.1	0.3	0.2

¹ Measured with TDR probes (Pile 1) or ECH₂O probes (Piles 2 and 3) ² From effluent flow gauges

³Measured with single-ring infiltrometers

⁴ Temporally constant and spatially uniform through pile, calibrated to Pile 2 outflow by Javadi et al. (2012) using MIN3P (Mayer et al., 2002)

⁵ From flux, assuming only gravity drainage and nearly uniform moisture content with depth, which likely underestimates K_{unsat} for Pile 1.

⁶ Calculated with volumetric moisture and effluent flux using average wet season (February) and dry season (August) values, which likely underestimate v for Pile 1

2.7 Figures



Figure 2.1. Cumulative annual precipitation, which is usually approximately 1250-1300mm/year with the exception of the very high precipitation water year (2008-2009).



Figure 2.2. Three-stage effluent flow patterns from Piles 1, 2, and 3 D Lysimeters.



Figure 2.3. Daily precipitation and effluent flow patterns for Sub-lysimeters A, B, and C and Lysimeter D for Piles 1, 2, and 3.



Figure 2.4. Precipitation and Pile 1 effluent flow and specific conductance (SC) during Stage I, with variable relationships between precipitation and SC (A). Some patterns include (B) rapid sharp drop in SC in response to heavy precipitation, indicating fast (>10m/day) preferential flow; (C) decrease in SC followed by an increase suggesting preferential flow followed by slower matrix response; and (D) an increase then stabilization of EC, suggesting matrix-dominated flow without activation of preferential flow paths.



Figure 2.5. Bromide breakthrough curves for Piles 1-3 D Lysimeters, showing evidence of preferential and matrix flow in Piles 1 and 3 and almost exclusively matrix flow in Pile 2.



Figure 2.6. Relative proportions of cumulative mass released from each pile (all lysimeters).



Figure 2.7. Breakthrough curves and cumulative bromide mass released from Piles 1, 2, and 3. Breakthrough curves are presented at the same scale for all three piles for comparative purposes; see Appendix A for full-scale plots.



Figure 2.8. Cyclops in-line fluorimeter voltage spike – and implicit sodium fluorescein and bromide concentration increase -- during the night following Pile 1 tracer application, during which no bromide samples were taken.



Figure 2.9. Comparison of total bromide removed from Sub-lysimeters A, B, and C for the three piles, suggesting a component of non-vertical flow toward the outer slopes (Sub-lysimeter C, above which no tracer was applied) in Piles 1 and 3, and less of evidence of non-vertical flow in Pile 2.



Figure 2.10. Daily normalized mass outflow (M/M_0) as a function of real time (days, on left) and flowcorrected time (τ , on right). Daily normalized masses from February 27, 2010 to April 9, 2010 are based on linearly interpolated concentration estimates.



Figure 2.11. Stage I wetting fronts moving consecutively downward for (A) Pile 1, Line 3; (B) Pile 2, Line 1; (C) Pile 2, Line 2; and (D) Pile 3, Line 1. TDR/TE1 is the lowermost probe and TDR/TE 5 is the uppermost probe.



Figure 2.12. Stage II wetting fronts moving consecutively downward for (A) Pile 1, Line 3; (B) Pile 2, Line 1; and (C) Pile 3, Line . TDR/TE1 is the lowermost probe and TDR/TE 5 is the uppermost probe.



Figure 2.13. Stage III wetting fronts usually dissipate before reaching bottom probes, e.g., in (A) Pile 1, Line 3; (B) Pile 2, Line 2; and (C) Pile 3, Line 1. TDR/TE1 is the lowermost probe and TDR/TE 5 is the uppermost probe.



Figure 2.14. Examples of fast flow reaching the bottom of the pile first, with wetting fronts reaching higher probes later in (A) Pile 2, Line 3; (B) Pile 3, Line 2; and (C) Pile 3, Line 3. TDR/TE1 is the lowermost probe and TDR/TE 5 is the uppermost probe.



Figure 2.15. Evidence of preferential flow, as a wetting front reaches the lowermost TDR probe (TDR1) at the same time as or before reaching upper probes (TDR2, TDR 3, and TDR4).



Figure 2.16. Soil water characteristic curves (SWCCs) for Piles 1, 2, and 3, based on average particle size distributions.



Figure 2.17. Soil water characteristic curves (SWCCs) for all tipping phases for Piles 1, 2, and 3 (after Speidel, 2011).

Chapter 3: Effect of material type and wind exposure on evaporation from three experimental waste-rock piles as measured by water balance and estimated by Penman-Monteith

3.1 Introduction

Constraining site- and rock-specific evaporation estimates from mine waste rock is an important step in the prediction and management of waste-rock effluent water quality and quantity. Waste rock is highly heterogeneous with complex hydrology, complicating evaporation predictions. Evaporation from waste rock can be determined using a water balance approach, which is accurate if a physical test site and appropriate data, such as quality measurements of rainfall infiltration, runoff, and storage fluxes, are available. These resources are not often available, so other approaches using analytical methods based on atmospheric and soil data may be beneficial tools for mine planners and operators for predictive and management purposes when direct evaporation measurements are not possible.

Research has been conducted concerning atmospheric-based analytical techniques for estimating evaporation under a variety of conditions for decades, especially in agricultural settings for irrigation purposes (Section 1.2.2). Two examples include the Penman (1948) and Penman-Monteith (Monteith, 1965) approaches. The Food and Agricultural Organization of the United Nations developed a modification of the Penman-Monteith based on standardized atmospheric, crop, and soil parameters (FAO-PM; Allen et al., 1998).

Some mine waste research has attempted to apply those analytic approaches to bare mine waste rock. For example, Carey et al., (2005) measured evaporation from the upper surface of a mine

waste-rock pile near Key Lake, Saskatchewan, Canada, using the eddy covariance method. They modeled evaporation using the Granger and Gray (1989) modified Penman method and found that the modeled results matched well with measured results. Fretz et al. (2012) calculated evaporation from the upper surface of an experimental waste-rock pile at a mine in the Northwest Territories, Canada. They used tensiometer-based flux estimates to validate the applicability of a modified FAO-PM method that considered the influence of the cold climate. Bay (2009) presented preliminary water balance evaporation calculations compared with pan evaporation, modified Penman-Monteith, and Soil Cover (2000) evaporation estimates from one type of waste rock at the Antamina Mine in Peru.

Two main factors make evaporation estimation for waste rock more difficult than estimation for agricultural fields, mine tailings, and some engineered soil covers. First, waste rock is highly heterogeneous, with particle size distributions often ranging from clay to boulders, as opposed to settings in which soils are comparatively homogeneous and fine grained. The variation in particle size in waste rock strongly influences surficial and internal flow regimes within waste-rock piles, for example by facilitating high-velocity and non-vertical preferential flow paths which directly influence the infiltration, and subsequently the evaporation of precipitation on waste rock (e.g., Eriksson et al., 1997; Smith and Beckie, 2003; Nichol et al., 2005; Blackmore et al., 2012). The heterogeneous nature of waste rock also influences air circulation within a pile (e.g. Amos et al., 2009, Chi et al., 2013).

Second, waste rock is often deposited on slopes using an 'end-dumping' method. This creates two distinct surfaces – flat, compacted upper traffic surfaces and looser, sloped sides – and internal interbedded sloping layers and coarse material segregated at into 'rubble zones' at the base of the pile (Figure 1.2; Smith and Beckie, 2003; Fala et al., 2005; Stockwell et al, 2006).

The estimation of evaporation from the upper flat surface of waste-rock piles has been successful using the FAO-PM method (Fretz, 2012) and the Granger and Grey modified Penman method (Carey et al., 2005), but waste-rock slopes pose several challenges to the applicability of those evaporation estimation techniques, and require further investigation (Figure 3.1).

The Antamina-Teck-UBC Waste-Rock Research Program includes work on the hydrology, geochemistry, and microbiology of several types of waste rock at the laboratory to dump scales, and provides an opportunity to study evaporation and infiltration on both the flat upper surfaces and the sloped sides of waste-rock piles. This study uses site-specific atmospheric data and outflow measurements for three 36 m x 36 m x 10 m experimental waste-rock piles (Piles 1, 2, and 3). The piles are composed of different types of waste rock with unique hydrological and geochemical properties, but are in the same location and are almost identical in size and orientation, so they experience essentially the same environmental forcings with the exception of wind exposure. Differences in evaporation from the piles can therefore be attributed mostly to the differences in material type.

The objectives of this study are to: 1) calculate the evaporation component of the water balance for three types of waste rock, including flat and sloped surfaces; 2) compare the water-balance results with evaporation estimates from the FAO-PM method using base-case laboratory- and software-derived or recommended soil parameter values; and 3) calibrate the FAO-PM model to water-balance evaporation calculations and evaluate conditions and parameters in waste-rock settings for which the FAO-PM method may and may not be applicable.

3.2 Methods

Evaporation was calculated (water balance) and estimated (FAO-PM) for three geometrically identical 36 m X 36 m X 10 m experimental waste-rock piles described in Chapter 1. Interpretation of evaporation results draws on the particle size analyses described in Chapters 1 and 2, including the coarser-grained nature of Pile 1, the finer-grained, relatively homogeneous waste rock in Pile 2, and the more heterogeneous, finer-grained waste rock containing large boulders in the outer slopes of Pile 3. Some observations from the tracer study (Section 2.4.2.4), which was applied via an artificial rainfall event to the crowns (above the A and B sublysimeters) but not the slopes (above the C sub-lysimeters) of the experimental piles, are also relevant to the evaporation discussion.

3.2.1 Water balance evaporation calculation

The study period for Pile 1 is July1, 2007 through June 30, 2011, and for Piles 2 and 3 it is July 1, 2008 through June 30, 2011. A 'water year' is considered to be July 1 through June 30. Water balances for each test pile were determined using recharge to combined Sub-lysimeters A, B and C, and Lysimeter D, and incorporate evaporation from the flat upper surfaces and sloping sides of the piles. Water balances for the three internal three sub-lysimeters were also calculated, with Sub-lysimeters A and B representing evaporation from the crowns of the piles and Sub-lysimeter C representing evaporation from the slopes.

Evaporation based on the water balance (E_{WB}) was calculated for each water year based on the equation

$$E_{WB} = P - Q - \Delta S - R$$

Eq. 3.1

where *P* is precipitation, *Q* is the total effluent flow from the base of the pile, ΔS is the change in water storage, and *R* is runoff. Berms were built around the tops of the piles, so while some ponding and runoff to surface depressions on the piles occurs, there is no loss in the water balance due to runoff outside of the piles. With negligible runoff the water-balance evaporation equation reduces to

$$E_{WB} = P - Q - \Delta S.$$

Eq. 3.2

The net infiltration and lysimeter effluent (Q) was measured with "tipping bucket" flow gauges as described in Corazao Gallegos (2007) and Bay (2009). Precipitation (P) was measured at the location of the experimental piles with an 8" rain gauge (Rainwise). Rain data was not available from the experimental piles rain gauge from February to June 2008, and was estimated over this time period from other mine-site weather stations located within four kilometers of the test site according to the methods in Bay (2009).

The annual and study period changes in storage (ΔS) were calculated through the conversion of changes in average volumetric moisture content (ΔVMC), which were measured with internal sensors in the piles. Pile 1 ΔVMC was measured with time domain reflectometry (TDR) probes constructed at the University of British Columbia according to the methods in Nichol et al. (2003) and a MoisturePoint MP-917 TDR instrument. Piles 2 and 3 ΔVMC was measured with Decagon Devices ECH₂O probes. Changes in volumetric moisture content were then converted to ΔS using the volume of waste rock in each pile. Volumetric measurements (Q and ΔS) were converted to area-normalized height of water according to the plan-view area of catchment lysimeters and are reported in mm.

3.2.1.1 Sources of error in water balance calculations

Errors are associated with the measurement of the individual components of the water balance. The rain gauges used for precipitation measurements are reported by the manufacturer to have an accuracy of +/- 1% (www.rainwise.com) but research shows that tipping bucket rain gauges similar to those used can have much lower accuracy, for example due to wind effects and rainfall intensity (e.g., Habib et al., 2001]; Ciach et al., 2003; Yang et al., 2005). Effluent flow volumes measured by the "tipping bucket" flow meters can change over time as a result of mechanical wear, so each tipping bucket was calibrated annually to ensure accuracy was maintained. Gaps in the flow or precipitation data records resulting from mechanical or electronic malfunction were estimated by linear extrapolations for periods less than one week or estimated using corresponding lysimeter flow relationships for longer periods (Appendix E).

Previous research has shown that obtaining an accurate water balance using lysimeters that are installed within soils and waste rock can be difficult because of the tendency for 'divergent flow' of water around lysimeters rather than through them (e.g., Gee et al., 2003). Research also indicates that the influence of capillary breaks and non-vertical preferential flow paths can induce lateral movement of water within a waste-rock pile (e.g., Nichol et al., 2005; Stockwell et al., 2006; Bay et al., 2009). While these problems do not apply to Lysimeter D, error could be introduced in the sub-lysimeter water-balance calculations due to the possibility of water gained or lost in non-vertical flow paths and as a result of divergent flow around lysimeters. Sub-lysimeter results will be most accurate, then, where matrix flow is dominant and lateral flow into or out of the sub-lysimeter catchment areas is limited. Bromide tracer results show very consistent matrix-dominated breakthrough curves for Pile 2 Sub-lysimeters A and B with almost no bromide mass reporting to the C lysimeter, above which bromide was no applied during the

tracer study, suggesting minimal influence on the water balance caused by non-vertical flow above those lysimeters (Figure 2.9). Since Sub-lysimeters A, B, and C were designed to evaluate hydrological and geochemical variability over a 10 m flow path, as opposed to surficial evaporation, water balance-derived evaporation values from the sub-lysimeters should be considered qualitatively rather than quantitatively, and are heretofore described as 'estimates' as opposed to 'calculations'. In this study, the error inherent to the sub-lysimeters from non-vertical flow is not applicable to water balance calculations for whole-pile evaporation because all water is captured among the four lysimeters. It is also assumed that there is no leakage through the impermeable basal liners, and that there is no lateral inflow of water from the slope above the piles.

3.2.2 Penman-Monteith: Base-case evaporation estimation

Evaporation was estimated from meteorological data and soil properties based on the FAO-PM method as outlined in Allen et al. (1998). Base-case values are laboratory- and software-derived from measured soil properties, or are recommended values from Allen et al. (1998). All terms used here for the FAO-PM formulation are listed in Table 3.1.

The FAO-PM approach is a capillary model and only applies to matrix pathways. The method calculates evapotranspiration for "*a hypothetical reference crop with an assumed crop height of* 0.12 m, a fixed surface resistance of 70 s m⁴ and an albedo of 0.23" (Allen et al., 1998), but has been successfully applied to cases without transpiration (Allen et al., 2005, Mutziger et al., 2005).

Daily reference evaporation (ET_0 , mm/day) was calculated using according to the equation

$$ET_0 = \frac{0.408(R_n - G) + \gamma \left(\frac{900}{T + 273.15}\right) u_2(e_s - e_a)}{\Delta + \gamma (1 + 0.34u_2)}$$

Eq. 3.3

where R_n is net radiation (MJ/(m²·day)), *G* is soil heat flux density (MJ/(m²·day)), *T* is mean daily air temperature at 2 m height (°C), u_2 is wind speed at 2 m height (m/s), e_s is saturation vapor pressure (kPa), e_a is actual vapor pressure (kPa), ($e_s - e_a$) is saturation vapor pressure deficit (kPa), γ is the psychrometric constant (kPa /°C) and equals 0.038 kPa/°C for this study, and Δ is the slope of saturation pressure curve (kPa/ °C) (Allen et al., 1998). Atmospheric data for the FAO-PM estimates were measured and collected hourly at Antamina's Yanacancha weather station, located less than four kilometers from the experimental piles site.

Daily actual evaporation (ET_c , mm/day) was calculated according to the dual crop coefficient methods in Chapter 7 of Allen et al. (1998) and according to the equation

$$ET_c = (K_{cb} + K_e)ET_0$$

Eq. 3.4

where K_{cb} is the dimensionless coefficient for crop transpiration and is considered to be zero for bare waste rock and K_e is the dimensionless coefficient of soil evaporation. The equation for FAO-PM evaporation from the bare surface, E_{PM} (mm/day), becomes

$$E_{PM} = ET_c = (K_e)ET_0.$$

Eq. 3.5

The coefficient of soil evaporation K_e accounts for soil properties and the amount of evaporable water in soil at variable drying stages after precipitation events according to the equation

$$K_e = K_r(K_{cmax} - K_{cb}) \le f_{ew}K_{cmax}$$
Eq. 3.6

where K_r is the dimensionless soil reduction coefficient; K_{cmax} is the dimensionless maximum value of the crop coefficient, recommended as 1.2 for bare soils; and f_{ew} is the fraction of soil that is both wetted and exposed, and is equal to 1 due to the absence of crop cover.

The soil reduction coefficient K_r is determined for two stages of drying: the energy limiting stage during which the soil is moist after a precipitation event and $K_r = 1$, and the falling rate stage, during which the evaporation rate is decreasing and $K_r < 1$. K_r is based on soil characteristics including total evaporable water (*TEW*, mm), readily evaporable water (*REW*, mm), and cumulative amount of evaporation from the soil surface layer at the end of the previous day, $(D_{e,i-1}, mm, where i$ represents the current day), according to the equation

$$K_r = \frac{TEW - D_{e,i-1}}{TEW - REW}, \quad for \ D_{e,i-1} > REW.$$
Eq. 3.7

TEW is based on soil moisture at field capacity (θ_{FC}) and wilting point (θ_{WP}), which can be determined from soil water characteristic curves, field data, or laboratory experiments, and by the depth of the soil layer which is susceptible to evaporation (Z_e), according to the equation

$$TEW = (\theta_{FC} - 0.5 \,\theta_{WP})Z_e$$

Eq. 3.8

Selection of θ_{FC} and θ_{WP} values is ambiguous and subject to user definition. For example, Allen et al. (1998) state "...it is assumed that the water content of [the] evaporating layer of the soil is at field capacity, θ_{FC} , shortly following a major wetting event...", while other sources describe θ_{FC} as the moisture content after which free drainage has ceased, usually two to three days after a wetting event (Veihmeyer and Hendrickson, 1949, Chesworth, 2007); the moisture content at specified soil suction (i.e., -33 kPa (-0.33 bar) for fine soils and -100 kPa (-0.1 bar) for coarse soils (from Ritchie, 1981)); and the moisture content as a function of flux (Nachabe 1998, Mayer and Gee, 1999). For this study, base-case values were obtained from soil-water characteristic curves (SWCCs) generated using SoilVision software (Fredlund, 1996) by the method of Speidel (2011) for waste-rock samples with particle diameters less than 10 cm. The SWCCs were converted from gravimetric moisture content to volumetric moisture content using dry density (Pile 1) and specific gravity (Piles 2 and 3) as measured by Golder Assoc., Peru. Soil-moisture probes within the pile measure higher field-capacity moisture contents than those determined in the laboratory, possibly because sensors in the field were installed in very fine-grained material (<0.5 cm) as opposed to the coarser-grained material (<10 cm) used in the laboratory for soilwater characteristic curve development. The values from the coarser (laboratory) material are likely more representative of the whole pile than those from the finer sieved material surrounding in-situ probes, so those values were used for θ_{FC} and θ_{WP} .

Base-case *REW* values were determined using typical *TEW:REW* relationships reported in Table 19 of Allen et al. (1998). A recommended value of $Z_e = 0.10$ m (Allen et al. 1998), was used in the base-case evaporation estimations. Subsequent calibration of Z_e , θ_{FC} and θ_{WP} was conducted.

The cumulative depth of evaporation (depletion) following complete wetting at the end of day i ($D_{e,i}$, mm), is modified in Eq. 3.9 for bare, non-agricultural soil without irrigation or runoff:

$$D_{e,i} = D_{e,i-1} - P_i + \frac{E_i}{f_{ew}} - DP_{e,i-1}$$
Eq. 3.9

where $D_{e, i-1}$ (mm) is the cumulative depth of evaporation following complete wetting from the exposed and wetted fraction of the soil at the end of day *i*-1; P_i (mm) is precipitation; E_i (mm) is evaporation; and $DP_{e,i}$ (mm) is deep percolation loss from the topsoil layer if soil water content exceeds field capacity. Once the total evaporable water (*TEW*) has been exhausted from the upper soil layer, daily evaporation will be zero until another wetting event, bounding $D_{e,i}$ to

$$0 \leq D_{e,i} \leq TEW.$$

Eq. 3.10

In the FAO-PM estimation, water lost to deep percolation $(DP_{e,i})$ is no longer available for evaporation and becomes recharge, and is calculated according to the modified equation

$$DP_{e,i} = P_i - D_{e,i-1} \ge 0.$$

Eq. 3.11

3.2.3 Penman-Monteith: Calibration

The base-case FAO-PM methods and values described above were followed in order to determine the suitability of the method in cases where complementary water balance methods are not available. A subsequent calibration of the evaporation model was performed to determine reasonable adjustments of parameter values based on physical soil properties and hypothesized mechanisms causing under- or over-prediction of observed evaporation calculated by the water

balance method. The base-case FAO-PM estimates were manually calibrated to the water balance calculations for the entire study period as opposed to individual water years. Base-case FAO-PM soil parameters that determine total evaporable water (θ_{FC} , θ_{WP} , and Z_e) were calibrated independently and in combination to reach a good match with the whole-pile three- or four-year water balance evaporation calculations.

The range of θ_{FC} values considered reasonable for FAO-PM calibration was 0.03 to 0.25, and θ_{WP} values were assigned as

$$heta_{WP}=rac{1}{3} heta_{FC}$$
 .

Eq. 3.12

The selection of Z_e for FAO-PM calculation is inherently more difficult in a waste-rock pile than in an agricultural setting, where Z_e is typically 0.10-0.15 m (Allen et al., 1998). Firstly, waste particle sizes can have very broad ranges, including very coarse materials that promote moisture movement in the gas phase deeper below the surface than would be expected in a conventional soil. Secondly, the depth of evaporation for a waste-rock pile is expected to vary spatially for different locations of the pile, especially along the loose, boulder- and gravel-filled slopes.

Fretz (2013) calibrated FAO-PM evaporation estimates to water balance estimates for the crowns of waste-rock piles using a Z_e of 0.05m. For this study, the FAO-PM evaporation estimations were calibrated to the water balance calculations considering values of Z_e from 0.01 m to 1.0 m.

3.3 Results

Cumulative precipitation for the 2007-08, 2008-09, 2009-10, and 2010-11 water years was 1281 mm, 1535 mm, 1290 mm, and 1274 mm, respectively (Table 3.2, Figure 3.2). The 2008-09 wet season had more rainfall than average years, including higher rainfall in September 2008, May 2009, and June 2009. The wet season started slightly later in 2010-11.

3.3.1 Change in storage: Initial and annual wet-up

A prominent unknown amongst mine planners is the length of time it takes for a full-scale wasterock pile to 'wet-up', i.e., for all of the waste rock to reach water contents exceeding field capacity, allowing flow rates to increase substantially and resulting in negligible annual change in storage. It is important to distinguish between initial wet-up that occurs after dump construction, and the annual wet-up which occurs at the beginning of each wet season and is balanced by the annual drain-down stage at the end of the wet season and through the dry season.

Bay (2009) reported that the initial wet-up of Pile 1 was 1-4 months. Pile 2 internal moisture content measurements and effluent flow rates were very similar for all average-precipitation years, indicating that the initial wet-up of the piles was complete by the first year after construction. Internal moisture content measurements from Pile 3 suggest that initial wet-up was complete within the second year after construction. Blackmore (in progress) reports that initial wet-up of Piles 4 and 5 is also less than two years. In general, then, in Antamina's climate, the initial wet-up period ranges for a few months to two years per ten meters of waste rock.

The volume of water going into initial wet-up can be estimated as the change in storage over the entire study periods (i.e., July 1, 2007 - June 30, 2011 for Pile 1, and July 1, 2008 - June 30,

2011 for Piles 2 and 3) because the study periods began soon after construction of each pile was completed. Under that assumption, initial wet-up was negligible for Pile 1 (0.2% of precipitation or 11 mm) and minor for Piles 2 and 3 (2.3% of precipitation or 93 mm and 3.1% of precipitation or 126 mm, respectively; Table 3.3). These values correspond to 0.1%, 1.1%, and 1.8% of the total volumes of Piles 1, 2, and 3, respectively. It is important to note that internal moisture measurements were not available until after construction was completed and monitoring systems were established, so there are likely additional volumes of water that went into initial storage between the time each pile was completed and the beginning of the study period.

Annual change in storage was variable, with 4%-9% of annual precipitation going into storage during the 2008-2009 water year – which had a prolonged wet season with high precipitation – and about the same amount of water coming out of storage during the following, average precipitation 2009-2010 water year (Table 3.3). The exception is for Pile 3, which had the highest overall increase in storage for the 2008-09 year (138 mm) that was not balanced by the decrease in storage the following year (-26 mm) nor in subsequent years. This is evident in two moisture probes at the bottom of the pile, which each register a distinct increase in volumetric moisture content during the 2008-09 year that remains steady in following years. The 2008-09 Pile 3 change in storage should therefore be attributed mostly to the initial wet-up of the pile.

3.3.2 Evaporation calculations from water balance: Entire pile

The four-year (Pile 1) and three-year (Piles 2 and 3) study period average evaporation values as determined by water balance (E_{WB}) for Piles 1, 2, and 3 were 59%, 41%, and 28% of precipitation, respectively (Table 3.2). These values correspond to highly variable inter-pile and

inter-annual evaporation that ranges from 302 mm/year (Pile 3 in 2010-2011) to 961 mm/year (Pile 1 in 2009-2010; Figure 3.3).

Yearly evaporation from Pile 1 calculated using the water balance method was 57%, 60%, 75%, and 44% of annual precipitation for the 2007-08, 2008-09, 2009-10, and 2010-11 years, respectively (Table 3.2, Figure 3.4). The range of yearly evaporation is greatest in this pile. Pile 2 evaporation was 36%, 48%, and 40% of precipitation for the 2008-09, 2009-10, and 2010-11 years, respectively, exhibiting moderate variability from year to year. Evaporation from Pile 3 was lowest of the three piles at 29%, 32%, and 24% of precipitation for the 2008-09, 2009-10, and 2010-11 years, with low variability among the water years.

3.3.3 Evaporation estimates from water balance: Sub-lysimeters

Acknowledging the possibility of errors from non-vertical flow, water balance estimates for Antamina's experimental pile sub-lysimeters can be useful to assess differences in evaporation between the slopes and the crowns of waste-rock piles. Additionally, smaller lysimeters such as those commonly used for pre-existing piles (e.g., O'Kane et al., 1998) and that are similar in function to Sub-lysimeters A, B and C could be useful estimation tools in cases where whole-pile water balance evaporation calculations are not available due to a lack of a complete basal lysimeter.

Water-balance evaporation estimates are extremely variable between Pile 1 sub-lysimeters located under the crown and slopes of the pile (Table 3.2, Figure 3.5). Very high evaporation is estimated above P1A (76% to 88% of precipitation) and P1B (84% to 95% of precipitation), which are located completely under the flat upper crowns. This is vastly different from the low evaporation estimated P1C (15% to 39% of precipitation), which is located under the outer slope

of the pile. For any given sub-lysimeter, annual evaporation estimates do not vary greatly from year to year, especially under the crown of the pile.

Pile 2 sub-lysimeter evaporation estimates from the water balance method are relatively consistent from sub-lysimeter to sub-lysimeter, but the individual sub-lysimeters exhibit less consistency from year to year than seen in the other two piles (Table 3.2, Figure 3.5). Over the three-year study period, P2A evaporation estimates range from 41% to 61% of precipitation, P2B evaporation estimates range from 31% to 51%, and P2C yearly evaporation estimates are higher and more consistent annually than the other sub-lysimeters, ranging from 55% to 63%.

Similar trends to those of Pile 1 are observed for evaporation estimated from the water balance method for Pile 3 sub-lysimeters, with high, consistent evaporation from Sub-lysimeters A and B, and lower evaporation from Lysimeter C (Table 3.2, Figure 3.5). Over the three year study period, P3A evaporation estimates ranged from 64% to 76% of precipitation, P3B evaporation estimates ranged from 62% to 74%, and P3C evaporation estimates ranged from 50% to 61%.

The striking difference in evaporation estimated from the internal (A and B) and external (C) sub-lysimeters in Piles 1 and 3 is likely caused largely by flow regimes that divert water toward the outer slopes rather than differences in evaporation. This is supported by Piles 1 and 3 tracer study results, where bromide mass reporting to the C sub-lysimeter was comparable to bromide mass reporting to the A and B sub-lysimeters, despite tracer application only on the crown of the pile (i.e., above Sub-lysimeters A and B but not Sub-lysimeter C; Figure 2.9).

3.3.4 Penman-Monteith evaporation: Base-case

Evaporation estimates from the FAO-PM method (Allen et al., 1998) are based only on meteorology and soil parameters for each pile, are therefore identical for all lysimeters and the entire pile.

The four-year (Pile 1) and three-year (Piles 2 and 3) evaporation estimates for Piles 1, 2, and 3 using the FAO-PM method with base-case parameter values are 53%, 56%, and 60% of precipitation, respectively (Table 3.2; Figure 3.4; Figure 3.5). The base-case FAO-PM method slightly underestimates observed evaporation in Pile 1 for the study period, and does not capture the annual variability that is observed in water-balance calculations. Annual evaporation estimates for Pile 2 using the FAO-PM method overestimate evaporation calculated using the water-balance method, but have similar inter-annual variability. Pile 3 FAO-PM evaporation estimates are much higher than evaporation calculated by water balance method, but exhibit a similar inter-annual variability.

The differences in the base-case FAO-PM results among the three piles are purely due to soil properties and we therefore have a prediction of the effect of soil type on evaporation. There are two hypotheses for why the base-case predictions are inconsistent in the estimation of evaporation from the three rock types. First, the base-case parameters, which have largely been developed for agricultural-type soils, may require adjustment for use in waste rock settings. That possibility is explored and discussed through model calibration below in Sections 3.3.5 and 3.4.3.1. A second possibility is that there are additional mechanisms that occur in waste-rock settings that are not accounted for with FAO-PM. That possibility – and specifically that of
preferential flow mechanisms that rapidly transport evaporable water away from the surface – is discussed in Section 3.4.3.2.

3.3.5 Penman-Monteith evaporation: Calibration

Penman-Monteith estimates were calibrated to water balance calculations by adjusting laboratory-derived values for moisture content at field capacity θ_{FC} (0.09, 0.18, and 0.31 for Piles 1, 2, and 3, respectively; Table 3.4) and moisture content at wilting point θ_{WP} (0.04, 0.08, and 0.14 for Piles 1, 2, and 3, respectively) as well as the recommended value for depth of the soil surface which is susceptible to evaporation Z_e (0.10 m for all three piles).

3.3.5.1 Moisture content at field capacity θ_{FC} and wilting point θ_{WP}

Calibrated θ_{FC} values were 0.16, 0.04, and 0.03 for Piles 1, 2, and 3, respectively, when using the recommended value for depth of the soil surface which is susceptible to evaporation (Z_e) of 0.1 m (Table 3.4). The corresponding calibrated θ_{WP} values for Piles 1, 2, and 3 are 0.05, 0.01, and 0.01. The calibrated moisture content values are not representative of the respective soil types based on known soil characteristics and measured soil moisture content. Therefore, calibration of the FAO-PM estimates by adjusting θ_{FC} and θ_{WP} is not considered to be as reasonable as calibration of Z_e values (below).

3.3.5.2 Depth of the soil surface which is susceptible to evaporation (Z_e)

The FAO-PM method can provide a good match with respect to the water-balance method for materials in the three piles over the course of the study period by adjusting Z_e values on the whole-pile scale and for the entire study period using base-case θ_{FC} and θ_{WP} values.

- A recommended Z_e of 0.10 m for Pile 1 underestimated evaporation by 6%, and increasing Z_e to 0.19 m provided a good match between the FAO-PM and water-balance methods.
- A recommended Z_e of 0.10 m for Pile 2 overestimated evaporation by 15%, and decreasing Z_e to 0.03 m provided a good match between the FAO-PM and water-balance methods.
- A recommended Z_e of 0.10 m for Pile 3 greatly overestimated evaporation by 32%, and a good fit between water balance and FAO-PM estimates was obtained by adjusting Z_e to the value of 0.01 m.

It is hypothesized that the low evaporation in Pile 3 is due to complex surficial and internal flow regimes that include higher-velocity preferential flow paths, as opposed to a very shallow depth of the soil layer which is susceptible to evaporation, and therefore the calibration of $Z_e = 0.01$ m for Pile 3 is unrealistic. A more physically-valid approach may be to include an additional term in FAO-PM method to account for precipitation that is rapidly removed from the surface of the pile as a result of preferential flow and is therefore not available for evaporation (see Section 3.4.3.2).

3.4 Discussion

The discussion below addresses initial wet-up and annual changes in storage followed by hypotheses of the processes controlling evaporation as calculated by the water balance, and ends with a discussion on the suitability of the FAO-PM method for estimating evaporation in waste rock setting.

3.4.1 Change in storage

The storage results from experimental Piles 1-3 suggest that the finer grained the material, the greater the changes in storage, both at initial wet-up and annually (Table 3.3). Depending on the material type, the net amount of water going into storage over the study period for the 10 m piles in this study ranged from 0.1% to 1.8% of the total pile volume, corresponding to 11 mm to 126 mm of water, or 0.2% to 3.8% of total precipitation.

Initial and annual changes in storage are site specific and will vary depending on climate, operations, topography, and waste-rock type. In a bi-modal wet/dry climate similar to Antamina's, the amount of time it takes for initial wet-up will depend on timing of dump construction: areas completed during the wet season with heavy daily precipitation are not as likely to have significant changes in storage over subsequent wet seasons as those completed during the dry season. Considering that the scale of the actual waste-rock dumps is much greater than the scale of the experimental piles, the variability of initial wet-up periods for areas constructed during the wet and dry seasons will be exacerbated. Regardless of the variations, it is reasonable to assume that, in a climate such as Antamina's:

- initial change in storage will range from 0.1% to 1.8% or more of the volume of the waste rock
- initial wet-up of the piles ranges from a month to two years per 10 m of waste rock, and initial wet-up is longer in the finer-grained the material
- annual changes in storage are negligible especially in average precipitation years, but a more drastic increase in annual storage can be expected during years of high precipitation

and a balancing decrease in storage can be expected in subsequent, average-precipitation years.

3.4.2 Evaporation based on the water-balance method

Results from the water-balance calculations for the piles highlight the effect of meteorology and material type on evaporation. Differences in annual evaporation observed in the individual piles show the effects of meteorological variability. Distinct pile results, such as the consistently low evaporation observed in Pile 3, show the effects of rock type. Finally, the two factors are linked: material type plays a role in how climate affects evaporation, with coarser-grained material impacted much more by meteorological variability than finer-grained material.

Of the three piles, coarsest-grained Pile 1 had the highest observed cumulative evaporation, which is counter-intuitive. Firstly, coarser grained materials tend to have higher matrix hydraulic conductivities and a greater tendency for preferential flow, both of which promote more rapid infiltration to depth (e.g., Nichol et al., 2005). Secondly, and central to the FAO-PM method, coarser-grained materials have larger pore sizes and therefore lower air-entry pressures, which lead to lower moisture contents and less evaporable water than fine-grained materials at field capacity. Finally, ponding was often observed during the wet season on the surfaces of finer-grained Piles 2 and 3. Despite increasing the Darcy flux due to saturated flow conditions and increased hydraulic head, the open-water surface area of ponding should increase evaporation, and yet both Piles 2 and 3 have higher measured infiltration and lower observed evaporation than the coarse Pile 1.

The higher evaporation from the coarser-grained Pile 1 is hypothesized to be due to higher air circulation within that pile, which is supported by measurements and observations. Firstly,

aqueous sulfate concentrations indicate that sulfide oxidation is occurring (sulfate loadings of 2.7 mg SO₄ per kilogram of waste rock per week in the wet season), but pore gas O_2 and CO_2 concentrations are near-atmospheric, indicating a lack of O_2 depletion or CO_2 enrichment (Singurindy et al., 2012; Bay et al., 2014 submitted; Lorca, in progress). Secondly, internal temperatures measured near the slopes of Pile 1 have seasonal averages that are about one degree lower than seasonal air temperature averages (Bay, 2009). The lower temperature could be explained by a loss of heat from the latent heat of evaporation, further suggesting high air circulation near the slopes in Pile 1 (Bay, 2009). Thirdly, the clast-supported, boulder and gravel-dominated rubble zones created during end-dumping of the marble and hornfels deposits in Pile 1 have large visible voids similar to those seen in Figure 3.1, which should inherently promote air circulation.

Also, wind direction in relation to location and orientation of the piles likely contributes to increased air circulation (and evaporation) within Pile 1. Bay (2009) observed that general wind patterns at two meteorological stations within four kilometers of the test piles site, stations Yanacancha and Puente Juproc, have dominant wind directions from the north and northeast (Figure 3.6). Pile 1 is located at the northern end of the row of experimental test piles, and both its northern and eastern slopes are exposed, while only the eastern slopes of Piles 2 and 3 are exposed. Chi et al. (2013) use internal waste-rock test pile pressure measurements to report that exposure of windward waste-rock slopes promotes higher advective gas transport within the pile. In this study, then, the Pile 1 exposed northern slope likely contributes to higher air circulation and hence lower evaporation.

Tracer-study results and internal moisture probe measurements suggest that non-vertical flow paths may divert infiltrating water toward the slopes of Pile 1 (Figure 2.9). This diversion results

in higher soil moisture near the slopes, which, combined with greater wind-driven air circulation in the coarse-grained material, should increase whole-pile evaporation even more.

Pile 3, which has the lowest evaporation of the three piles, has a relatively broad particle size distribution (Figure 1.9), ranging from boulders exceeding 1 m in diameter within the outer-most tipping phase of the pile to high amounts of fine-grained waste rock (up to 8% silts and clays). Despite more large particles in the outer tipping phase, the large visible clast-supported voids that likely increase air circulation in Pile 1 are not observed in Pile 3, since the latter contains enough fines to be matrix supported. The coarser particles in Pile 3 – and specifically the boulders under the outer slope – may, however, increase the potential for preferential flow, which has been observed in a variety of settings (e.g., Eriksson et al., 1997; Pruess, 1999; Tokunaga & Wan, 2001), leading to higher infiltration and lower evaporation compared to the other piles during the beginning of the wet season (Stage I, Figure 3.7). The finer grained particles sustain higher flows during the middle of the wet season (Stage II) and into the dry season (Stage III). It is hypothesized that Pile 3 has very low evaporation as a result of these sustained, high preferential and matrix flow regimes through all three stages of the water year, in conjunction with low wind-driven air circulation.

Sub-lysimeter evaporation estimation is complicated by the possibility of non-vertical flow, which is a missing component of the water balance. Indeed, the Pile 1 and Pile 3 sub-lysimeter water balance evaporation calculations, which suggest much lower evaporation for the slopes than the crowns, are most likely skewed by high infiltration on the slopes and water being diverted toward the slopes via non-vertical flow paths, which is supported by tracer evidence (Figure 2.9). Evaporation from the slopes and crowns of Pile 2 (for which there is sparse evidence of non-vertical flow) is the opposite, i.e., higher evaporation from the slopes than the

crowns. This is the effect to be expected as a result of the high surface area of the slope, which equates to increased wind exposure and solar radiation, and decreased precipitation per footprint area. High evaporation on the slopes of piles has also been reported at the Pierina Mine, which is also located in Ancash, Peru and experiences a very similar climate to Antamina (Milczarek et al., 2011). Likewise, comparatively low evaporation has been observed for Antamina's test cover study plots, which are enclosed except at the surface and therefore have no slope effect (Urrutia et al., 2011; Urrutia, 2012).

3.4.3 Suitability of using FAO-PM for waste rock evaporation calculations

A comparison between the water balance and FAO-PM shows that, for whole-pile estimates of evaporation using the non-calibrated, laboratory- and modeling-derived base-case parameters listed in Table 3.4, the FAO-PM method slightly underestimated evaporation for Pile 1 for the study period but did not capture inter-annual variability; overestimated evaporation for Pile 2; and greatly overestimated evaporation for Pile 3.

3.4.3.1 Evaluation of FAO-PM soil property values

For FAO-PM model calibration, it was determined that calibration of θ_{FC} and θ_{WP} is not as physically realistic as calibration of Z_e values. The calibrated values of Z_e are best-fit values for the whole pile, including the crowns and slopes.

The deeper Z_e value for Pile 1 (0.19 m) is reasonable when observing the large voids created by the coarse gravel and boulders that comprise the slopes and some areas of the crown of that pile. The shallower value of $Z_e = 0.03$ m is quite low but may be reasonable for Pile 2 considering the fine-grained, relatively homogeneous nature of the crown and slopes of that pile, and is similar to the $Z_e = 0.05$ m value the crowns of an experimental waste-rock pile at the Diavik mine (Fretz, 2013).

The FAO-PM evaporation can be calibrated to achieve the very low observed evaporation from Pile 3 by decreasing Z_e from 0.10 m to 0.01 m. However, the very low parameter values required to calibrate the model to the observed evaporation are not physically realistic of the broader range of particle sizes of material in that pile. Pile 3 is different from the other two piles in that the interior tipping phases are comprised almost entirely of finer-grained waste rock and the final, outer tipping phase is coarser, including boulders larger than one meter. The wide and spatially variable particle sizes induce strong preferential flow on the slopes and highly variable surface and internal flow. Therefore, adjusting the soil parameter values in order to calibrate the model for Pile 3 may not be as valid as directly accounting for the water lost to preferential flow directly, for example by including an additional term in the model (below).

3.4.3.2 Preferential flow

Proportions of matrix and preferential flow depend on material type, location within pile (i.e., slope vs. crown), conditions on the infiltration surface, magnitude of precipitation events, and antecedent moisture content (e.g., Nichol et al., 2005; Bay et al., 2009; Blackmore et al., 2012). While the FAO-PM approach to estimating evaporation accounts for deep percolation when the moisture content of surface soil exceeds field capacity (Equation 3.11), it does not account for non-capillary flow paths and preferential flow.

Preferential flow could be accounted for within the FAO-PM evaporation calculation through the use of a separate parameter that independently removes a percentage of precipitation as a preferential flow after precipitation events of a specified magnitude. A resulting modification to

the FAO-PM estimation would be to modify Equation 3.11 to increase deep percolation $DP_{e,i}$ by a specified percent of precipitation (or coefficient of preferential flow, K_{PF}) on days that exceed a specified threshold daily precipitation, $P_{i,TH}$.

$$DP_{e,i} = P_i - D_{e,i-1} + K_{PF}P_i \ge 0 \text{ for } P_i \ge P_{i,TH}$$

Eq. 3.13

The values for K_{PF} and $P_{i,TH}$ are site- and material- specific, as the amount of precipitation required to activate preferential flow and the degree of preferential flow depends on several factors as described above. While it is currently difficult to quantitatively define these parameters, a growing body of physical- and modeling-based research is lending insight into waste-rock flow regimes, including the proportions of preferential flow to matrix flow and threshold precipitation events (e.g., Eriksson et al., 1997; Blackmore et al., 2012; Broda et al., 2013; Blackmore, in progress). With an eventual sound conceptual understanding of flow regimes in waste rock and an ample database of hydrological parameters for a variety of waste rock types, the modification of FAO-PM to account for preferential flow when predicting evaporation could be a useful tool for mine planners, managers, and closure specialists.

3.4.3.3 Dump geometry and orientation

Dump geometry affects evaporation in several ways besides the spatial particle size variability of materials of the slopes – and subsequent variability in the depth of evaporable soil – and the decreased permeability resulting from the compaction of the crowns. Additionally, the proportion and orientation of slopes of a dump directly affect the surface area and locations exposed to precipitation, solar radiation, and wind effects.

The exposed surface area of waste rock slopes that is subject to evaporation is much greater than the horizontal footprint for which precipitation is measured. In Antamina's experimental wasterock piles the evaporable surface area of the slopes is 2.5 times greater than the footprint of the slopes. One method to account for the discrepancy in surface area to footprint area could be to adjust f_{ew} , or fraction of exposed and wetted soil for the slopes of piles. The value of f_{ew} could be increased to above 1.0 to account for the increased surface area of the pile slopes.

Results of this study suggest that air circulation can significantly impact evaporation from coarse-grained waste dumps, and that, in general, evaporation can be higher on slopes of waste rock. This effect is likely exacerbated in situations where slopes are exposed to the dominant wind direction (Chi et al., 2013), promoting air circulation at a greater depth in waste rock as compared to flat surfaces for which the reference evapotranspiration E_0 calculation is intended. For evaporation estimated by the FAO-PM method in waste-rock settings, observations of wind direction and exposed dump slope orientation should be carefully considered when applying a value for wind speed (u_2).

3.4.3.4 Internal heat from sulfide oxidation

Within reactive waste-rock piles that contain large amounts of sulfides, exothermic sulfide oxidation can increase internal pile temperatures, sometimes up to dozens of degrees above ambient (Lefebvre et al., 1993; Sracek et al, 2004), and can trigger chimney-like convective chambers (Lefebvre et al., 2001a,b; Wels et al., 2003) or contribute to expansive and contractive air flow (Lahmira et al., 2009). Increased temperature and convection-driven air flow in these reactive waste-rock piles could bring moist air from deeper within the piles closer to the surface, possibly increasing total evaporable water. For 2-D simulations of slope-dominated waste rock

dumps at the Questa Mine in New Mexico, Lefebvre et al. (2002) found that significant moisture was transported by convection from the center of the pile to the outer parts of the pile where it condensed, and that about 2% was removed from the pile by convection. While the modeling results suggest that moisture is not removed from the pile physically by convection itself, the transport of significant moisture toward the surface by convection coupled with wind-induced air circulation near the surface of the pile could promote an increase in overall evaporation.

3.4.3.5 Summary of FAO-PM recommendations

If no prior water balance or other evaporation data is available but soil properties and atmospheric data are available, FAO-PM can be used to predict evaporation from waste rock while taking site- and material-specific considerations into account. For the case of Antamina's waste rock and climate, the most appropriate use of and adjustments to the laboratory-derived and recommended FAO-PM parameters to achieve a good fit with water balance evaporation calculations consisted of:

- using software-derived (SoilVision, Fredlund (1996)) soil-water characteristic curves based on laboratory-measured soil properties from <10 cm samples for the selection of θ_{FC} and θ_{WP} ;
- using $Z_e = 0.19$ m for coarser-grained, blocky marble and hornfels waste rock
- using $Z_e = 0.03$ m for relatively homogeneous, finer-grained, friable intrusive quartz monzonite waste rock;
- and accounting independently for preferential flow, if possible, or a low $Z_e = 0.01$ m for heterogeneous, finer-grained skarn waste rock with boulders in the outermost slope layer.

Additional recommendations for the application of FAO-PM in various waste-rock settings include consideration of dump geometry and possible reactive waste-rock dump characteristics.

- Dump geometry:
 - Evaporation generally increases as slope-to-crown ratio increases due to higher wind exposure and solar radiation and lower precipitation on slope surfaces compared to footprint area.
 - Slope orientation with respect to dominant wind directions likely impacts internal air circulation and hence, evaporation.
- Reactive waste-rock dump characteristics
 - Exothermic sulfide oxidation in highly reactive materials can increase internal air circulation, bringing moist air near dump surfaces where, coupled with windinduced air circulation, it may be available for evaporation.

3.5 Conclusions

The evaporation component of the water balance was calculated including initial and annual changes in storage for three waste-rock piles almost identical in size, at the same location and, with the possible exception of wind exposure, under identical atmospheric conditions. The experimental set-up isolates the effect of the material type in each pile, including unique particle size distributions. The calculated water balance evaporation was compared to FAO-PM (Allen et al., 1998) evaporation estimates. The broad variability in calculated water balance evaporation among waste rock types (and inter-annually within certain waste rock types) under nearly identical meteorological conditions is similar to the broad variability observed for other waste rock types in a variety of climates (Carey et al, 2005; Fretz et al., 2012; Neuner, 2009),

highlighting the importance of empirical site- and material-specific evaluation of evaporation from bare waste rock.

In Antamina's climate with distinct wet and dry seasons, initial changes in storage ranged from 0.1% to 1.8% or more of the volume of the waste rock and initial wet-up of the piles ranges from a month (coarser-grained) to two years (finer-grained) per 10 m of waste rock. After initial wet-up, annual changes in storage were low to negligible in average precipitation years, but a more substantial increase in annual storage was observed during a year of high precipitation and was followed by a balancing decrease in storage the following year.

Water-balance results indicate that the particle size distribution of a waste-rock pile has a significant control on evaporation. The coarse-grained waste-rock pile (Pile 1) had higher evaporation with greater annual variability than evaporation from the finer-grained waste-rock piles. The higher evaporation and temporal variability is attributed to greater efficiency of wind-driven air circulation within the coarser-grained pile. The movement and evaporation of moisture from deeper within the pile, not just from the soil surface, must be considered when estimating evaporation using an analytical approach for coarser-grained waste rock.

Water-balance results further suggest that for Antamina's climate, relatively homogeneous, finegrained waste rock that shows little evidence of preferential flow (Pile 2) has relatively consistent and moderate evaporation (36%-48% of precipitation in a three-year period). The FAO-PM method generally overestimates evaporation for this type of waste rock, and the depth of the soil susceptible to evaporation ($Z_e = 0.03$ m) is lower than values suggested by Allen et al. (1998) for use in agricultural settings ($Z_e = 0.10$ m) but similar to that determined for the crown of a similar waste-rock pile ($Z_e = 0.05$ m; Fretz, 2013).

The finer-grained waste-rock pile with a broad particle size distribution including boulders (Pile 3) shows low and consistent evaporation (24%-32% of precipitation in three years) which could not be accounted for by the FAO-PM method without adjusting soil parameters outside a realistic range of values. Effluent flow patterns and results of a tracer study indicate that the influence of preferential flow on increased infiltration and decreased evaporation should be considered when using an atmospheric model to predict evaporation. The inclusion of a coefficient for preferential flow, K_{PF} , may be effective in model calibration for this type of waste rock by attributing a specified percentage of evaporable water from large precipitation events to deep percolation when hydrological data is available.

Infiltration measured by sub-lysimeters that are representative of smaller areas of a waste-rock piles can be used in the water-balance method to calculate evaporation if the amount of non-vertical flow is minimal. Non-vertical flow will have less of an impact on infiltration measurements and subsequent evaporation calculations if lysimeters are below material that supports matrix-dominated flow. Evaporation calculated by water balance using the sub-lysimeters below the flat upper surfaces of the experimental piles are much higher than whole-pile calculations from coarsest-grained waste rock (Pile 1) and fine-grained waste rock with a broad particle size distribution (Pile 3), and comparable or slightly higher than the whole-pile calculations from relatively homogeneous, fine-grained waste rock (Pile 2). Tracer study results and effluent flow patterns suggest that for Piles 1 and 3, high infiltration on the slopes and non-vertical flow being diverted towards the slopes have skewed the water-balance evaporation estimates, and that, in general, evaporation is expected to be higher on the slopes than on the crowns of waste-rock piles.

The FAO-PM evaporation estimation method is likely accurate in estimating evaporation from the surfaces of waste-rock piles, but there are several complicating factors that render the method less effective for estimating overall evaporation and subsequently, recharge to the bottom of a waste-rock pile, including:

- the fraction and orientation of a dump that is occupied by slopes, which have the greatest component of non-capillary flow and spatially variable particle size distributions, and greatly impact air circulation within the pile and precipitation and solar radiation exposure on the surface;
- surficial and internal hydrology and preferential flow paths;
- internal heat from exothermic reactions (sulfide oxidation).

Complex internal and surficial hydrology that leads to preferential flow within waste-rock piles is very difficult to predict. As a result, the application of an analytical method such as FAO-PM becomes more difficult as the degree of material heterogeneity and subsequent complexity of flow regimes increase.

3.6 Tables

Table 3.1. List of terms used in Penman-Monteith formulat

$D_{e,i}$	cumulative depth of evaporation (depletion) following complete wetting at the end of day i
$D_{e,i-1}$	cumulative amount of evaporation from the soil surface layer at the end of the previous day
$DP_{e,i}$	deep percolation loss from the topsoil layer on day <i>i</i> if soil water content exceeds field capacity
e_a	actual vapor pressure
E_i	evaporation on day <i>i</i>
E_{PM}	FAO-PM evaporation
e_s	saturation vapor pressure
$e_s - e_a$	saturation vapor pressure deficit
ET_0	daily reference evaporation
ET_c	daily actual evaporation
E_{WB}	evaporation as calculated through the water balance method
f_{ew}	fraction of soil that is both wetted and exposed
G	soil heat flux density
K_{cb}	coefficient for crop transpiration
K _{cmax}	maximum value of the crop coefficient
K_e	coefficient of soil evaporation
K_{PF}	coefficient of preferential flow
K_r	soil reduction coefficient
Р	precipitation
P_i	precipitation on day <i>i</i>
$P_{i,TH}$	threshold daily precipitation
Q	total effluent flow from the base of the pile
R	runoff
REW	readily evaporable water
R_n	net radiation
Т	temperature
TEW	total evaporable water
<i>u</i> ₂	wind speed
Z_e	depth of the soil layer which is susceptible to evaporation
γ	psychrometric constant
Δ	slope of saturation vapor pressure curve
ΔS	change in storage
ΔVMC	volumetric moisture content
$ heta_{FC}$	soil moisture at field capacity
$ heta_{\scriptscriptstyle WP}$	soil moisture at wilting point

Table 3.2. Cumulative annual precipitation (ppt), water balance evaporation (E_{WB}), and base-case FAO-PM evaporation (E_{PM}) results. Recommended (Z_e) and measured (θ_{FC} and θ_{WP}) values used for FAO-PM estimates.

	Precipitation (ppt)	E _{wв} : % of ppt	E _{WB} : % of ppt	E _{wв} : % of ppt	E _{WB:} % of ppt	Base-case E _{PM} : % of ppt
	mm	%	%	%	%	%
		Pile 1 A	Pile 1 B	Pile 1 C	Pile 1 E _{WB}	Pile 1 E _{PM}
Four-year	5381	79	89	28	59	53
2007-08	1281	77	94	30	57	62
2008-09	1535	77	84	15	60	51
2009-10	1290	88	95	39	75	55
2010-11	1274	76	86	30	44	46
		Pile 2 A	Pile 2 B	Pile 2 C	Pile 2 E _{WB}	Pile 2 E _{PM}
Three-year	4099	50	40	60	41	56
2008-09	1535	41	31	63	36	56
2009-10	1290	61	51	61	48	61
2010-11	1274	51	41	55	40	51
		Pile 3 A	Pile 3 B	Pile 3 C	Pile 3 E _{WB}	Pile 3 E _{PM}
Three-year	4099	70	67	55	28	60
2008-09	1535	64	62	53	29	60
2009-10	1290	76	74	61	32	64
2010-11	1274	70	66	50	24	54

Table 3.3. Precipitation and change in storage (Δ S) annually and for the study period. Positive Δ S values represent water going into storage within the piles, and negative values represent water coming out of storage and being released from the piles.

	Precipitation ΔS %		ΔS: % of precipitation	
	mm	mm	%	
Pile 1				
Four-year	5381	11	0.2	
2007-08	1281	0	0.0	
2008-09	1535 66		4.3	
2009-10	1290	-61	-4.7	
2010-11	1274	6	0.5	
Pile 2				
Three-year	4099	93	2.3	
2008-09	1535	111	7.2	
2009-10	1290	-92	-7.1	
2010-11	1274	73	5.8	
Pile 3				
Three-year	Three-year 4099		3.1	
2008-09	2008-09 1535		9.0	
2009-10	2009-10 1290		-2.0	
2010-11	1274	14	1.1	

	Calibrated	θ_{FC}	θ_{WP}	Ze	E _{PM}	E _{WB}	
	parameter(s)	-	-	m	mm	mm	
				Pile 1			
Base-case	-	0.09	0.04	0.10	2875		
Calibration #1	$ heta_{FC}$, wp	0.16	0.05	0.10	3169	3169	
Calibration #2	Z _e	0.09	0.04	0.19	3169		
		Pile 2					
Base-case	-	0.18	0.08	0.10	2301		
Calibration #1	$ heta_{FC}$, wp	0.04	0.01	0.10	1687	1687	
Calibration #2	Z _e	0.18	0.08	0.03	1687		
		Pile 3					
Base-case	-	0.31	0.14	0.10	2442		
Calibration #1	$ heta_{FC}$, wp	0.03	0.01	0.10	1156	1156	
Calibration #2	Z _e	0.31	0.14	0.01	1156		

Table 3.4. Base-case and calibrated parameter values used in FAO-PM evaporation estimations. Base-case values are laboratory- and software-based ($\theta_{FC, WP}$) and recommended (Z_e).

3.7 Figures



Figure 3.1. Conceptual model of infiltration (I) and evaporation (E) on the slopes and crowns of slopedominated waste-rock piles, where $E_{CROWN} \neq E_{SLOPE}$.



Figure 3.2. Cumulative annual precipitation at the experimental test piles site.



Figure 3.3. Annual precipitation and whole pile evaporation as determined by the water balance (E_{WB}) in mm for the three experimental waste-rock piles. Daily E_{WB} calculations use precipitation and effluent flow for the same day, despite the inherent delay for precipitation event water to reach the base of the pile.



Figure 3.4. E_{WB} and base-case E_{PM} as percent of precipitation for individual water years and the study periods (2007-2011 for Pile 1 and 2008-2011 for Piles 2 and 3).



Figure 3.5. Precipitation and evaporation (E_{WB} and E_{PM}) from Piles 1, 2, and 3: whole piles and sublysimeters.



Figure 3.6. Satellite image (©Google Earth & DigitalGlobe) of the experimental piles site showing the exposed northern slope of Pile 1. Rose diagrams (quarterly, from 2007) as evidence of dominant N-S and NE-SW wind directions (from Bay, 2009).



Figure 3.7. Weekly flow from the D lysimeters of all three piles, showing evidence of high infiltration in Pile 3 during all three stages of the wet season.

Chapter 4: Rapid seasonal transition from neutral to acidic drainage as a result of carbonate depletion and material heterogeneity ¹

4.1 Introduction

The ability to predict a shift from neutral to acidic drainage is critical for mine planners, as is the prediction of the associated solute concentrations and mass loadings (i.e., mass of solute per mass of waste rock per unit time; e.g., mg/(kg·wk)) that are controlled largely by drainage pH. Concentrations of some dissolved metals can vary significantly with slight changes in pH, which may dictate the water management decisions necessary to mitigate elevated solute concentrations and remove metals from the dissolved load. For example, neutral pH waters may tend to transport As, Mo, Se, and Sb while slightly acidic waters will carry Zn and Cu, and strongly acidic waters will transport Fe. In a system where effluent water from waste dumps has a variable pH, especially one that changes substantially on a seasonal basis, management options must be sufficiently robust to adapt to fluctuations in chemistry, and monitoring plans must be designed to detect rapid changes.

A variety of standard static and kinetic tools such as acid-base accounting (ABA) including the ratio of neutralization potential to acid production potential (NP/AP), sequential leach tests, and humidity cell tests can be used to estimate the potential for mine waste to produce acidic drainage. However, there are several variables which complicate the prediction of neutral and acidic drainage. Variables such as hydrology, oxygen availability, and heterogeneous

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mineralogy and particle size distributions are associated with the large-scale nature of the waste rock dumps and are difficult to reproduce in a laboratory setting (e.g., Smith and Beckie (2003); Lefebvre et al. (2001); Jambor (2003); Malmström et al. (2000)).

The Antamina experimental pile program provides an excellent opportunity to study the processes controlling neutral drainage in mine waste rock under field conditions. The Antamina polymetallic skarn deposit generates a large amount of limestone and marble waste rock that is not potentially net acid generating (NAG) with high carbonate buffering capacity, in addition to other carbonate and intrusive and skarn waste rock with a higher sulfide content, that can lead to acid production. The two waste dumps at Antamina are geochemically heterogeneous, with one dump containing predominantly NAG rock and the other containing higher percentages of potentially net acid generating (PAG) rock.

One of the single rock type, large-scale experimental waste-rock piles, Pile 2, constructed in 2007-2008, was developed to study the processes occurring in PAG waste rock that initially produce circumneutral effluent waters. Pile 2 is composed of intrusive rock with relatively high sulfide and low carbonate contents. Three wet seasons after pile construction, drainage from the experimental test pile underwent a rapid transition from a near neutral pH (7.7) to slightly more acidic effluent water during the 2010-2011 wet season. The effluent water pH decreased about 1.3 pH units in two months, including about 0.9 pH units in just two weeks. During those same time periods dissolved copper and zinc concentrations increased significantly (Table 4.1). Substantial accumulation of a bright blue predominantly amorphous precipitate containing gypsum and malachite coincided with the pH drop (Figure 4.1). A similar precipitate was observed during a laboratory experiment using material from Pile 2. The rapid changes in this field scale experimental waste-rock pile provide valuable insight into how the combined

influence of geochemical and hydrologic processes on the transition from circum-neutral to more acidic geochemical conditions.

4.2 Methods and materials

Details of Pile 2 construction, and locations and nomenclature of lysimeters and instruments are presented in Chapter 1, and methods pertaining to the analysis of Pile 2 aqueous geochemistry, mineralogy, solid-phase elemental composition, and particle size distributions are presented below.

4.2.1 Analytical techniques

Solid phase waste rock samples from Pile 2 were analyzed by ALS Labs in Lima, Peru. Analyses included solid phase trace metal concentrations using whole rock digestion and ICP-MS; acid-base accounting, including acid production potential (AP) and neutralization potential (NP) using the unmodified Sobek et al. (1978) method without siderite correction; and solid phase S and C by Leco. Precipitate samples were analyzed for trace metal concentrations using whole rock digestion and ICP-MS and solid phase S and C by Leco by ALS Labs in North Vancouver, BC, or Acme Labs in Vancouver, BC. All samples were also examined using a Philips XI-30 Scanning electron microscope (SEM) fitted with a Princeton Gamma-Tech Energy-dispersive X-ray spectroscopy (EDS) system in the Department of Earth and Ocean Sciences at the University of British Columbia (UBC). Identification of mineral phases was performed by powder X-ray diffraction (XRD) on a Siemens D8000 Diffractometer. Qualitative identification of phases was carried out using EVA software, and quantitative analyses – i.e., the relative proportions of the minerals present – were determined using Rietveld refinement with Topas v.3.0 software. The lowest amount of a mineral quantifiable by XRD and Rietveld refinement is 0.1 % wt.pt., but it is possible to observe the presence of a mineral in lower quantities on XRD chromatograms. A 10% corundum spike was used in conjunction with the normalized reference intensity ratio, or 'matrix-flushing', method (Chung, 1974) to calculate the relative abundance of amorphous material of secondary mineral samples with XRD

4.2.2 Solid phase elemental and mineralogical properties summary

The intrusive rock that comprises Pile 2 is classified as reactive Class A (Table 1.2). Rocks from the individual tipping phases have variable solid phase elemental compositions (Table 4.2). The dominant minerals in the intrusive rock in Pile 2 as determined by XRD are quartz [SiO₂] orthoclase [KAlSi₃O₈] and plagioclase [NaAlSi₃O₈ – CaAl₂Si₂O₈] feldspars. The dominant sulfides are pyrite [FeS₂] and chalcopyrite [CuFeS₂] with trace molybdenite [MoS₂]. The only carbonate detected in some of the intrusive rock samples was siderite [FeCO₃] at weight percents below 1%. The garnet andradite [Ca₃Fe₂(SiO₄)₃] was abundant in sample 2-1B, but was not detected, or had a low abundance in the other samples. Micas, oxides, amphiboles, and diopsides are present in some of the samples at low percentages.

4.2.3 Particle size distributions

Particle size analysis was completed for each tipping phase. There is variability from tipping phase to tipping phase; samples 2-1B, 2-2A and 2-3A are finer-grained than samples 2-0A and 2-1A (Figure 4.2). The average composition of Pile 2 is relatively fine-grained and homogeneous in comparison to the other large-scale test piles (Figure 1.9), with an average D_{20} of 1.68 mm (i.e., 20% of the material is finer than 1.68mm), D_{10} of 0.12mm, and 28.0% smaller than 4.75 mm, resulting in a flow regime is matrix-dominated with very little evidence of preferential flow (Chapter 2). Particles < 0.25 mm contribute most significantly to sulfide and

silicate weathering (Strömberg and Banwart, 1999). Therefore, the relatively fine-grained nature of waste rock in Pile 2 has implications for infiltration rates of pore waters, residence time, sulfide oxidation rates and carbonate and silicate buffering capacities.

4.3 Results

In 2010-2011, which was the third full wet season since Pile 2 construction and the year in which the distinct pH shift was observed, cumulative precipitation was approximately 1300mm (Figure 4.3). During high Stage II (Chapter 2) flows in April 2011, a rapid accumulation of a solid-phase precipitate in the drainage pipes that convey water to the P2D flow meters caused a disruption in the flow measurements (Figure 4.3). The flow rate returned to its previous state after manual cleaning of the pipes.

4.3.1 Effluent chemistry: Piles

Solute concentrations and pH from Pile 2 effluent fluctuate on an annual cycle with the precipitation and flow patterns described in Chapter 2 and shown in Figure 4.3. The pH of P2D effluent tends to be most alkaline under lowest flow conditions (at the end of Stage III in October), and most acidic under highest flow conditions (at the peak of Stage II in March). Correspondingly, an observed direct relationship between dissolved Zn and Cu concentrations and flow was observed. Other elements such as Mo and As, which are generally less mobile in moderately acidic waters, increase to maximum concentrations during the first flush of each wet season (Stage I), usually in November or December, and decrease to minimum concentrations at the end of each wet season in May. These relationships started for most solutes in 2008-2009 and repeated in 2009-2010, and were enhanced greatly in 2010-2011.

In February 2011 the pH of P2D began to drop rapidly. In previous years, the pH of P2D was generally near pH 7.8 during lowest flow periods and usually dropped to about pH 7 over three months with the onset of the wet season high flow. In 2011 the pH dropped lower than in previous years and at a faster rate. The pH dropped from pH 7.7 to pH 6.4 between December and February, including a 0.9 pH unit drop from pH 7.3 to pH 6.4 over two weeks in February 2011.

Despite the pH dropping less than a unit lower than it had in previous years, concentrations of several dissolved metals rapidly increased significantly more in February 2011than in previous years. Notably, dissolved Cu concentrations increased from 0.01 mg/L in December 2010 to 67 mg/L in February 2011 (Table 4.1, Figure 4.4). Over the same time period, dissolved Zn concentrations increased from 5.9 mg/L to 75 mg/L, and dissolved SO₄ concentrations increased from 1500 mg/L to 1850 mg/L.

Other elements, Mo and As, which tended to exhibit lowest concentrations in May in previous years, showed sharp drops in March and April 2011, slightly later than the peaks in Cu, Zn, and Mn, but while the pH remained below pH 6.5. The 2010-2011 maximum Mo concentration (13 mg/L) was observed in December 2010 and the minimum (6.3 mg/L) in April 2011. The maximum concentration of As (0.051 mg/L) was reported in December 2010, and concentrations fell below the detection limit of 0.001 mg/L from late February to mid-April 2011. The decrease in these oxyanion-forming element concentrations is expected based on the tendency for oxyanions to sorb at lower pH (Stumm and Morgan, 1996).

As flow declined during Stage III, the pH of P2D increased to 6.7, and Cu and Zn concentrations decreased to 4.4 mg/L and 42 mg/L, respectively. The P2D Mo concentration increased to 9.2 mg/L and As increased to 0.025 mg/L. Sulfate remained around 2000 mg/L through June 2011.

The effluent chemistry of P2C, which is the lysimeter under the outer slope of the pile and represents Tipping Phase III, follows similar seasonal trends as P2D, although often not to the same degree. Important differences to note for P2C in the 2010-2011 wet season include a minimum pH 6.6, a dramatic spike in SO₄ to 5400mg/L, the limited mobility of dissolved Mo, and a smaller decrease of As than seen in P2D.

4.3.2 Effluent chemistry: Field barrels

The field barrels do not flow in the dry season. When the rainy season begins each year there is a flushing of solutes, generally resulting in maximum initial concentrations decreasing to minimum concentrations at the end of the wet season. Drainage pH for Field Barrel 2-3A (corresponding to the material that is located above Lysimeter C) was consistently lower than the other field barrels (Figure 4.5). Drainage from this field barrel also contained the highest Cu and Zn concentrations, and very low Mo and As concentrations. Three-year trends from all field barrel data indicate that Cu and Si concentrations are generally increasing, SO₄ and Zn concentrations have reached an apparent steady state , and Mo and As concentrations are generally decreasing.

4.3.3 Solid-phase precipitate

A significant increase in accumulation of a solid-phase precipitate coincided with the pH drop and concentration and loading increases from the Pile 2 lysimeter D effluent. Prior to February 2011, small amounts of gypsum with low metal content had accumulated on the P2D outflow structures. After February 2011 large amounts of blue precipitate with a high metal content accumulated rapidly on flow gauges and in discharge areas (Table 4.3, Figure 4.1).

Mineralogical analysis of the post-shift precipitate revealed that the precipitate is mostly amorphous material (73.8 %) and gypsum [CaSO₄·2H₂O] (22.0%). Malachite [Cu₂CO₃(OH)₂] was also detected by XRD in small amounts (4.2%). Results from SEM and EDS analyses support the presence of the minerals detected by XRD. The dominant sulfate is gypsum, with little evidence of Cu-Zn sulfates. Copper was observed associated with spheres forming in the amorphous material, possibly as the carbonate malachite. The amorphous material contained variable amounts of Zn, Cu, Si, Al, Mn, Mg, S, and C, among other elements. A thin Cu-Zn-Si layer was observed on some surfaces of gypsum and the bulk amorphous material. Zinc was primarily found associated with Cu in the spheres or associated with Cu and Si in the surficial layer, but was also rarely associated with S.

4.4 Discussion

A potential control on the decline in drainage pH during the 2010-2011 wet season is the depletion of carbonate neutralization capacity within isolated areas in the pile. Mineralogical and elemental analyses indicate that Pile 2 contains very minor (<1%) amounts of carbonates. According to the ABA data, waste rock from Tipping Phase III, which corresponds to Sub-lysimeter C and Field Barrel 2-3A has an NP/AP of 0.14. This signifies that carbonate depletion and acid generation is likely to occur over time. In general, silicate weathering may contribute to pH-buffering following the depletion of carbonate phases. Although this process is effective buffering in terms of moles of proton consumption, it is typically kinetically constrained, and

therefore significantly slower than carbonate dissolution and sulfide oxidation. Previous studies (e.g., Jurjovec et al. (2002), Moncur et al. (2005)) have shown that silicate buffering occurs at significantly lower pH values than what is observed in Pile 2. Evidence of silicate dissolution was inferred based on increased dissolved Si concentrations in effluent from Field Barrel 2-3A and lysimeters P2C and P2D, as well as the presence of Si in the solid-phase precipitate samples from the Pile 2 outflow structures. There is a possibility, then, that there are small zones within the pile where carbonate depletion and silicate weathering are occurring, and that low-pH water from those zones has a strong influence on the overall aqueous geochemistry of the outflow.

A second hypothesis concerning the distinct seasonal pH shift, which is exhibited clearly in the field barrels, is a flushing of the water that remained in storage in the pile for the duration of the dry season. This "dry season" water would have a longer residence time than the component of the water in the wet season which migrates with a higher velocity resulting from macropore flow, increased water content, and ponding-induced increased heads and gradients. Seasonal flushing contributes to the yearly fluctuations in drainage chemistry since 2008, and is more dramatic during the 2010-2011 wet season. A more detailed analysis of the hydrological controls of seasonal flushing on effluent geochemistry for Piles 1, 2, and 3 can be found in Chapter 5.

Localized carbonate depletion and seasonal flushing of lower-pH water may be exaggerated by longer residence times in the finer-grained matrix. Indeed, water discharging from the pile during the 2010-2011 wet season may have had a 2- to 3-year or longer residence time, based upon preliminary tracer-study results. Again, the material in Tipping Phase III not only has lower carbonate content and higher sulfide and Cu content than most of the other tipping phases, but it also relatively fine-grained, increasing pore-water residence time.

The similarities between the aqueous concentrations in lysimeters P2C and P2D – and indeed the strong differences between those lysimeters and the A and B lysimeters – suggest that one material type has a disproportionately strong influence on overall drainage chemistry. Tipping Phase III comprises only about one quarter of the pile by mass and volume, yet drainage chemistry for lysimeter P2D, which is representative of the entire pile, follows the effluent chemistry trends of lysimeter C very closely for pH, Zn and Cu. Field Barrel 2-3A also exhibits concentrations sometimes orders of magnitude higher than seen in the other field barrels. There is a possibility that the sub-type of rock that is present in Field Barrel 2-3A may not necessarily be located in the flow paths above P2C but is creating an acidic environment in certain areas within the pile. Strong spatial variations in pore gas composition in the pile (Singurindy et al., ICARD 2012) also support the hypothesis that small amounts of reactive waste rock may dominate drainage chemistry of much larger areas despite dilution through the pile and at the base.

Variable mineralogy in waste rock also plays a role in drainage chemistry. For example, the presence of siderite as a main carbonate – rather than just calcite or dolomite – complicates the interpretation of net buffering capacity. Iron is released during siderite dissolution and then hydrolyzes, producing acid which counteracts the neutralization from carbonate dissolution. A second example of the importance of mineralogy is the differences in weathering rates and Cu released in chalcopyrite and bornite. The XRD analysis performed for this study has provided baseline knowledge of material mineralogy, and is being complemented by other techniques in order to examine both primary and secondary mineralogy in more detail.

Examples of the techniques that are being used to characterize Antamina minerals include mineral liberation analysis (MLA) (Blaskovich, ICARD 2012), optical microscopy, focused ion

beam transmission electron microscopy (Dockrey 2010), synchrotron methods and extraction methods. Methods such as these can be used to better identify the types and quantities of carbonates in the system in order to refine the forms of NP in this type of waste rock and better characterize the quantities and types of sulfides.

The full-scale dumps at Antamina are still wetting and accumulating water into storage. Concentrations of metals and sulfate in seeps from those dumps also fluctuate with season, but have not shown rapid changes by orders of magnitude such as the ones seen in experimental Pile 2. On-going research is being conducted with laboratory scale experiments, field barrels, experimental piles, and full-scale waste dumps to determine scaling factors that will assist in predictive water quality monitoring.

4.5 Conclusions

The distinct wet and dry seasons at Antamina support discrete periods of high and low water flow through the waste rock. These shifts in flow generally exhibited an inverse relationship with Pile 2 drainage pH, As and Mo concentrations, and a direct relationship with Cu and Zn concentrations. These shifts were gradually more pronounced each year, and after three years became more dramatic, significantly changing solute concentrations within weeks.

Reasons for the shifts may include depletion of carbonate phases, seasonal flushing, and variable residence times among flow paths. The study shows that small amounts of acidic water from reactive material may strongly influence overall outflow chemistry despite dilution with large volumes of less acidic water.

The findings of strong seasonal influences and impacts of reactive zones that have the ability to control the quality of large volumes of water both have important implications for water quality management. Rapid shifts in pH and solute concentrations require flexibility in water management programs and monitoring vigilance, especially at the onset of rainy seasons. The results of this study in combination with other studies and the overall Antamina mine plan are being evaluated to implement appropriate measures. Scenarios are focused on investigating waste rock management strategies in the form of either complete waste segregation, as generally occurs now, or encapsulation and blending. Both scenarios have the objective of localizing the drainage produced from the highly reactive material types that are known to create "hot spots" and minimize the effect of these "hot spots" downstream.
4.6 Tables

Table 4.1. Sur	nmary of ra	pid aqueous com	positional changes in	n Pile 2 basal l	vsimeter outflow.
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Date	Field pH (pH unit)	Dissolved Cu (mg/l)	Dissolved Zn (mg/l)
23-Dec-2010	7.71	0.01	5.9
1-Feb-2011	7.25	2.6	21.4
17-Feb-2011	6.37	67.0	75.3
23-Jun-2011	6.64	4.3	41.9

Table 4.2. Select solid phase analytical results for Pile 2 materials.

Field barrel ID	Tipping Phase	Associated Lysimeter	NP/AP	S (%)	C (%)	As (ppm)	Cu (ppm)	Mo (ppm)	Zn (ppm)
2-0A	Protective layer	P2D	1.49	0.62	0.17	167	3340	265	187
2-1A	Tipping Phase I	P2B	1.90	0.20	0.15	54	612	429	33
2-1B	Tipping Phase I	P2B	0.06	4.26	0.09	21	1710	329	439
2-2A	Tipping Phase II	P2A	0.40	0.64	0.08	70	2680	393	186
2-3A	Tipping Phase III	P2C	0.14	1.56	0.05	228	7140	282	310

Table 4.3. Selected solid phase analysis of P2D precipitate forming on outflow structures in August 2011.

Al	As	С	Ca	Cu	Mn	Мо	Pb	S	Zn
(%)	(ppm)	(%)	(%)	(ppm)	(ppm)	(ppm)	(ppm)	(%)	(ppm)
0.83	1182.33	1.02	6.07	>10000	4960	>4000	666	5.87	>10000

4.7 Figures



Figure 4.1. Accumulation of bright blue precipitate from effluent water.



Figure 4.2. Particle size distributions for the individual tipping phases in Pile 2.



Figure 4.3. Daily and cumulative precipitation and P2D outflow for 2008 to 2011 (top) and 2010 to 2011 (bottom). Precipitation is reported as height of rain, and effluent flow as specific discharge, i.e. volumetric flux normalized to the area of the lysimeter. The apparent decrease in effluent flow in April 2011 is an artifact of abundant precipitation of secondary minerals that blocked the outflow structures. Linear interpolation was used to calculate cumulative outflow during that period.



Figure 4.4. Aqueous geochemistry for Pile 2 lysimeters: (A) pH (B) SO₄ (C) Cu (D) Zn (E) Mo (F) As (G) Si (H) Al.



Figure 4.5. Aqueous geochemistry for Pile 2 field barrels: (A) pH (B) SO4 (C) Cu (D) Zn (E) Mo (F) As (G) Si (H) Al.

Chapter 5: Linking the hydrological and geochemical processes that control mine waste rock effluent water quality

5.1 Introduction

One focus of research and development groups for mines that produce high volumes of waste rock, as many surface mining operations do, is the management of the water that discharges as seeps at the bases of waste rock dumps. Mine managers need to know the timing and volume of effluent discharge water to expect on a seasonal and long-term basis in order to manage handling and storage of effluent water (Chapters 2 and 3). If the effluent water contains high concentrations and/or loads of dissolved metals, managers must also plan for treatment of effluent water prior to re-use in the mine or discharge to the environment. This becomes more challenging if effluent water chemistry undergoes strong seasonal variability (Chapter 4). Several types of active and passive water treatments are currently used for solute removal (e.g., INAP, 2009; Johnson and Hallberg, 2005), and new technologies for treatment and prevention are constantly being researched, developed and improved upon. Eventually, mines may be able to optimize dump construction, combining and stacking waste rock in such a way that mineral weathering is minimized, inhibiting dissolution and mobilization of metals and metalloids, or if solutes are mobilized, that they are then permanently attenuated through precipitation of secondary minerals or sorption (Linklater et al., 2006).

Typical waste dump effluent water quality concerns from sulfide ore deposits include low pH and high sulfate, metal, and metalloid concentrations that result from sulfide oxidation (e.g., Blowes et al., 2003; Evangelou and Zhang, 1995). When the acidity produced from sulfide oxidation is neutralized by carbonate buffering, the resulting effluent water will be pH-neutral,

yet may still contain solutes that are mobile under neutral conditions, including sulfate, oxyanions such as Mo and As, and moderate concentrations of the more mobile trace metals, such as Zn. If the acidity is not neutralized, acid rock drainage perpetuates with sulfide oxidation rates increasing as pH decreases due to increased microbiological activity, and less soluble metals such as Fe, Cu, and, Pb become mobile. Removal of metals and metalloids from the water is solute-specific, and water treatment often involves changing the pH to remove metals from solution (e.g., Cravotta and Trahan, 1999; INAP, 2009; Johnson and Hallberg, 2005). In a system where effluent water ranges from neutral to acidic at different locations in the dump, and several types of metals and metalloids are therefore mobile, it is crucial for mine planners to understand which types of waste rock are prone to release certain solutes and the mechanisms that control the release and attenuation of the solutes within the dump. Additionally, seasonal fluctuations in pH, solute concentrations, and loadings from each of those waste rock types are also important for mine water management.

The variables that contribute to mine waste rock dump effluent water are numerous. Simplified, they include waste rock elemental and mineralogical composition, particle size, hydrological properties, microbiology, and meteorology. Many of the variables are all strongly linked, and while there are ample studies on the geochemistry of acid mine drainage (e.g., Blowes et al., 2003; Moncur et al., 2005) and a growing number of studies on the hydrology of mine waste rock (e.g., Eriksson et al., 1997; Nichol et al., 2005; Neuner et al., 2009; Smith et al., 1995; Smith and Beckie, 2003;), research that seeks a link between the two at a mechanistic level is less abundant (e.g., Sracek et al, 2004; Stockwell et al., 2006; Wagner et al., 2006). Researchers are now using reactive transport modeling, which includes coupled hydrological and geochemical processes, in waste rock settings (Da Silva et al., 2007; Demers et al., 2013; Fala et

al., 2013; Gerke et al., 1998; Gerke et al., 2001; Lefebvre et al., 2001; Linklater et al., 2005; Molson et al., 2005; Stromberg and Banwart, 1994). As researchers begin to compile more evidence regarding the interactions between hydrology, material type, reaction rates, and metal release and attenuation, reactive transport models will become more robust and uncertainty associated with water quality predictions will be reduced.

The objectives of this research are to determine and present seasonal loading and concentration patterns for select solutes for three types of waste rock at the Antamina Mine in Peru, and determine the dominant controls on those patterns. The data for this research comes from three 36 m x 36 m x 10 m experimental piles (Piles 1, 2, and 3), and the reader is referred to Chapter 1 for details on piles construction, material placement, lysimeter and instrumentation locations and nomenclature, sampling, and effluent water collection. The analyses are based on the conceptual hydrological models of the three waste rock types presented in Chapter 2; solid phase geochemical properties from the basal protective layers and all tipping phases; and effluent water aqueous chemistry from the large, 36 m x 36 m D Lysimeters that capture the majority of effluent flow from the experimental piles. The results can be used to assist water management professionals at Antamina and other mines in the prediction of full-scale dump seasonal concentration and loading trends based on material properties; as guidelines in parameter estimation for reactive transport modeling; and eventually in geochemically based waste rock dump optimization.

5.2 Methods

The reader is referred to Chapter 1 for details of piles construction, and locations and nomenclature of lysimeters and instrumentation.

5.2.1 Solid-phase and aqueous chemistry analyses

Solid-phase waste-rock samples from each tipping phase were analyzed to characterize elemental (e.g., solid-phase elemental concentrations and acid-base accounting) and mineralogical properties (e.g., mineralogical assemblages by XRD and Rietveld refinement). The reader is referred to Chapter 4 for waste rock solid phase elemental and mineralogical analysis methods, to Table 5.1 for mineral names and formulae, and to Appendix F for detailed results.

Lysimeter D effluent water was collected and analyzed weekly for 'field parameters' – pH, temperature, dissolved oxygen, and specific conductance (SC) – using a WTW Model 340i multi-parameter meter. On a weekly to monthly basis, additional samples were collected, filtered and acidified as needed, refrigerated, and analyzed for anions, cations, dissolved and total metals, and alkalinity by external laboratories (2007-2009: Envirolab S.A, Lima Peru; 2010-2013: SGS Del Per, S.A.C.). Sampling intervals were shortest in the year following pile construction and gradually became longer as the piles aged.

5.2.2 Calculation of loading rates and minimum sulfide oxidation rates

Mass loading rates $(M_L, \text{mg/(kg·wk)})$ – i.e., the mass of a solute that is released from the pile per kg of waste rock per week – are calculated using the equation

$$M_L = \frac{C * V}{M_{WR}}$$

Eq. 5.1

where *C* is the solute concentration during a given week (mg/L), *V* is the volume of effluent flow for that week (L), and M_{WR} is the mass of the waste rock above the lysimeter (kg). In this chapter, only Lysimeter D loadings are considered because that lysimeter occupies 96.4% of the pile plan view area, collects a similar percentage of pile effluent water, and is considered to be representative of whole-pile processes. Details and comparisons of Pile 2 sub-lysimeter and field barrel aqueous chemistry are presented in Chapter 4.

Minimum sulfide oxidation rates per kg waste rock per second (Ox_s , mol/(kg·sec)) can be estimated from sulfate loadings by first using the molar mass of sulfate (MM_s , mg/mol) to convert sulfate mass loadings ($M_{L,s}$, mg/(kg·wk)) into a sulfate release rate per kg waste rock per second (R_s , mol/(kg·sec)) according to the equation

$$R_{S} = \frac{M_{L,S}}{MM_{S} * 604800 \frac{sec}{week}}$$

Eq. 5.2.

Assuming pyrite as the dominant sulfide in the waste rock, one can then use the pyrite (FeS_2) /sulfate (SO_4) molar ratio to calculate the minimum sulfide oxidation rate.

$$Ox_s = \frac{R_s}{2}$$

Eq. 5.3

There are several assumptions and exclusions that must be considered when examining the results of this estimation.

- Seasonal rates do not account for sulfate storage within the pile during the dry season (i.e., more sulfate is produced than reports to the bottom of the pile) and flushing in the wet season (i.e., additional sulfate that was produced during the dry season reporting to the bottom of the pile).
- 2. The rates do not account for precipitation and dissolution of secondary sulfate minerals such as gypsum, which can have strong concentration controls on aqueous sulfate.
- 3. The rates are based on the sulfur molar ratio for pyrite/sulfate, as opposed to other minor sulfides such as sphalerite or galena, which have different sulfide/sulfate molar ratios.

Acknowledging these limitations, estimated apparent sulfide oxidation rates can be considered minimum rates under the conditions of the experimental piles, and can be useful in the comparison of rates among waste rock material types and as a starting point for more detailed sulfide oxidation rate investigations.

5.2.3 PHREEQC speciation modeling

Speciation modeling was performed using PHREEQC Interactive Version 3.0.0.7430 (Parkhurst and Appelo, 2013) to determine saturation indices (SIs) for the minerals listed in Table 5.2. The simulations employed a database based on WATEQ4F (Ball and Nordstrom, 1991) with revised arsenic data from Nordstrom and Archer (2002). Revised Mo data by Kaback and Runnells (1980), Essington (1990), and Smith and Martell (1976) were compiled and added to the database by Conlan (2009), and revised Mo data from Minteq.v4 (Charlton and Parkhurst, 2002) were compiled and added to the database by Laurenzi (in progress).

The simulations were conducted using the SOLUTION_SPREAD keyword in PHREEQC, which allowed for the import of spreadsheet data containing results from laboratory chemical analyses and field-based temperature and pH from Lysimeter D effluent water. Redox conditions were set to an open system with a $pO_2(g) = 0.21$ atm. Carbonate was inputted from alkalinity measurements except when Pile 2 field pH <5.5, in which case pCO₂ was set to 10^{-3} atm, which is consistent with average pile-internal pore gas compositions.

The computed saturation indices (SIs) for the effluent water were analyzed and mineral phases were flagged as possible solubility controls when $-0.05 \ge SI \le 0.05$; minerals were considered undersaturated with respect to a mineral when SI < -0.05 (lack of solubility control); and supersaturated with respect to a mineral when SI > 0.05 (kinetic inhibition). Minerals tend to dissolve at negative SIs and precipitate at positive SIs.

Although the PHREEQC results are valid for outflow chemistry, they may not be indicative of internal pore-water chemistry at the same temporal scale because of the time required for pore water to flow from the pile. Similarly, results may be skewed in cases of heavy dilution of higher-concentration pore water by lower-concentration fresh water travelling through higher-velocity, lower-reactivity flow paths. Finally, internal pore water chemistry is highly spatially variable due to heterogeneities within waste rock types, as evidenced by solute concentration measurements from soil water solution samplers varying up to several orders of magnitude at various locations throughout the piles (Appendix G).

5.3 Solid phase waste rock material description

Elemental composition and mineralogy of the three material types is the fundamental basis for differences in outflow aqueous geochemistry from the three experimental piles. While solid

phase metal concentrations are not strictly proportional to aqueous concentrations (e.g., Golder 2004) and acid base accounting (ABA) tests are not flawless (e.g., Sherlock et al., 1995), they provide knowledge of possible elements of concern and a rough prediction whether or not acidic conditions can develop.

As an overview of the detailed results discussed below, the marble and hornfels of Pile 1 have relatively low sulfides and high carbonates resulting in high neutralization potential to acid production potential (NP/AP) ratios and low probability of acidic conditions, but some elemental concentrations such as As, Mn, Pb, and Zn are high enough that the possibility of metal release through carbonate and sulfide dissolution nevertheless exists. Pile 2 has very low carbonates and enough sulfides to result in low NP/AP ratios, including three material types with NP/AP<1. The elemental concentrations of As, Cu, Mn, Mo, and Zn are high in the intrusive samples, and are most likely associated with sulfide minerals. Finally, Pile 3 also has relatively low NP/AP ratios with waste rock from two tipping phases with NP/AP<1, and the skarns of that pile have by far the highest elemental concentrations of most metals and metalloids of concern, including As, Cd, Cu, Fe, Mn, Pb, and Zn.

5.3.1 Solid phase elemental compositions

Solid phase elemental composition analyses reveal strong geochemical heterogeneity among waste rock samples from the individual tipping phases of each pile (Table 5.3). This is the case for solid phase sulfides (as represented by S) and carbonates (as represented by C); for solid phase elemental concentrations of metals and metalloids of concern such as As, Cu, Mo, and Zn; and for NP/AP. The aqueous effluent geochemistry, then, presents an integrated picture of the

weathering of all materials – and specifically, highly heterogeneous materials – within a single pile.

Pile 1 waste rock (grey hornfels, black marble, and diopside marble) is consistently net neutralizing (i.e., NP/AP >1), with NP/AP values ranging widely from 5.3 to 291.2. Mo concentrations range from 1.6 ppm (i.e., mg of the element per kg of waste rock) to 104 ppm among tipping phases, and Zn concentrations range from 440 ppm to 2220 ppm. Mn concentrations are highest in the high sulfide-bearing samples, while Zn concentrations are highest in the high carbonate-bearing samples. Samples 1-2A and 1-2B, which represent the Tipping Phase II in Pile 1, are by far the highest in sulfides and lowest in carbonates, with the lowest NP/AP ratios of all Pile 1 waste rock (5.72 and 5.30). This waste rock also has the highest solid phase Mn and Pb concentrations in Pile 1, and was considered by Aranda (2010) to be the most reactive material in Pile 1.

According to NP/AP calculations, Pile 2 intrusives include some materials that are predicted to be net neutralizing (P2-0A and P2-1A) and others that are predicted to be net acid generating (P2-1B, P2-2A, and P2-3A). The sulfur content of Pile 2 samples ranges from 0.20% to 4.26%. The solid phase carbonate content as evidenced by C is very low in Pile 2 (0.05% - 0.17% C), and specifically Ca content, which could be used as a surrogate for calcite, is also very low. For Pile 2 samples, Cd, Cu, Mn, and Zn are all highest in the high-sulfide bearing samples, and there are no strong correlations between concentrations of C and metals of concern.

The skarns of Pile 3 have very high sulfide and metal concentrations, especially for Zn (4980 ppm - 46000 ppm) and Cu (1445 ppm – 23200 ppm). Samples from two tipping phases (represented by Field Barrels P3-1A and P3-2A) are predicted to be net acid producing and the

other three samples are predicted to be net neutralizing according to NP/AP ratios. Due to the combination of comparatively high and consistent sulfide and carbonate contents in the skarn materials, correlations between solid phase metals, sulfides, and carbonates are not clear.

5.3.2 Solid phase mineralogical compositions

Mineralogical analysis of Pile 1 waste rock was completed using Mineral Liberation Analysis (minimum detection limit 0.01 wt%) by Randy Blaskovich (Teck Metals) and was presented by Aranda (2010) and summarized by Bay (2009). The Pile 1 waste rock is dominated by carbonates with calcite being the most abundant carbonate by far (Table 5.4; see Section 5.10 for mineral formulae). Silicates are also abundant in Pile 1 waste rock, including feldspars, quartz, pyroxene, and clay minerals. Samples contain between 0.5 wt.% and 4.5 wt.% sulfides. Pyrite is the most abundant sulfide and chalcopyrite is the second most abundant. The diopside marble waste rock from Tipping Phase II (samples 1-2A and 1-2B) is anomalous; it is comparatively low in carbonates (11.1%), high in silicates (82.2%), and high in sulfides (4.5%).

The XRD method used to characterize Piles 2 and 3 mineralogy detects only crystalline minerals, and has a higher minimum quantification limit (0.1 wt%) and lower precision than the MLA technique used for Pile 1 mineralogical analysis (0.01 wt%). Nevertheless, the XRD method is sufficient for baseline mineralogical characterization, and elucidates the strong geochemical heterogeneities within the intrusive and skarn lithologies, which are illustrated in Figure 5.1.

Pile 2 intrusive waste rock samples (Table 5.5) are dominated by quartz and orthoclase feldspars with significant plagioclase feldspars. The dominant sulfides in the intrusive samples are pyrite and chalcopyrite. A molybdenite peak is present in the diffractograms for most samples, but the calculated weight percent of that mineral is usually less than 0.05%, which is below the

minimum detection limit. The only carbonate detected in some of the intrusive samples is siderite (0.0% -0.5%). Micas, oxides, amphiboles, and diopsides are present in some of the samples. Sample 2-1B is mineralogically similar to skarns, with a high percentage of the garnet andradite, lower percentage of orthoclase feldspar, and very high sulfide content.

Pile 3 skarn waste rock samples (Table 5.5) are dominated by the garnets andradite and grossular and the disilicate vesuvianite. Diopside is also a significant mineral in all of the samples. The skarns contain variable amounts of other silicates and carbonates. Calcite was detected in all samples, and siderite and pyroaurite were each detected in one sample. The dominant sulfides in the skarns are pyrite, sphalerite, and pyrrhotite (which is the first and fastest sulfide to weather, Moncur et al. (2005)). Molybdenite was detected only in sample 3-0A.

5.4 Results

Salient results from the aqueous geochemical analysis completed for Piles 1, 2, and 3 include mass loading and sulfide oxidation rates, seasonal peak concentration timing, correlation of effluent concentrations and flow rates, and PHREEQC speciation modeling.

5.4.1 Mass loading and sulfide oxidation

For all experimental piles, highest mass loadings occur during times of peak flows (Stage II) in January through April for almost all solutes (Figure 5.2). One exception to this pattern is Mn loadings in Pile 1, which tends to be highest during the first flush (Stage I) from October through December.

The ranges between minimum and maximum loading rates differ by about one to two orders of magnitude between the wet and dry seasons for most solutes in all three piles (Table 5.6). A

major exception to loading fluctuations is Cu loadings in Pile 2, which vary up to six orders of magnitude between the wet and dry seasons in 2010-2011.

5.4.2 Peak concentration timing

Peak solute concentration patterns for the three materials are much more complex than peak loading patterns (Figure 5.3). Depending on the material type and the solute, concentrations peak when effluent flow begins to increase during Stage I; at peak flows during Stage II, or when flows are lowest at the end of Stage III.

In general, Pile 1 solute concentrations peak at the end of Stage III when flows are lowest (Figure 5.4). Exceptions to this behavior are Mo and Sb concentrations, which are generally highest during peak flows in Stage II. Pile 1 pH does not exhibit strong seasonal patterns save occasional decreases throughout Stage III and increases throughout Stage II. Clearly observable longer-term concentration trends for Pile 1 are gradually decreasing Mg and Sb concentrations.

Peak solute concentration timing is complex in Pile 2. Concentrations of the oxyanion-forming elements Mo, As, and to a lesser extent, Sb, are highest during the Stage I first flush just before peak flows begin in Pile 2 (Figure 5.5). Concentrations of Cd also increased during Stage I in November-December 2009, but in subsequent years increased with peak flows during Stage II. The concentrations Mo, As, and Sb typically decrease rapidly at the beginning of Stage II. The majority of solute concentrations are highest during Stage II, including Cd, Cu, Mn, Se, SO₄, and Zn. Pile 2 Mg concentrations are highest at the end of Stage III. Pile 2 pH is lowest during Stage II at lowest flows.

Longer-term trends for Pile 2 include rapidly decreasing pH; moderately to rapidly increasing Cd, Cu, Mg, Mn, SO₄ and Zn concentrations; several years of steadily increasing Mo concentrations, followed by a rapid decrease during Stage II in 2013; and steadily decreasing Sb concentrations. In general, As concentrations also decline throughout the study period, which is consistent with the tendency for As to sorb at lower pH. Starting in August 2012, however, As concentrations begin to gradually increase to maximum levels in May 2013, and a definitive long-term trend for that solute was not yet apparent by that time.

Pile 3 concentrations are generally highest at the end of Stage III at lowest flows, similar to Pile 1 (Figure 5.6). Concentrations of Se and Pb are sometimes highest during Stages I and II, and Mo concentrations tend to decrease during Stage II. Pile 3 pH remains circumneutral through the study period and does not fluctuate seasonally. Notable longer-term concentration trends in Pile 3 are steady decreases in Se, Mn, and Pb concentrations and increases in Mo concentrations.

When comparing solutes among the three piles side by side, the difference between peak concentration patterns is striking. While alkalinity and Mg concentrations are highest for all three piles at the end of Stage III (Figure 5.7), peak concentrations of most other solutes are not consistent among the piles. For example, Cd, Cu, Mn, SO₄, and Zn concentrations all peak during Stage II in Pile 2, but they peak during Stage III for Pile 1 (Mn, Zn, and SO₄) and/or Pile 3 (Cd, Cu, and Zn; Figure 5.8, 5.9, and 5.10). Concentrations of Mo peak during Stage I in Pile 2 and during Stage II for Pile 1 (Figure 5.10). These behaviors result from both hydrological controls such as degree of matrix and preferential flow and geochemical controls such as pH and secondary mineral precipitation and dilution, as discussed in Section 5.5.

5.4.3 Correlation of effluent properties and solute concentrations

The pH range in Pile 1 is relatively narrow and always circumneutral, so seasonal solute concentration fluctuations are not strongly correlated with changes in pH (Figure 5.11). Dissolved Mg and Zn concentrations increase linearly with increasing specific conductance, and dissolved SO₄ and Ca, which may be evidence of Ca-Mg and Ca-Zn solid solutions. Dissolved Mn concentrations increase exponentially with increasing dissolved Ca. Dissolved Mn concentrations also increase with specific conductance and dissolved SO₄, and are only high at low effluent flow rates.

Pile 2 dissolved Cd, Co, Cu, Mn, and Zn concentrations are all strongly positively correlated with specific conductance and dissolved SO₄ and are highest at low pH values (Figure 5.12). The same metal concentrations are negatively correlated with alkalinity. Dissolved As concentrations are positively correlated with bicarbonate alkalinity and negatively correlated with specific conductance and SO₄. None of the metals of interest have notable relationships with dissolved Ca. It is difficult to discern meaningful relationships between effluent flow and dissolved solutes from the Figure 5.12 cross plots because solute concentrations vary significantly from year to year resulting from long-term geochemical trends, while effluent flow rates are consistent from year to year. Effluent flow rates versus dissolved solutes for individual flow years provide clearer evidence of the increase of Cd, Co, Cu, Mn, and Zn with increasing flow rates and the very strong inverse relationship between those solutes and pH (Figure 5.13). Following the pattern of the dissolved metals on a yearly basis, increasing SO₄ and SC is observed with increasing flow and decreasing pH, and the opposite pattern occurs for alkalinity (Figure 5.14).

Pile 3 dissolved Co, Mg, Mn, and Zn concentrations are positively correlated with specific conductance and negatively correlated with effluent flow (Figure 5.15). None of the dissolved metals have notable relationships with bicarbonate alkalinity, dissolved Ca, or dissolved SO₄, which – under the assumption that metals are dissolving from sulfides – is strong evidence of sulfate precipitation in the pile. Like Pile 1, the range of pH values in Pile 3 is relatively narrow and always circumneutral, and there does not appear to be a strong relationship between pH and dissolved solutes.

5.4.4 PHREEQC speciation modeling

Speciation calculations were performed in order to better understand what minerals may be precipitating and attenuating metals through the seasons and over the years. Effluent water saturation indices with respect to minerals from Table 5.2 are presented in four groups: oxides, hydroxides, and molybdates; carbonates; sulfates; and silicates. Only minerals with saturation indices higher than -2 are shown graphically and discussed. The saturation indices of all other minerals listed in Table 5.2 are less than -2. The PHREEQC speciation results for those minerals can be found in Appendix H.

5.4.4.1 Pile 1

Graphical results from PHREEQC speciation modeling for Pile 1 are in Figure 5.16.

5.4.4.1.1 Pile 1 oxides, hydroxides, and molybdates

Pile 1 effluent water is supersaturated with respect to goethite throughout the course of the study and regardless of the season. It is supersaturated or at equilibrium with respect to Fe (III) hydroxide, suggesting that this phase provides solubility control for Fe. Pile 1 effluent water is always slightly undersaturated with respect to wulfenite (SI \sim -2.0 to 0.0), and more undersaturated with respect to powellite and amorphous zinc hydroxide (SI<-1.5), suggesting a weak solubility control for Pb and Mo, but no mineral solubility control for Zn.

5.4.4.1.2 Pile 1 carbonates

Pile 1 effluent water is near equilibrium with respect to calcite and undersaturated with respect to dolomite, rhodochrosite, smithsonite, strontianite, and hydrous zinc carbonate. Pile 1 effluent water approaches equilibrium with respect to rhodochrosite (SI~ -2.5 to 0.0) and hydrous zinc carbonate (SI~ -1.0 to 0.0) during Stage III. These results suggest active pH-buffering by calcite dissolution, and potentially seasonally limited attenuation of Mn and Zn through the formation of secondary carbonate phases.

5.4.4.1.3 Pile 1 sulfates

Pile 1 effluent water is undersaturated with respect to all sulfates (including metal sulfates, e.g., ZnSO₄ and CuSO₄) except for gypsum and occasionally jarosite. The effluent is near equilibrium with respect to gypsum throughout the course of the study, with slight seasonal variations: a tendency towards supersaturation during the dry seasons and undersaturation during the wet seasons. These results strongly suggest that gypsum acts as a solubility control for SO₄, and that SO₄ release rates are not representative of sulfide weathering rates. The variations of the SIs may be indicative of gypsum accumulation during the dry season, and re-dissolution during the wet season.

5.4.4.1.4 Pile 1 silicates

Pile 1 effluent water is highly supersaturated with respect to zinc silicate and undersaturated with respect to amorphous SiO_2 throughout the course of the study and regardless of the season. While the Zn-silicate $ZnSiO_3$ is highly supersaturated in all piles during all three flow stages, it likely does not precipitate in that form under the temperatures and pressures in the experimental piles. However, it is shown here as a surrogate for Zn-silicates that are believed to be precipitating based on mineralogical evidence (see Section 5.5.2.2).

5.4.4.2 Pile 2

Graphical results from PHREEQC speciation modeling for Pile 2 are in Figure 5.17.

5.4.4.2.1 Pile 2 oxides, hydroxides, and molybdates

Pile 2 effluent water is supersaturated with respect to goethite throughout the course of the study and regardless of the season. It is slightly supersaturated with respect to Fe (III) hydroxide, especially during the wet seasons (SI ~ 2.0), and can be closer to equilibrium during the dry seasons (SI ~ 0.0). Similar to Pile 1, these results suggest that Fe (III)-hydroxides provide a solubility control for Fe. Pile 2 effluent water is undersaturated with respect to Cu hydroxide until January 2011, when the saturation index of that mineral increases and remains near equilibrium (SI ~ -1.0 to 0.0) for the remainder of the study period. Pile 2 effluent water becomes more undersaturated with respect to amorphous zinc hydroxide, is consistently supersaturated with respect to wulfenite throughout the course of the study, and is generally at equilibrium or slightly supersaturated with respect to powellite. These results indicate that powellite may provide a solubility control for Mo in Pile 2, with limited solubility controls for Cu, and no solubility controls for Zn and Pb, by oxides and hydroxides.

5.4.4.2.2 Pile 2 carbonates

From January 2008 to January 2011, Pile 2 effluent water is at equilibrium or supersaturated with respect to rhodochrosite (SI ~ 0.0-2.0), and at equilibrium or undersaturated with respect to with respect to calcite, dolomite, azurite, malachite, smithsonite, otavite, strontianite, and hydrous zinc carbonate. In January 2011, the saturation indices of most of those minerals remain stable or decrease and the saturation indices of the copper carbonates malachite and azurite dramatically increase (SI ~ 0.0 to 6.0), suggesting strong solubility controls on Cu. The original seasonal trend of rhodochrosite saturation (i.e., higher saturation indices in the wet season, and lower indices in the dry season) is inverted in January 2011. In January 2012, there is a sharp increase in Cu carbonate saturation indices and coincident sharp decrease in all other carbonate saturation indices, suggesting constant solubility controls on Cu through variable minerals, possibly as a result of mixing of waters from spatially variable locations within the pile (Section 5.5.2.2).

Calcite is most definitely dissolving and not precipitating at the pH values in Pile 2, so any instances where the SI> 0 are likely a result of CO_2 degassing during sampling and before pH measurement because site sampling procedures do not include flow-through cells. This would result in slightly higher pH values in the effluent water than in the pore water, and hence slightly higher calcite saturation indices. At later times, the calcite saturation indices are also affected by calcite depletion.

5.4.4.2.3 Pile 2 sulfates

Pile 2 effluent water is near equilibrium with respect to gypsum throughout the course of the study, with no apparent seasonal variation. Beginning in January 2011, Pile 2 effluent water becomes supersaturated with respect to antlerite and brochantite (SI \sim 0.0 to 8.0), suggesting that sulfates also provide solubility controls on Cu in Pile 2. For both of those minerals, saturation indices tend to be highest during the wet seasons. Jarosite saturation indices also increase in 2011, reaching equilibrium or supersaturation mostly during the wet seasons.

5.4.4.2.4 Pile 2 silicates

Pile 2 effluent water is supersaturated with respect to zinc silicate and undersaturated with respect to amorphous SiO_2 throughout the course of the study and regardless of the season. The saturation index of dioptase increases starting in January 2011 but does not reach equilibrium.

5.4.4.3 Pile 3

Graphical results from PHREEQC speciation modeling for Pile 3 are in Figure 5.18.

5.4.4.3.1 Pile 3 oxides, hydroxides, and molybdates

Pile 3 effluent water is supersaturated with respect to goethite, Fe (III) hydroxide, and wulfenite (wulfenite SI ~ 0.5 to 1.5) throughout the course of the study and regardless of the season. It is undersaturated with respect to amorphous zinc hydroxide, copper hydroxide, and powellite (all SIs ~ -2.0 to -1.0) throughout the course of the study and regardless of the season. These results suggest solubility controls on Fe by hydroxides and on Pb and Mo by wulfenite.

5.4.4.3.2 Pile 3 carbonates

Pile 3 carbonate saturation indices are usually higher during the dry seasons and lower during the wet seasons. Effluent water is near equilibrium with respect to calcite, smithsonite, and hydrous zinc carbonate throughout the course of the study. It is slightly undersaturated with respect to dolomite and otavite throughout the course of the study. Long term trends for Pile 3 effluent water include a shift from supersaturation to undersaturation with respect to rhodochrosite (from SI ~ 0.5 to SI ~ -1.5) and a less-dramatic shift from slightly supersaturated to slightly undersaturated with respect to cerrusite (from SI ~ 0.2 to SI ~ -0.5), which could be due to depletion of Mn and Pb in the source, or for Pb could be due to preferential sequestrations onto wulfenite due to changes in the Pb/Mo ratios. Finally, a shift from undersaturated to near-equilibrium with respect to malachite occurs through the study period (from SI ~ -1.5 to SI ~ -1.5 to SI ~ 0.0), suggesting a possible solubility control on Cu by carbonates.

5.4.4.3.3 Pile 3 sulfates

Pile 3 effluent water is near equilibrium with respect to gypsum throughout the course of the study with no apparent seasonal variation, suggesting a constant solubility control on SO_4 . Saturation indices of antlerite, brochantite, jarosite, and anglesite are generally below saturation, although jarosite sometimes reaches equilibrium with no distinct seasonal pattern.

5.4.4.3.4 Pile 3 silicates

Pile 3 effluent water is supersaturated with respect to zinc silicate and undersaturated with respect to amorphous SiO_2 throughout the course of the study and regardless of the season.

5.5 Discussion

Seasonal variations in solute loadings and concentrations are affected by the accumulation of solutes in pore water during the dry season. All three piles have much slower flow velocities and longer residence times during Stage III (Chapter 2), so accumulation of solutes (and therefore higher concentrations) in the pore water can be expected during that time. The time required for pore water to flow through the pile to the effluent drainage points is hydrologically controlled and material-specific, though, resulting in variable seasonal concentration patterns. Pore-water accumulation and effluent release of solutes are just two of several factors that affect seasonal concentration trends, which are also complicated by dilution at the bases of the piles, secondary mineral formation, pH, and sorption.

Another possible explanation for observed highly variable seasonal concentrations and loading trends could be seasonally variable sulfide oxidation rates. For all three piles, however, there is very little internal evidence of seasonal fluctuation in sulfide reaction rates. That is, ambient and internal temperatures do not vary by more than one or two degrees seasonally (Appendix I), oxygen is readily available year-round at all points within the piles (with the possible exception of isolated areas in Pile 2 during the wet season; Lorca, in progress; Singurindy et al., 2012) and sufficient water for oxidation is available year-round (with the possible exception of surficial regions near the slopes of Pile 1 during the dry season; Chapters 2 and 3). Therefore, it is not likely that sulfide oxidation varies significantly from season to season, and variation in oxidation rate with season is not believed to provide a major control on seasonal concentration patterns.

5.5.1 Seasonal loading trends

Mass loadings are controlled by flow volume regardless of internal flow regimes: the higher the effluent flows, the more water is moving through the pile and the more accumulated solutes are transported through and released from the pile. Highest loadings during Stage II peak flows prevail for all solutes in all three piles, with the exception of Mn in Pile 1. The occasional Stage I peak in Mn loadings is most likely due to the extreme seasonal variation in Mn concentrations in Pile 1 – i.e., more than two orders of magnitude difference between the wet and dry seasons (Figure 5.4), most likely affected by the dissolution and precipitation of rhodochrosite. In this case, seasonal Mn concentration variability is on the same order of magnitude as flow variability, so concentrations do significantly contribute to the timing of peak loadings. All other cases where concentrations fluctuate seasonally by several orders of magnitude are in Pile 2, where concentrations and flows are both highest during Stage II, augmenting loadings during that stage up to six orders of magnitude for Cu over Stage III loadings.

The seasonal numbers are strongly skewed by hydrological processes, especially the delay in sulfate release from the piles and they are likely not representative of actual seasonal pyrite oxidation rates. Furthermore, PHREEQC speciation calculations suggest that effluent water is supersaturated with respect to gypsum year-round for Piles 2 and 3 and seasonally for Pile 1. Gypsum is likely providing a solubility control on sulfate, then, resulting in underestimated pyrite oxidations rates.

5.5.2 Seasonal concentration trends

Acknowledging relatively consistent year-round sulfide oxidation rates and accumulation of solutes due to longer residence times in the dry season for all three piles, it is proposed that the

sometimes dramatically different seasonal fluctuations in effluent sulfate and dissolved metal and metalloid concentrations observed among the piles are controlled by a combination of the following factors:

- the displacement of high concentration water that accumulates during periods of lower flow and longer residence times through matrix flow paths, both through uniformvelocity flow paths and as bleeding/pistoning from slower velocity flow paths into higher velocity flow paths (Chapter 2);
- 2. dilution at the base of the pile: higher-concentration water travelling through lowervelocity flow paths diluted by lower-concentration fresh water travelling through highvelocity, low-reactivity flow paths (Chapter 2);
- seasonal fluctuations in pH resulting from variations of CO₂ degassing as a function of the fluctuations in air permeability caused by changes in moisture content (Appendix J);
- 4. attenuation and release of dissolved solutes through secondary mineral precipitation/dissolution and sorption/desorption; and
- seasonal pH fluctuations resulting from secondary mineral precipitation/dissolution reactions (Appendix K).

Through the observation and comparison of solute concentrations and loadings, mineral saturation indices, and the tracer study and hydrologic patterns described in Chapter 2, it is possible to determine the relative degree of influence of the mechanisms on seasonal concentration trends.

5.5.2.1 Pile 1

As expected based on longer residence times and accumulation of solutes during the dry season, Pile 1 concentrations increase throughout the dry season and are highest at the end of Stage III. Based on the dominant inverse relationship between solute concentrations and mass loadings, it is hypothesized that the consistent Stage II concentration decreases observed in Pile 1 are strongly controlled by the dilution of higher-concentration water at the base of the pile by water flowing to the base through high-velocity, low-reactivity flow paths. Evidence of the presence of these higher-velocity flow paths is observed in the tracer study and specific conductance results outlined in Chapter 2 and is supported by Bay (2009).

Pile 1 speciation calculations suggest that the precipitation and dissolution of secondary minerals do not strongly influence pH and rarely influence seasonal fluctuations in metal concentrations. The speciation results for goethite and Fe (III) hydroxide indicate active formation of amorphous or low-crystalline forms of Fe hydroxides year-round, which act as sorption sites for metals as discussed below. One mineral saturation index that does exhibit seasonal trends in Pile 1 is gypsum, which is prone to precipitate during Stage III (Figure 5.16) most likely as a result of longer residence times and higher solute accumulation during that stage. Gypsum is prone to dissolve during Stage II, which differs from the constant year-round equilibrium with respect to gypsum that is observed in Piles 2 and 3. This is indicative that the overall sulfide oxidation rate is lower in Pile 1 than in Piles 2 and 3 (i.e., higher oxidation rates induce year-round gypsum precipitation in the latter two piles), which is consistent with estimates (Table 5.6). Gypsum dissolution may add to SO₄ and Ca loadings during Stage II in Pile 1.

Although Pile 1 effluent water is generally undersaturated with respect to rhodochrosite and hydrous zinc carbonate, the SIs of those minerals do approach equilibrium during Stage III. There is a possibility that these minerals provide intermittent solubility controls for Mn and Zn in Pile 1. Furthermore, secondary rhodochrosite dissolution during the first flush of the wet season likely contributes to peak Mn loadings during Stage I.

While the Zn-silicate ZnSiO₃ is highly supersaturated during all three flow stages and could then be considered a solubility control on Zn, it likely does not precipitate in that form under the temperatures and pressures in the experimental piles and has been shown as a surrogate for other Zn-silicates that have been observed. However, in Pile 1 at circum-neutral pH the sources of aqueous silica – primary silicates – are likely not weathering rapidly and secondary silicate controls on metals are less likely than they are, for example, in Pile 2 (Section 5.5.2.2).

Two solutes that may experience seasonal attenuation through weak sorption in Pile 1 are the oxyanion-forming elements Mo and Sb. Concentrations of those solutes are low and seasonal patterns are not as distinct as they are for some other solutes, but it appears that Mo and Sb concentrations peak during Stage II flows. Since pH is the major sorption control, and Pile 1 does not undergo strong seasonal pH transitions, it is hypothesized that the decrease of solid to water ratio (e.g., Limousin et al., 1997; Plante et al., 2010) may be responsible for the desorption of Mo and Sb during Stage II. Sorption is also likely attenuating metals such as Cd, Cu, and Zn – all of which have a high tendency for surface complexation at circumneutral pH (e.g., Stumm and Morgan, 1996; Figure 5.19) – during both the wet and dry seasons. Sorption may therefore be an important factor in the mobility of those metals prone to surface complexation in Pile 1, but does not have a strong influence on seasonal concentration trends of due to relatively consistent seasonal pH trends.

There are no strong seasonal pH fluctuations caused by CO_2 degassing in Pile 1 because the coarse materials comprising the pile permit air flow (Chapter 3) preventing CO_2 accumulation even at higher moisture contents during the wet season (Lorca, in progress). The seasonal secondary mineral precipitation/dissolution trends in Pile 1 for gypsum, wulfenite, rhodochrosite, and hydrous zinc carbonate have the potential to cause minor seasonal pH fluctuations, but acid neutralization through primary carbonates in that pile dominate the pH of the system and a circumneutral pH is maintained in Pile 1 through both the wet and dry seasons.

5.5.2.2 Pile 2

Pile 2 effluent solute concentrations trends are complex, and are influenced most strongly by seasonal flushing of high-concentration pore waters through relatively uniform-velocity matrix flow paths and seasonal pH shifts caused by CO₂ degassing and acid buffering sequences from primary and secondary minerals. Attenuation and release of metals through secondary mineral precipitation/dissolution and sorption/desorption also likely play roles in seasonal concentration fluctuations in Pile 2, and those reactions may contribute to minor seasonal changes in pH as well.

The relatively matrix flow that dominates the hydrology of Pile 2 is likely the strongest control on the seasonal concentration patterns observed in Pile 2. The smooth bromide breakthrough curves of Pile 2 during the wet season following tracer study application (Chapter 2, Figure 2.7) supports the hypothesis that accumulated dry season pore water is flushed out through flow paths with a relatively narrow range of velocities during the wet season. Another line of evidence is an inverse relationship between internal electrical conductivity (EC) and volumetric moisture content (VMC) during the wet season (Figure 5.20). Solutes accumulate during the dry season when flows are low, as evidenced by high internal EC. That water is flushed out and displaced by fresh (low EC) water during the wet season. Furthermore, the strong positive correlations between Cd, Co, Cu, EC, Mn, SO₄, and Zn with effluent flow rates also suggest solute flushing during the wet season. Finally, based on sparse evidence of preferential flow in Pile 2 observed from the tracer study, it is evident that basal dilution of higher-concentration water by lowerconcentration water travelling through preferential flow paths does not have a significant impact on Pile 2 seasonal concentration trends.

Based on Pile 2 seasonally variable internal CO₂ concentrations (Singurindy et al., 2012) and the strong correlations between solute loadings and pH (Figure 5.12-5.14), it is hypothesized that seasonal concentration fluctuations are also controlled by pH changes that result from seasonal CO₂ fluctuations in the pile. Specifically, internal CO₂ concentrations increase substantially in the wet season as pile moisture contents increase, inhibiting CO_2 loss to the atmosphere and driving the pile towards a closed system resulting in lower pore water pH values (Lorca, in progress; Appendix J). Conversely in the dry season, moisture content decreases, internal CO₂ concentrations decrease, and CO₂ degassing to the atmosphere occurs more readily, resulting in higher pore water pH. In support of this hypothesis, two PHREEQC simulations were conducted that simulate the dissolution of calcite in contact with a pH 3 sulfuric acid solution under two different pCO₂ conditions of 10^{-3} atm and 10^{-2} atm (Appendix J), which are representative of wet and dry season pCO₂ values within Pile 2, respectively (Lorca, in progress). The simulations yield pH values of 7.9 and 7.2 for these conditions, respectively, supporting the argument that CO₂ degassing within the pile during the dry season can lead to pH increases exceeding 0.5 pHunits. This is also consistent with what is seen in the internal pCO₂ and pH effluent data. The

fluctuations in pH in turn have significant impacts on metal attenuation and release by secondary mineralization and sorption, as discussed below.

Speciation calculations suggest that the precipitation and dissolution of secondary minerals play significant roles in metal attenuation and release in Pile 2. After the rapid pH decrease in January 2011, Pile 2 effluent water became supersaturated with respect to several Cu-bearing minerals, including copper hydroxide (Cu(OH)₂), carbonates (malachite and azurite), and sulfates (antlerite and brochantite). The saturation index of the Cu silicate dioptase, a secondary mineral that forms in the oxidized zones of some copper deposits (Mindat.org, 2013) is generally undersaturated or nearing equilibrium, but XRD analysis showed the presence of dioptase in one of the P2D effluent precipitate samples (Chapter 4), so some precipitation of that mineral within the pile is also likely.

Secondary mineralization can also partially explain the high concentrations of Cu released from the pile during each wet season. The Cu released from primary sulfides during the first several years after pile construction were likely being sequestered inside the pile by the precipitation of Cu carbonates and hydroxy-carbonates in areas of highly reactive material (in which supersaturation and precipitation would not be represented by the composite effluent flow PHREEQC simulations). With the depletion of primary carbonates and the subsequent pH drop in January 2011, the secondary carbonates likely began to dissolve, augmenting Cu concentrations and loadings. That is, elevated wet-season concentrations that originate from flushing of high concentration accumulated waters from the previous dry season are enhanced by the re-dissolution of secondary Cu-carbonates and hydroxides due to lower pH conditions present under the higher wet-season moisture contents.

It is hypothesized that these processes are not properly represented in the Pile 2 Lysimeter D PHREEQC speciation calculations, to some extent because of the hydrological delay of pore water arrival to the lysimeters, and to a greater extent because of the strong spatial heterogeneity in that pile and subsequent mixing of variable-composition water at the base. Since material in the outer tipping phase (represented by Field Barrel 2-3A and Sub-lysimeter C) is so much more reactive than the material in the rest of the pile (Chapter 4; Singurindy et al., 2012), and because the effluent water pH from that material is much lower than in other materials (Chapter 4; Laurenzi, in progress) it is likely that secondary mineral dissolution and precipitation reactions are different in that area of the pile, and that the Lysimeter D speciation calculations are a representation of mixing of waters at the base of the pile in addition to processes occurring in the pore water in spatially distinct regions in the pile. This hypothesis can be tested by carrying out mixing calculations involving outflow waters from field barrels representing the different tipping phases. It is found that the effect of mixing low-pH, high-concentration 2-3A water with higherpH, lower concentration water is profound and results in supersaturation with respect to Cubearing sulfates and carbonates (Appendix L). Notably, the same phases that are found to be supersaturated in the effluent of Lysimeter D are identified by these mixing calculations. The Pile 2 speciation calculations from Lysimeter D, then, present a composite picture of solubility controls at the base of the pile, once mixing has already occurred.

One implication of this finding is that the presence of copper carbonates provides – if only temporarily and on a minor scale – sustained carbonate buffering capacity in the pile through secondary carbonates even after primary carbonates have been depleted or passivated, as well as a sustained source of Cu. Eventually, secondary Cu-sulfates will also re-dissolve, releasing additional Cu. After complete re-dissolution of these phases, Cu loading rates are expected to

decrease, but will remain substantial and be representative of Cu-sulfide weathering rates within the pile.

Zn-bearing carbonates (smithsonite and ZnCO₃:H₂O) are supersaturated in Pile 2 speciation calculations and are therefore likely solubility controls on Zn concentrations, whereas Znsulfates likely are not. As noted before, while the Zn-silicate ZnSiO₃ is highly supersaturated during all three flow stages, it likely does not precipitate in that form under the temperatures and pressures in the pile but is included here as a surrogate for other secondary Zn-silicates that have been observed in Pile 2 and in the full-scale waste rock dumps. Scanning Electron Microscopy (SEM) has revealed surficial associations between Zn and Si in Pile 2 (Appendix F). Additionally, in a concurrent study, Laurenzi (in progress) has observed mineralogical evidence that the hydrated Zn-silicate hemimorphite may be precipitating as a secondary mineral within the full-scale waste rock dumps at Antamina. The lower pH likely leads to higher primary silicate weathering in Pile 2 than the other piles, possibly providing a source of aqueous silica and increasing the likelihood of Zn (and Cu) solubility controls by secondary silicates.

The precipitation of wulfenite and possibly powellite may control Mo and Pb mobility in Pile 2, as water is supersaturated with respect to both of those minerals. Related studies at Antamina and elsewhere have demonstrated evidence of the solubility controls of powellite and wulfenite on Mo and Pb in both laboratory (Conlan et al., 2012; Petrunic et al., 2006) and field settings (Hirsche, 2012). The computed supersaturation of Pile 2 effluent water with respect to rhodochrosite suggests that secondary rhodochrosite may be a solubility control on Mn, at least through the first several years after construction. Seasonally variable saturation indices suggest rhodochrosite precipitation through Stages II and III and dissolution during Stage I, but again the

delay of the hydrology and spatial differences in material types and mixing complicate the interpretation of the reactions occurring within the pore water.

In addition to the PHREEQC speciation calculations, direct observations of metal-bearing secondary mineral precipitates is observed in the Pile 2 effluent water every year during Stage II (Chapter 4). The predominantly amorphous precipitates have extremely high metal concentrations, and Synchrotron analyses suggest that Cu is mostly associated amorphously with SO₄, and to a lesser degree with the crystalline carbonates malachite and azurite (Matt Lindsay, personal communication; Chapter 4). These observations are consistent with the SI calculations and mixing calculations discussed above. These solid carbonate, hydroxy-carbonate, and hydroxyl-sulfate precipitates form rapidly and abundantly in effluent flow structures, which is likely enhanced by CO₂ degassing and increased pH in effluent waters once exiting the pile (Appendix J).

In addition to clear long-term pH drops resulting from depletion of buffering minerals (5.5.3; Chapter 4) and dry season increases in pH resulting from CO_2 degassing, dissolution and precipitation of secondary minerals may also contribute to both seasonal and long-term pH trends (Javadi, in progress). Since different aqueous species are dominant at different pH values and since there are so many simultaneous processes occurring in Pile 2 (e.g., precipitation and dissolution of antlerite, azurite, brochantite, jarosite, malachite, rhodochrosite, and wulfenite), it is difficult to determine the net effect of the combined reactions, but an example of the precipitation and dissolution of jarosite is given here to elucidate possible effects of secondary mineralization on pore water pH (Appendix K). At pH 4, 5, and 6 the dominant Fe species in solution is Fe $(OH)_2^+$ and the dominant dissolution-precipitation reaction for jarosite is pH – neutral:
$$KFe^{3}(OH)_{6}(SO_{4})^{2} < = > K^{+} + 3Fe(OH)_{2}^{+} + 2SO_{4}^{2-}$$

Eq. 5.4

At pH 4, the minor Fe species is $Fe(OH)_2^+$, and jarosite dissolution increases pH, while jarosite precipitation generates acidity:

$$KFe^{3}(OH)_{6}(SO_{4})^{2} + 3H^{+} < = >K^{+} + 3Fe(OH)_{2}^{+} + 3H_{2}O + 2SO_{4}^{2-}$$

Eq. 5.5

At pH 6, when the minor Fe species is $Fe(OH)_3$ and jarosite tends to dissolve, the opposite occurs; jarosite dissolution generates acidity:

$$KFe^{3}(OH)_{6}(SO_{4})^{2} + 3H_{2}O < = >K^{+} + 3Fe(OH)_{3} + 3H^{+} + 2SO_{4}^{2-}$$

Eq. 5.6

The dissolution and precipitation of jarosite and other mineral phases with seasonal fluctuations in observed SIs may therefore impact pore-water pH.

The Pile 2 secondary mineral system is temporally and spatially complex. The dominant cause for the drop in effluent pH is primary buffering mineral depletion (Chapter 4; Section 5.5.3) and the less dramatic dry season increases in pH that are very likely caused by CO_2 degassing, but there is also a possibility that seasonal precipitation and dissolution of secondary minerals such as the jarosite example above also contributes to the seasonal pH patterns observed in the effluent water. Since sorption through surface complexation is highly-pH dependent, the significant seasonal pH shifts in Pile 2 caused likely drive seasonal sorption and desorption, contributing to seasonal solute concentration fluctuations. Additionally, sorption increases with clay mineral content, which is higher in intrusive waste rock than marble, hornfels, or skarn. In a concurrent sequential leaching study of Antamina waste rock, Laurenzi (in progress) observed Zn released in the amorphous and crystalline iron oxide extraction steps of sequential leaches of similar waste rock, indicating that Zn is likely sorbed to iron oxides.

Pile 2 effluent pH drops to approximately pH 6 during the 2011-2012 wet season, does not reach more than 6.5 in the following dry season, and drops to 4.5 in the 2012-2013 wet season. At those lower pH values, sorption on substrates such as iron oxides plays a minor role in Zn and Cd attenuation, but is still a major factor in Cu attenuation (Figure 5.19). It is hypothesized that pH-controlled sorption and desorption of Zn and Cd contribute to seasonal concentration trends during the carbonate buffering stage and until pH decreases to about pH 5.5 to 6. At lower pH values, the magnitude of seasonal Zn and Cd may decrease as seasonal fluctuations in pH have less of an impact on sorption and desorption.

Additional metals that may be affected by sorption onto iron oxides in Pile 2 are As, Mo, and Sb. The concentrations of these metals increase during Stage I, when Pile 2 pH values are at their highest and when solid to solution ratios drop. As effluent pH drops in Stage II, concentrations of As, Mo, and Sb decrease, indicating that, as expected, higher sorption at lower pH values likely controls oxyanion mobility in that pile (Stumm and Morgan, 1996).

5.5.2.3 Pile 3

Similar to Pile 1, the dominant seasonal inverse relationship between concentrations and loadings suggests that seasonal concentration patterns in Pile 3 are strongly controlled by basal dilution of higher-concentration water travelling through lower-velocity flow paths by lower-concentration water that reaches the bottom of the pile through high-velocity, low-reactivity pathways. Although the majority of Pile 3 by volume is fine-grained material and therefore has longer residence times and high solute accumulation, the boulders in the outer slope of that pile strongly influence the overall hydrology, contributing to fast preferential flow (Chapter 2) and increasing dilution at the bottom of the pile.

Additionally, the broader particle size distribution in Pile 3 contributes to a slightly wider range of matrix flow velocities (Chapter 2). Displacement of accumulated higher-solute pore water through variable-velocity matrix pathways may lead to more complex seasonal concentration fluctuations in the outflow.

PHREEQC speciation analyses suggest that solute attenuation and release through precipitation and dissolution of secondary minerals also contribute moderately to Pile 3 seasonal concentrations. Specifically, the hydrous zinc carbonate ZnCO₃:H₂O is prone to precipitate during the dry season and dissolve during the wet season, providing a solubility control on aqueous Zn. Seasonal SI fluctuations in the non-hydrated polymorph smithsonite are similar, but slightly lower, suggesting equilibrium during the dry season and dissolution during the wet season. An implication is that Zn concentrations during the dry season may be lower than expected based on sulfide oxidation rates. Pile 3 results also indicate formation of amorphous or low-crystalline forms of Fe hydroxides year round, providing sorption sites for other metals and metalloids. Pile 3 water is occasionally supersaturated with respect to jarosite, but the circumneutral pH of Pile 3 likely inhibits jarosite precipitation. Effluent waters are consistently undersaturated with respect to powellite, suggesting that Mo mobility is not likely controlled by the precipitation and dissolution of powellite in skarns. Wulfenite is prone to precipitate year-round, however, possibly limiting both Mo and Pb mobility in that pile. Another solubility control for Pb in the skarns is cerrusite, with precipitation of the mineral more likely in the first several years after pile construction and dissolution more likely in the second half of the study period.

Similar to Pile 1, Pile 3 has relatively consistent circumneutral pH year round, so surface complexation likely plays an important control on metal mobility – for example Zn and Cu sorption to iron oxides – without contributing to seasonal concentration fluctuations. Sorption may be a factor, however, on seasonal concentrations of weakly-sorbed oxyanion-forming elements such as Se in Pile 3 skarns. Concentrations of Se increase during Stages I and II, indicating easily-exchangeable sorption most likely controlled by decreasing solid to solution ratios.

While CO₂ concentrations in Pile 3 do vary seasonally (Appendix J) the variations as of the end of the study period have not been strong enough to induce the open system/closed system degassing that partially controls pH fluctuations in Pile 2. This is likely due to lower sulfide oxidation rates and a higher degree of air circulation. Finally, primary carbonate mineral buffering maintains a year-round circumneutral pH in Pile 3.

5.5.3 Notable long-term trends

Observable long-term concentration trends for Pile 1 are gradually decreasing Mg and Sb concentrations. The decrease in Mg may be an indication of gradual depletion of dolomite, of which low quantities are present in Pile 1 (Table 5.4). The decrease in Sb is likely from depletion of a primary Sb-bearing sulfide such as stibnite (Sb₂S₃) or watanabeite (Cu₄(As,Sb)₂S₅).

The most striking long term trend for Pile 2 is the rapidly decreasing pH that results from primary carbonate depletion. The carbonate content in Pile 2 waste rock is very low (<1%) and the only carbonate detected by XRD was siderite, which is likely a primary mineral due to its very low saturation index (Appendix H), and the dissolution of which is not necessarily net neutralizing (Chapter 4). Considering the low pH values observed in effluent flow water (as low as pH 4.5, and possibly even lower in internal pore water than effluent water; Chapter 4), it is likely that "hot spots" in the pile are completely depleted of primary carbonate buffers, so the main buffering minerals in those areas have likely become secondary carbonates (e.g., malachite, and rhodochrosite), primary and secondary hydroxides (e.g., alumino-hydroxides, ferrihydrite, and goethite). As each of the minerals becomes depleted (with the highest reactivity carbonates first and the slowest reactivity silicates last), the pH of the effluent waters will drop sequentially (e.g., pH 6-7 for carbonates, pH 4.0-4.5 for alumino-hydroxides, pH 3.5 and pH 2.5 for ferrihydrite and goethite; Blowes et al., 2003; Jurjovec et al., 2002, 2003, 2004). The buffering sequence is complicated by secondary carbonate buffering as discussed earlier.

Coincident with the decreasing pH in Pile 2 are moderately to rapidly increasing Cd, Cu, SO₄ and Zn concentrations, likely resulting from increasing dissolution of metal-bearing primary

sulfides as internal pile temperatures rise and acidophilic microbial populations thrive; previously attenuated metals released from the dissolution of secondary carbonates and sulfates; and decreasing sorption at lower pore water pH. Increasing Mg concentrations in Pile 2 likely result from increasing dissolution of primary silicates at lower pH values.

Concentrations of Mn also increase through the study period in Pile 2. The primary mineralogical source of Mn is unknown, but it is hypothesized that the source of Mn is not a primary carbonate (rhodochrosite) because if that were the case a decrease, not increase, in Mn concentrations would be expected as carbonate depletion occurred. It is possible that isolated areas of the pile are abundant in primary rhodochrosite and that mineral has still not been depleted in those areas, or that Mn is associated with sulfides and/or silicates, which both appear to be dissolving at increasing rates.

Mo and Se concentrations held steady for several years in Pile 2 and are decreasing as of 2013 as pH decreases and oxyanion sorption increases. A long-term implication is that there is a persistent, pH- and redox-dependent source of Mo and Se within the pile that could desorb and become mobile if pore water pH were to increase.

Notable long-term concentration trends in Pile 3 include an increase in Mo concentrations, likely resulting from increased molybdenite oxidation or from saturation of sorption sites. Conversely, Se and Pb concentrations steadily decrease through the study period. The decrease in Pb may be caused by a depletion of the primary sulfide galena, by increasing Mo concentrations and subsequent sequestration of Pb through the precipitation of wulfenite, or by immobilization through another secondary phase. The primary source of Se is unknown in skarns for this study, but the gradual decrease in concentrations of that element suggests that the primary mineral is

likely becoming depleted. Mn concentrations rapidly decrease within two years of Pile 3 construction, which is likely a result of primary rhodochrosite depletion.

Finally, while Pile 3 skarns are not as carbonate-rich as the marble and hornfels of Pile 1, there are enough primary carbonates in the skarns to have maintained circumneutral pore water in that pile through the end of the study period. However, certain areas of the pile have very low primary carbonate concentrations, and almost all samples have very high sulfide and metal concentrations (Table 5.3). It is therefore possible that sulfide oxidation will still be occurring if carbonates are passivated or depleted. If that occurs, the acid buffering sequence including secondary carbonates, and primary and secondary hydroxides and silicates discussed above would be initiated. The resulting sequential pH drops would affect CO₂ and metal release, secondary mineralization and sorption. These processes might then become the dominant controls on concentrations over dilution, and dramatic decreases in pH and corresponding increases in solute concentrations could occur.

5.6 Conclusions

Seasonal concentration and loading patterns for dissolved solutes are strongly controlled not only by solid phase elemental, mineralogical, and physical characteristics of waste rock, but also by the flow regimes in each material type and the three flow stages that result from Antamina's distinct wet/dry-season climate (Chapter 2). Sulfide oxidation rates are not highly variable on a seasonal basis.

Solute loadings are controlled mostly by flow volume and are almost always highest during Stage II, when flows are highest from about January through April. The exception is when seasonal concentrations fluctuations are on the same order of magnitude as seasonal flow fluctuations and peak solute concentrations do not occur during peak flow periods, such as the case of Mn in Pile 1.

Seasonal concentration patterns are much more complex and result from both hydrological and geochemical forcings (Figure 5.21). Significant differences in seasonal concentrations result from internal flow regimes, which are in turn strongly controlled by material grain size distribution. For a pile with greater percentages of high-velocity, low-reactivity preferential flow (i.e., Pile 1 marble and hornfels and Pile 3 skarns), seasonal concentrations are controlled most strongly by basal dilution. That is, higher-concentration water that accumulates solutes as it travels through lower-velocity paths is diluted at the base by lower concentration water that travels through higher-velocity, lower-reactivity flow paths with low solute accumulation save minor 'bleeding in' of higher concentration water from the finer-grained matrix. The result is higher solute concentrations and lower solute loadings during the dry season, and lower solute concentrations and higher solute loadings during the wet season. Conversely, for relatively homogeneous finer-grained material (i.e., Pile 2 intrusives) seasonal concentration fluctuations are controlled by pore water accumulation of solutes during the dry season followed by matrix flushing during the wet season with little dilution as the base by low-concentration preferential flow water. The result is lower solute loadings and concentrations during the dry season and higher solute loadings and concentrations during the wet season.

The seasonal fluctuations in moisture content in Pile 2 create shifts from an open system to a closed system with CO_2 degassing to the atmosphere occurring during the dry season. This phenomenon was simulated using PHREEQC, the results of which suggest an increase of more than a half a pH unit when degassing from internal wet season CO_2 concentrations (10⁻³ atm) to

dry season CO₂ concentrations (10^{-2} atm; Appendix J; Lorca, in progress). The effect is aggravated in Pile 2 both by fine grain sizes and high oxidation rates.

Solute concentrations are also controlled by the dissolution and precipitation of secondary minerals. This is especially true for Pile 2 minerals, in particular Cu-bearing carbonates and sulfates. The dry-season effect of pH increases with CO₂ degassing and mixing of spatially variable concentration waters at the base of Pile 2 complicate the secondary mineralization processes. The effect of CO₂ degassing on secondary mineral precipitation and dissolution is evidenced by rapid accumulation of high metal-bearing predominantly amorphous precipitates in the Pile 2 outflow structures after atmospheric interaction (Chapter 4) and is supported by PHREEQC simulations (Appendix J). Secondary mineral precipitation and dissolution also affect solute concentrations, including on a seasonal level, in Piles 1 and 3, but to a lesser extent than in Pile 2. In all three piles, precipitation of secondary minerals may lead to persistent long-term metal, metalloid, and sulfate sources in waste rock dumps, as well as additional sources of carbonate buffering and hydroxide buffering after primary carbonates have been depleted.

Sorption onto actively forming iron oxides is controlled most strongly by pH and to a lesser extent by seasonal changes in solid to solution ratios, and likely plays a role in the attenuation and release of metals and metalloids. Sorption impacts the attenuation of Zn and Cu in all three piles, but likely only plays a strong role in seasonal concentration fluctuations of those elements in Pile 2 when the pH fluctuates between about 5.5 and 7. In circum-neutral Piles 1 and 3, sorption of Zn and Cu likely remains constant year-round. Oxyanions are also likely controlled by sorption in all three piles, and seasonal concentrations of As, Mo, Sb, and Se tend to increase either during the first flush (Stage I) or to a lesser extent during peak flows (Stage II). The long-term transition towards acidic conditions in Pile 2 likely results from carbonate depletion and subsequent acid buffering sequences discussed above and in Chapter 4. If carbonates were to become passivated or depleted and hot-spots of high acid generation were to develop in Pile 3 (which is possible for some skarn sub-types based on NP/AP ratios), high solute loadings and concentrations, including Cd, Cu, Mn, Mo, and Zn, may occur and pH-related processes could become the dominant controls on seasonal concentration fluctuations.

This project serves to increase our holistic understanding of the geochemical processes controlling effluent water chemistry – including metal release and attenuation through primary and secondary mineralogical assemblages and sorption, as well as acid production and neutralization – in light of the hydrology that partially controls them. The links between hydrological and geochemical processes in waste rock are extremely complex. They are highly site- and scale-dependent, and involve multiple interacting, temporally and spatially variable processes that are difficult to characterize. Semi-empirical models based on site-specific observations will likely continue to be instrumental to predictive efforts. The up-scaling of findings from smaller scale studies (laboratory and field barrel) to larger-scale studies (experimental piles) and to the operational waste dump scale is the logical next step in this research. The increased understanding of the connections between hydrological and geochemical processes through this and similar research is key to the implementation and assessment of viability of those efforts.

5.7 Tables

Table 5.1. All referenced mineral names and formulae

Mineral Name	Mineral Formula
Actinolite	Ca ₂ (Mg,Fe) ₅ Si ₈ O ₂₂ (OH) ₂
Albite	NaAlSi ₃ O ₈
Amorphous silicate	SiO ₂ (a)
Amorphous zinc hydroxide	Zn(OH) ₂ -a
Anglesite	PbSO ₄
Anorthite	CaAl ₂ Si ₂ O ₈
Antlerite	Cu ₃ (OH) ₄ SO ₄
Aragonite	Ca(CO) ₃
Azurite	$Cu_{3}(CO_{3})_{2}(OH)_{2}$
Biotite	K(Mg,Fe) ₃ AlSi ₃ O ₁₀ (F,OH) ₂
Bornite	Cu ₅ FeS ₄
Brochantite	Cu ₄ (OH) ₆ SO ₄
Calcite	CaCO ₃
Cerrusite	PbCO ₃
Chalcanthite	CuSO ₄ ·5H ₂ O
Chalcopyrite	CuFeS ₂
Chlorite	$(Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2 \cdot (Mg,Fe)_3(OH)_6$
Copper (I) sulfate	Cu_2SO_4
Copper (II) sulfate	CuSO ₄
Copper carbonate	CuCO ₃
Copper hydroxide	Cu(OH) ₂
Dioptase	CuSiO ₃ ·H ₂ O
Diopside	MgCaSi ₂ O ₆
Dolomite	CaMg(CO ₃) ₂
Galena	PbS
Goethite	FeOOH
Goslarite	ZnSO ₄ :7H ₂ O
Gypsum	CaSO ₄ ·2H ₂ O
Hydrous zinc carbonate	ZnCO ₃ :H ₂ O
Hydrous zinc sulfate	ZnSO ₄ :H ₂ O
Fe (III) hydroxide	Fe(OH) ₃
Jarosite-K	(K _{0.77} Na _{0.03} H _{0.2})Fe ₃ (SO ₄) ₂ (OH) ₆
Kaolinite	$AI_2Si_2O_5(OH)_4$
K-Feldspar	KAISi ₃ O ₈
Magnetite	Fe ₃ O ₄
Malachite	Cu ₂ CO ₃ (OH) ₂
Manganese (II) sulfate	MnSO ₄
Manganese (III) sulfate	$Mn_2(SO_4)_3$
Melanterite	FeSO ₄ :7H ₂ O
Molybdenite	MoS ₂
Muscovite	$KAI_2(Si_3AI)O_{10}(OH,F)_2$
Otavite	CdCO ₃
Powellite	CaMoO ₄
Pyrite	FeS ₂
Pyrrhotite	$Fe_{(1-x)}S(x=0-0.17)$

Mineral Name	Mineral Formula
Quartz	SiO ₂
Realgar-Orpiment	AsS - As_2S_3
Rhodochrosite	MnCO ₃
Siderite	FeCO ₃
Smithsonite	ZnCO ₃
Sphalerite	(Zn,Fe)S
Strontianite	SrCO ₃
Titanite	CaTiSiO₅
Watanabeite	Cu ₄ (As,Sb) ₂ S
Wulfenite	PbMoO ₄
Zinc silicate	ZnSiO ₃
Zincosite	ZnSO ₄

Mineral Name	Mineral Formula
Amorphous silicate	SiO ₂ (a)
Amorphous zinc hydroxide	Zn(OH) ₂ -a
Anglesite	PbSO ₄
Antlerite	Cu ₃ (OH) ₄ SO ₄
Aragonite	Ca(CO) ₃
Azurite	Cu ₃ (CO ₃) ₂ (OH) ₂
Brochantite	Cu ₄ (OH) ₆ SO ₄
Calcite	CaCO ₃
Cerrusite	PbCO ₃
Chalcanthite	CuSO ₄ ·5H ₂ O
Copper (I) sulfate	Cu ₂ SO ₄
Copper (II) sulfate	CuSO ₄
Copper carbonate	CuCO ₃
Copper hydroxide	Cu(OH) ₂
Dioptase	CuSiO ₃ ·H ₂ O
Dolomite	CaMg(CO ₃) ₂
Goethite	FeOOH
Goslarite	ZnSO ₄ :7H ₂ O
Gypsum	CaSO ₄ ·2H ₂ O
Hydrous zinc carbonate	ZnCO ₃ :H ₂ O
Hydrous zinc sulfate	ZnSO ₄ :H ₂ O
Fe (III) hydroxide	Fe(OH) ₃ (a)
Jarosite-K	(K _{0.77} Na _{0.03} H _{0.2})Fe ₃ (SO ₄) ₂ (OH) ₆
Malachite	Cu ₂ CO ₃ (OH) ₂
Manganese (II) sulfate	MnSO ₄
Manganese (III) sulfate	$Mn_2(SO_4)_3$
Melanterite	FeSO ₄ :7H ₂ O
Otavite	CdCO ₃
Powellite	CaMoO ₄
Rhodochrosite	MnCO ₃
Siderite	FeCO ₃
Smithsonite	ZnCO ₃
Strontianite	SrCO ₃
Wulfenite	PbMoO ₄
Zinc silicate	ZnSiO ₃
Zincosite	ZnSO ₄

Table 5.2. Minerals examined for PHREEQC speciation analysis.

	As	Ca	Cd	Cu	Fe	Mn	Мо	Pb	Zn	S	С	AP	NP	NP/AP
	ppm	%	ppm	ppm	%	ppm	ppm	ppm	ppm	%	%	tCaCO3/ 1000t	tCaCO3/ 1000t	
Pile 1														
P1-0A	194	31.6	3.82	845	1.06	589	9.8	852	2220	0.15	8.71	4.7	769	163.6
P1-0B	74	33.1	1.26	331	0.67	348	1.6	255	525	0.12	9.14	3.8	838	220.5
P1-1A	73	29.1	1.40	878	1.33	836	104.0	366	653	0.26	6.72	8.1	605	74.7
P1-2A	41	18.9	1.59	824	3.51	2240	43.0	1010	590	1.11	1.58	34.7	184	5.3
P1-2B	47	19.5	1.19	610	3.58	2360	52.6	634	440	0.98	1.62	30.6	175	5.7
P1-3A	34	32.6	3.34	642	1.57	762	62.8	730	1360	0.65	7.91	20.3	707	34.8
P1-4A	23	36.1	1.51	203	0.29	205	5.7	170	528	0.11	11.10	3.4	990	291.2
							Р	ile 2						
P2-0A	167	1.3	<0.02	3340	1.57	698	265.0	33	187	0.62	0.17	19.4	29	1.5
P2-1A	54	0.8	<0.02	612	1.00	461	429.0	20	33	0.20	0.15	6.3	12	1.9
P2-1B	21	5.5	1.39	17100	10.10	1715	329.0	51	439	4.26	0.09	133.1	8	0.1
P2-2A	70	1.0	<0.02	2680	1.49	467	393.0	36	186	0.64	0.08	20.0	8	0.4
P2-3A	228	1.5	0.14	7140	3.22	763	282.0	30	310	1.56	0.05	48.8	7	0.1
							P	ile 3						
P3-0A	67	19.3	15.45	1445	7.00	2660	306.0	1220	6850	2.48	1.00	77.5	126	1.6
P3-1A	36	15.8	40.00	6180	12.30	2120	132.0	101	16000	7.53	0.25	235.3	36	0.2
P3-2A	77	17.2	71.90	11900	13.00	1910	68.3	202	28600	9.28	1.04	290.0	135	0.5
P3-3A	1050	21.7	44.40	23200	6.20	2200	156.0	1290	46000	1.52	3.06	47.5	366	7.7
P3-4A	46	21.0	13.60	2050	8.98	3260	115.5	487	4980	1.11	0.67	34.7	122	3.5

Table 5.3. Solid phase elemental composition and acid-base accounting results for waste rock in Piles 1, 2, and 3.

	1-0A & 1-0B (wt	1_1Δ	1-24 & 1-2B (wt	1-34	1-40				
	%)	(wt %)	-2A & 1-2D (wt. %)	(wt %)	(wt %)				
	70)	Sulfide	20	(₩ 70)	(Wit: 70)				
Bornite	0.00	0.02	0.00	0.00	0.00				
Galena	0.00	0.02	0.00	0.06	0.00				
Sphalerite	0.00	0.00	0.00	0.00	0.01				
Chalconvrite	0.00	0.20	0.10	0.21	0.07				
Pyrrhotite	0.11	0.00	0.73	0.00	0.07				
Realgar-Orniment	0.00	0.00	0.00	0.00	0.00				
Watanabeite	0.00	0.00	0.00	0.00	0.00				
Pvrite	0.19	0.72	3 42	1 49	0.49				
Molybdenite	0.00	0.04	0.05	0.01	0.00				
Others	0.00	0.03	0.01	0.00	0.00				
Total sulfides	0.00	1.98	4 53	2 44	0.67				
	0.10	Carbon	1.00	2.11	0.07				
Calcite	55.22		10.51	65 50	90.61				
Otavite	0.00	0.00	0.00	0.00	0.01				
Siderite	0.00	0.00	0.00	0.00	0.00				
Dolomite	0.01	0.00	0.04	0.02	0.00				
Others	0.04	0.05	0.01	0.00	0.12				
Total carbonates	55.63	47.54	11.04	65.67	90.78				
Total carbonates	00.00	Silicot	11.04	00.07	50.70				
Piotito	1.60	1 50	0.54	1 / 2	1 22				
Diulite	1.00	1.50	0.04	1.42	1.32				
K Foldenor	0.30	7.06	12.00	0.04	0.11				
Koolinito	0.52	7.00	13.00	2.50	0.30				
Mugaovito	0.00	0.23	0.20	0.00	0.04				
Diagioglass	5.21	2.06	0.00	0.17	1.04				
Playiociase	7.04	<u> </u>	5.55 15./3	5.70	1.99				
	8 30	8.73	0.78	2.02	1.43				
Mico	0.30	2.12	5.16	2.91	0.42				
Titanita	4.00	0.12	0.88	0.34	0.42				
Others	5.89	17.05	32.00	12 02	0.13				
Total silicates	41.00	/0.57	82.03	30.96	8.01				
Total Silicates	41.00	Phoenby	02.20	50.50	0.01				
Total phosphatas	1.04	Phospha		0.30	0.00				
Total phosphates	1.04	0.35	0.43	0.30	0.09				
F. O	4.00	Oxides/Hyd		0.05	0.00				
Fe-Oxynydroxides	1.09	0.35	1.21	0.25	0.33				
Others	0.10	0.04	80.0	0.03	0.01				
l otal	1.40	0.00	4.00	0.00	0.04				
oxides/hydroxides	1.19	0.39	1.29	0.28	0.34				
Sulfates									
Fe-Sulfate	0.32	0.06	0.35	0.17	0.04				
Gypsum	0.01	0.00	0.00	0.01	0.00				
Others	0.00	0.00	0.00	0.00	0.00				
I otal sulfates	0.33	0.07	0.35	0.18	0.05				
		Other	S						
Total others	0.35	0.13	0.14	0.17	0.07				
Total	100.00	100.00	100.00	100.00	100.00				

Table 5.4. Pile 1 mineralogy in weight percent (wt. %), as determined by Mineral Liberation Analysis and reported by Aranda (2010). For Pile 1 analysis, a value of 0.00 means that there is a trace of <0.01 wt.%.

	2-0A	2-1A	2-1B	2-2A	2-3A	3-0A	3-1A	3-3A	3-4A	
	(wt.%)									
Sulfides										
Chalcopyrite	1.2	0.8	4.1	1.0	2.4	N/D	N/D	N/D	N/D	
Molybdenite	<0.05	0.1	<0.05	<0.05	<0.05	0.1	N/D	N/D	N/D	
Pyrite	0.5	0.5	5.0	0.7	2.7	1.3	9.0	0.1	0.7	
Pyrrhotite	N/D	N/D	N/D	N/D	N/D	0.7	0.2	0.6	0.3	
Sphalerite	N/D	N/D	N/D	N/D	N/D	0.8	0.4	1.9	0.8	
Total sulfides	1.7	1.3	9.2	1.8	5.2	2.8	9.6	2.7	1.7	
Carbonates										
Calcite	N/D	N/D	N/D	N/D	N/D	4.6	2.8	30.7	7.8	
Pyroaurite	N/D	0.6	N/D							
Siderite	0.2	0.2	N/D	0.5	N/D	N/D	N/D	N/D	0.2	
Total carbonates	0.2	0.2	N/D	0.5	N/D	4.6	2.8	31.3	8.0	
			Silic	ates						
Actinolite	N/D	N/D	1.4	N/D	1.0	N/D	N/D	N/D	N/D	
Albite	2.8	2.8	1.5	6.7	1.0	<0.05	0.7	N/D	0.9	
Albite low, calcian	N/D	N/D	N/D	N/D	N/D	2.9	0.5	N/D	0.4	
Andradite	1.0	N/D	22.1	2.1	8.5	37.7	44.7	22.1	36.7	
Biotite	3.3	2.8	2.1	3.0	2.0	N/D	N/D	N/D	N/D	
Clinochlore	N/D	N/D	N/D	N/D	N/D	0.5	N/D	N/D	N/D	
Diopside	N/D	1.9	N/D	N/D	2.7	10.8	13.1	10.3	11.8	
Grossular	N/D	N/D	N/D	N/D	N/D	14.4	15.1	10.7	22.4	
Hemimorphite	N/D	3.1	N/D							
Kaolinite	1.1	1.0	N/D	1.6	N/D	N/D	N/D	N/D	N/D	
Microcline	N/D	3.7	N/D							
Muscovite	2.3	2.2	N/D	N/D	0.9	N/D	N/D	N/D	N/D	
Oligoclase	8.4	6.4	6.1	8.7	6.2	N/D	N/D	N/D	N/D	
Orthoclase	41.9	42.3	22.4	40.1	34.2	11.2	3.6	N/D	1.5	
Phlogopite	N/D	N/D	N/D	N/D	N/D	0.6	N/D	N/D	N/D	
Quartz	37.3	38.8	31.9	35.7	35.2	3.2	5.4	3.2	0.9	
Vesuvianite	N/D	N/D	N/D	N/D	N/D	7.5	3.0	7.6	14.7	
Wollastonite	N/D	N/D	N/D	N/D	2.1	3.9	1.4	5.3	1.0	
Total silicates	98.0	98.3	87.4	97.8	93.9	92.6	87.6	66.1	90.2	
Oxides/hydroxides										
Ferrihydrite	N/D	0.2	N/D							
Magnetite	N/D	N/D	3.4	N/D	0.7	N/D	N/D	N/D	N/D	
Total oxides/hydroxides	N/D	0.2	3.4	N/D	0.7	N/D	N/D	N/D	N/D	
			Sulf	ates						
Melanterite	N/D	N/D	N/D	N/D	0.2	N/D	N/D	N/D	N/D	
Total sulfates	N/D	N/D	N/D	N/D	0.2	N/D	N/D	N/D	N/D	
Total	100.0	100	100.0	100.0	100.0	100.0	100.0	100.0	100.0	

Table 5.5. Piles 2 and 3 mineralogy reported in weight percent (wt. %) as determined by XRD. N/D is 'not detected'.

		Cu	Мо	SO ₄	Zn	FeS ₂					
		mg/(kg•wk)	mg/(kg•wk)	mg/(kg•wk)	mg/(kg•wk)	mol/(kg•sec)					
Pile 1											
2007-08	Min	2.0 x 10 ⁻⁷	4.0 x 10 ⁻⁷	6.1 x 10 ⁻²	5.4 x 10⁻⁵	5.3 x 10 ⁻¹³					
2007 00	Max	4.1 x 10 ⁻⁵	6.9 x 10 ⁻⁵	3.5	4.4 x 10 ⁻³	3.0 x 10 ⁻¹¹					
2008-09	Min	2.6 x 10 ⁻⁷	5.8 x 10 ⁻⁷	6.5 x 10 ⁻²	9.7 x 10 ⁻⁵	5.6 x 10 ⁻¹³					
2000 00	Max	1.8 x 10 ⁻⁵	2.6 x 10 ⁻⁵	2.2	2.8 x 10 ⁻³	1.9 x 10 ⁻¹¹					
2000-10	Min	4.3 x 10 ⁻⁷	7.0 x 10 ⁻⁷	1.2 x 10 ⁻¹	1.4 x 10 ⁻⁴	1.0 x 10 ⁻¹²					
2003-10	Max	3.1 x 10 ⁻⁵	2.7 x 10 ⁻⁵	1.8	3.5 x 10 ⁻³	1.5 x 10 ⁻¹¹					
2010-11	Min	2.0 x 10 ⁻⁷	2.5 x 10 ⁻⁷	4.5 x 10 ⁻²	6.9 x 10 ⁻⁵	3.9 x 10 ⁻¹³					
2010 11	Max	1.2 x 10 ⁻⁵	4.7 x 10 ⁻⁵	2.7	3.3 x 10 ⁻³	2.3 x 10 ⁻¹¹					
			Pile	2							
2008-00	Min	1.92 x 10 ⁻⁵	1.81 x 10 ⁻⁴	1.19 x 10 ⁻¹	4.28 x 10 ⁻⁴	1.0 x 10 ⁻¹²					
2000-03	Max	5.81 x 10 ⁻⁴	1.82 x 10 ⁻²	5.15	3.40 x 10 ⁻²	4.4 x 10 ⁻¹¹					
2000-10	Min	8.70 x 10 ⁻⁶	9.00 x 10 ⁻⁴	2.29 x 10 ⁻¹	6.82 x 10 ⁻⁴	2.0 x 10 ⁻¹²					
2003-10	Max	1.07 x 10 ⁻³	2.14 x 10 ⁻²	4.86	5.63 x 10 ⁻²	4.2 x 10 ⁻¹¹					
2010-11	Min	1.78 x 10 ⁻⁷	6.19 x 10 ⁻⁴	1.16 x 10 ⁻¹	3.68 x 10 ⁻⁴	9.9 x 10 ⁻¹³					
2010 11	Max	1.55 x 10 ⁻¹	2.37 x 10 ⁻²	4.33	1.79 x 10 ⁻¹	3.7 x 10 ⁻¹¹					
2011-12	Min	1.61 x 10 ⁻⁴	6.59 x 10 ⁻⁴	1.51 x 10 ⁻¹	2.59 x 10 ⁻³	1.3 x 10 ⁻¹²					
2011 12	Max	4.43 x 10 ⁻¹	1.41 x 10 ⁻²	4.48	1.85 x 10 ^{⁻1}	3.9 x 10 ⁻¹¹					
2012-13	Min	2.05 x 10 ⁻³	3.10 x 10 ⁻⁴	1.46 x 10 ⁻¹	6.55 x 10 ⁻³	1.3 x 10 ⁻¹²					
2012 10	Max	2.30	1.25 x 10 ⁻²	1.36 x 10 ⁺¹	5.65 x 10⁻¹	1.2 x 10 ⁻¹⁰					
			Pile	3							
2008-09	Min	6.57 x 10 ⁻⁶	1.52 x 10 ⁻⁶	1.08 x 10 ⁻¹	3.32 x 10 ⁻³	9.3 x 10 ⁻¹³					
2000 00	Max	2.34 x 10 ⁻⁴	6.44 x 10 ⁻⁵	7.23	8.49 x 10 ⁻²	6.2 x 10 ⁻¹¹					
2009-10	Min	1.30 x 10 ⁻⁵	1.35 x 10 ⁻⁶	2.08 x 10 ⁻¹	5.41 x 10 ⁻³	1.8 x 10 ⁻¹²					
2000 10	Max	3.73 x 10 ⁻⁴	8.70 x 10 ⁻⁵	8.21	1.38 x 10-1	7.1 x 10 ⁻¹¹					
2010-11	Min	1.14 x 10 ⁻⁵	1.44 x 10 ⁻⁶	1.36 x 10 ⁻¹	4.41 x 10 ⁻³	1.2 x 10 ⁻¹²					
2010 11	Max	1.92 x 10 ⁻⁴	8.70 x 10 ⁻⁵	6.13	7.84 x 10 ⁻²	5.3 x 10 ⁻¹¹					
2011-12	Min	7.70 x 10 ⁻⁷	1.64 x 10 ⁻⁷	1.43 x 10 ⁻²	2.37 x 10 ⁻⁴	1.2 x 10 ⁻¹³					
	Max	2.10 x 10 ⁻⁴	6.37 x 10 ⁻⁵	4.24	5.51 x 10 ⁻²	3.6 x 10 ⁻¹¹					
2012-13	Min	8.56 x 10⁻ ⁶	2.05 x 10 ⁻⁶	1.46 x 10⁻¹	2.36 x 10 ⁻³	1.3 x 10 ⁻¹²					
2012-10	Max	5.27 x 10 ⁻⁴	9.03 x 10 ⁻⁵	6.76	6.19 x 10 ⁻²	5.8 x 10 ⁻¹¹					

 Table 5.6. Mass loadings (mg solute/(kg waste rock • week)) for selected solutes, and estimates of

 minimum pyrite oxidation rates (mol pyrite/(kg waste rock • sec)).

5.8 Figures



Figure 5.1. Bulk mineralogy of samples from Piles 2 and 3, reported in weight % and determined by XRD.



Figure 5.2. Mass loadings are generally highest during the peak flow season (Stage II) from January through April for all three piles. The exception is Mn loadings in Pile 1, which are highest during the first flush from October through December (Stage I).



Figure 5.3. Solute concentrations for Piles 1, 2, and 3.



Figure 5.4. Pile 1 solute concentrations, exhibiting strong seasonal variability with most solute concentrations highest at the end of Stage III (upper graph), with the exception of Mo and Sb concentrations, which are generally highest during Stage II (lower graph). The consistent Mo concentrations of 0.01 mg/L and 0.02 mg/L until mid-2009 are an artifact of laboratory measurement precision. Data points below the minimum detection limit for Mo (<0.01 mg/L prior to mid-2009) are not shown.



Figure 5.5. Pile 2 solute concentrations are highly variable, with peak solute concentrations occurring during Stage I (upper graph), Stage II (middle graph), and Stage III (lower graph).



Figure 5.6. Pile 3 solute concentrations are generally highest at the end of Stage III (upper graph), with the exception of Se concentrations and to a lesser extent Pb concentrations, which can peak during Stage II, and Mo Concentrations which sometimes decrease during Stage II (lower graph). The consistent Mo concentrations of 0.01 mg/L and 0.02 mg/L until mid-2009 are an artifact of laboratory measurement precision. Data points below the minimum detection limit for Mo (<0.01 mg/L prior to mid-2009) are not shown.



Figure 5.7. Piles 1, 2, and 3 alkalinity (mg/L) and Mg concentrations (mg/L) are highest at the end of Stage III at lowest effluent flows.



Figure 5.8. Highest Zn and Mn concentrations in Pile 1 occur during Stage III. Highest Zn and Mn concentrations in Pile 2 occur during Stage II. Highest Zn concentrations in Pile 3 occur during Stage III.



Figure 5.9. Pile 2 Cd and Cu concentrations are highest during Stage II, while Pile 3 concentrations of the same solutes are highest at the end of Stage III. Pile 1 Cd and Cu concentrations do not exhibit clear seasonal trends.



Figure 5.10. Pile 1 sulfate concentrations are highest at the end of Stage III. Initial sulfate concentrations for Piles 2 and 3 do not show strong seasonal trends. Pile 2 sulfate concentrations peak during Stage II during the third year after pile construction. Pile 1 Mo concentrations are highest during Stage II, while Pile 2 Mo concentrations are highest during Stage I.



Pile 1, Lysimeter D

Figure 5.11. Cross plots of Pile 1 solute concentrations, specific conductance, and effluent flow for 2006-2012. Notable relationships are increasing Mg, Mn, and Zn with increasing dissolved Ca, specific conductance, and dissolved SO₄. Additionally, Mn concentrations are high only when Pile 1 effluent flows are low. There are no strong relationships between pH and solute concentrations.



Pile 2, Lysimeter D

Figure 5.12. Cross plots of Pile 2 solute concentrations, specific conductance, and effluent flow for 2007-2012. In general, Cd, Co, Cu, Mn, and Zn concentrations are highest at low pH values with low alkalinity, high specific conductance, and high dissolved SO₄. Dissolved As concentrations and, to a lesser extent dissolved Mo concentrations, exhibit the opposite behavior. Flow relationships are not easily discernible from multi-year cross plots due to the rapidly changing annual solute concentrations versus relatively consistent annual effluent flow rates.



Pile 2, Lysimeter D, Yearly Effluent Flow

Figure 5.13. Pile 2 Lysimeter D effluent flow versus dissolved metals for each water year, with evidence of increasing Cd, Co, Cu, Mn, and Zn with increasing flow rates and decreasing pH.



Pile 2, Lysimeter D, Yearly Effluent Flow

D Lysimeter Effluent Flow (I/week)

Figure 5.14. Pile 2 Lysimeter D effluent flow versus dissolved SO_4 and Ca, specific conductance (SC), and alkalinity for each water year, with evidence of increasing SO_4 and SC with increasing flow rates and decreasing pH.



Pile 3, Lysimeter D

Figure 5.15. Cross plots of Pile 3 solute concentrations, specific conductance, and effluent flow for 2007-2012. Dissolved Co, Mg, Mn, and Zn concentrations increase with increasing specific conductance and decreasing effluent flow. There are no strong relationships between pH and solute concentrations.



Figure 5.16. Pile 1 PHREEQC saturation indices for mineral groups, starting with the top graph: Oxides, hydroxides, and molybdates; carbonates; sulfates, silicates; and field pH and D lysimeter effluent flow.



Figure 5.17. Pile 2 PHREEQC saturation indices for mineral groups, starting with the top graph: Oxides, hydroxides, and molybdates; carbonates; sulfates, silicates; and field pH and D lysimeter effluent flow.



Figure 5.18. Pile 3 PHREEQC saturation indices for mineral groups, starting with the top graph: Oxides, hydroxides, and molybdates; carbonates; sulfates, silicates; and field pH and D lysimeter effluent flow.



Figure 5.19. Surface complexation tendencies are highly dependent on pH, for example in this solution containing dissolved metals in a NaNO₃ solution with Fe present as the sorbent. (After Stumm and Morgan, 1996.)



Figure 5.20. Examples of the inverse relationship between internal SC and volumetric water content in Pile 2, showing higher-solute pore water displaced by lower-solute fresh water during the wet season.


Figure 5.21. Schematic of hypothesized processes concurrently and sometimes interdependently controlling waste rock effluent water chemistry.

Chapter 6: Summary and conclusions

One of the primary purposes of this dissertation is the synthesis and analysis of unprecedented multi-scalar, multi-parameter hydrologic and geochemical data from end member waste rock types producing acidic and neutral drainage in a distinct two-season wet/dry climate. To that end, field and laboratory experiments were conducted and hydrological, meteorological, and geochemical data from three 10-m experimental wasterock piles and to a lesser extent, corresponding 1-m field barrels, were compiled and presented. The hypotheses regarding processes controlling effluent water quantity and quality have been addressed in four chapters focusing on 1) internal unsaturated flow regimes, 2) evaporation, 3) waste rock systems that transition from neutral to acidic conditions and the effect of material heterogeneity in those systems, and 4) the links between hydrological and geochemical controls on water quality.

The waste rock types in each of the three experimental piles have unique physical and chemical properties, and there is high heterogeneity within and among each waste rock type. Pile 1 is composed of blocky marble and hornfels and has a coarse particle size distribution, dominated by gravel and cobbles with significant amount of boulders. The marble and hornfels generally have relatively high carbonate content (11.0 wt.% to 90.8 wt.%), lower sulfide content (0.5 wt.% to 4.53 wt.%), and lower metal content. Pile 2 is composed of friable intrusive waste rock that has a finer particle size distribution dominated by the sand size fraction with up to 22% silts and clays. The intrusive material generally contains extremely low carbonates (<1 wt.%), moderate sulfides (1.3 wt.% to 9.2 wt.%) and high metal and metalloid concentrations. Pile 3 is composed of friable skarn waste rock that is

generally finer-grained but that is highly variable within the pile, including a significant proportion of boulders near the outermost slope. The skarns have moderate carbonate content (2.8 wt.% to 31.3 wt.%), moderate sulfide content (1.7 wt.% to 9.6 wt.%), and very high metals and metalloid contents (e.g., up to 23,200 ppm Cu and 46,000 ppm Zn).

6.1 Unsaturated hydrology

Two objectives of this dissertation were to determine and present hydrological parameters such as hydraulic conductivities and matrix, preferential and wetting front flow velocities, and to develop conceptual models of flow regimes for three waste rock types, including relative proportions of matrix and preferential flow and the relationships between pore-water velocities and wetting-front velocities. To those ends, internal and effluent flow patterns were observed in conjunction with a tracer study for all three piles. A summary of the hydrological parameters and conceptual models as well as relevant meteorological conditions that impact the findings are described below.

Annual precipitation at Antamina was 1281 mm, 1535 mm, 1290 mm, and 1274 mm for the 2007-08, 2008-09, 2009-10, and 2010-11 water years, respectively. Almost all precipitation falls between September and April, and effluent flow for the three piles responds correspondingly with a 'first flush' of low flows during Stage I (about October through December), peak flows during Stage II (about January through mid-April), and draindown and low flows during Stage III (about late April through September). The flow stages, in turn, affect aqueous geochemistry of pore water and effluent water.

Of the three material types, the marble and hornfels from Pile 1 have the highest measured saturated hydraulic conductivity (1.5×10^{-5} m/s). Flux-based calculations likely

underestimate unsaturated hydraulic conductivities for the wet and dry seasons (4 x 10^{-8} m/s and 2 x 10^{-9} m/s, respectively). Pile 1 has the fastest, broadest range of matrix flow (velocities 3.6 cm/day to 12.4 cm/day) and the largest proportion of preferential flow of the three piles (velocities 0.4 m/day to 20 m/day). Measured internal wetting front velocities range from 15 cm/day in the dry season to 105 cm/day in the wet season.

Internal flow regimes in Pile 1 are matrix dominated but complex, with strong preferential flow near the slopes and moderate preferential flow below the crown of the pile and nonvertical flow diverting water toward the outer slope. Pile 1 effluent flow has fast response to precipitation and evidence of preferential flow path activation during the beginning of the wet season (Stage I), followed by flashy flow during the peak of the wet season (Stage II) and a rapid decline in flow as observed by a steep draindown curve during the dry season (Stage III).

Pile 2 exhibits the most spatially consistent effluent and internal flow patterns of the three piles. Matrix flow is relatively consistent spatially throughout the pile (velocities 2.0 cm/day to 2.6 cm/day) and internal wetting front velocities range from 7 cm/day in the dry season to 88 cm/day in the wet season. The average saturated hydraulic conductivity is 4.8×10^{-6} m/s as measured by single-ring infiltrometers, and flux-based calculated unsaturated hydraulic conductivities are 6×10^{-8} m/s in the wet season and 6×10^{-9} m/s in the dry season.

Flow regimes in Pile 2 are matrix dominated with sparse evidence of fast vertical preferential flow or non-vertical flow in the pile. Pile 2 has the most delayed and muted response to precipitation during Stage I, followed by high sustained flows with muted increases and

decreases in flows during Stage II, and high sustained flows and a gradual draindown curve during Stage III.

Pile 3 exhibits a slightly broader range of matrix flow velocities (<2 cm/day to 4 cm/day); evidence of preferential flow on the pile's outer slope (velocities 0.6 m/day to 2.5 m/day); and internal wetting front velocities range from 7 cm/day in the dry season to 44 cm/day in the wet season. The average saturated hydraulic conductivity for that pile is 3.7×10^{-6} m/s and average calculated unsaturated hydraulic conductivities for the wet and dry seasons are 8×10^{-8} m/s and 6×10^{-9} m/s, respectively.

Flow regimes in Pile 3 are matrix dominated and complex, including evidence of moderate preferential flow near the slopes of the pile and non-vertical flow. Pile 3 effluent flow responds moderately to precipitation with some evidence of preferential flow path activation during Stage I; exhibits flashy, high effluent flow during Stage II; and has high sustained flows and a gradual draindown curve in Stage III.

One hypothesis of this dissertation was that coarse particle size fractions (i.e., gravel, cobbles, and boulders) can strongly influence waste rock flow regimes. The observations summarized above highlight the importance of particle size on hydrological flow regimes, including that the presence of boulders may contribute to fast preferential flow, possibly as flow over the surfaces of the larger clasts, even in waste rock that is otherwise relatively finer-grained. Saturated hydraulic conductivities measured with ring infiltrometers reflect differences observed in the three waste rock types, while flux-based estimated unsaturated hydraulic conductivities do not. Future analysis of bromide tracer samples from after the end of the study period considered in this study will help further refine

hydrological parameters including residence times and the mass of bromide remaining in very slow paths in the piles.

6.2 Evaporation

Evaporation from the three experimental piles was calculated using the water balance, following the objective of the evaporation study that proposed to augment the dataset of the relatively few large-scale studies that have, to date, addressed evaporation from bare waste rock. The results were compared to the Food and Agricultural Organization of the United Nation's modified Penman-Monteith method (FAO-PM; Allen et al., 1998) using base-case and calibrated soil parameters. Since the piles are almost identical in size, are at the same location and are under identical atmospheric conditions with the possible exception of wind exposure, the effect of material type is isolated. Finally, conditions and parameters in wasterock settings for which the FAO-PM method may and may not be applicable were evaluated. The research findings are summarized below.

Initial changes in internal water storage ranged from 0.1% to 1.8% or more of the volume of the waste rock and initial wet-up period for the piles ranges from a month (coarser-grained) to two years (finer-grained) per 10 m of waste rock. Annual changes in storage were low to negligible in average precipitation years, but a more substantial increase in annual storage was observed during a year of high precipitation and was followed by a balancing decrease in storage the following year.

Waste rock particle size distributions have a significant impact on evaporation. Wind exposure in relation to slope orientation also plays a significant role in wind-induced air circulation (Chi et al., 2013) and hence, may impact evaporation from deeper below the soil

surface. The coarse-grained waste-rock pile (Pile 1) had high evaporation and high annual variability (44% - 75% of precipitation), which is attributed to greater efficiency of winddriven air circulation within the coarser-grained pile. Pile 2 had relatively consistent and moderate evaporation (36%-48% of precipitation in a three-year period). Pile 3 had low and consistent evaporation (24%-32% of precipitation in three years), possibly due to increased infiltration from preferential flow in conjunction with decreased wind-induced air circulation. These findings do not support the hypothesis that finer-grained waste rock should have higher evaporation than coarser-grained waste rock, and suggest that the effect of air circulation and evaporation from deeper within coarser-grained waste rock should be accounted for when attempting to predict evaporation from bare waste rock.

One research questions pertaining to this topic was how the water balance calculations differ between the outer slopes and upper surfaces of waste-rock piles. Evaporation calculated by water balance using the sub-lysimeters below the crown of coarsest-grained Pile 1 is much higher than evaporation calculated below the slopes. Calculated evaporation from the crown of Pile 3 was also higher than calculated evaporation from the slopes. Pile 2 calculated evaporation was the opposite, with lower evaporation observed on the crown than on the slopes. Tracer study results and effluent flow patterns suggest that for Piles 1 and 3, high infiltration on the slopes and non-vertical flow being diverted towards the slopes have skewed the sub-lysimeter water-balance evaporation estimates, and that, in general, evaporation is expected to be higher on the slopes than on the crowns of waste-rock piles. The experimental set-up of the smaller sub-lysimeters at 10-m depth was not ideal for comparison of evaporation from the slopes and crowns of the pile because of the high probability of non-vertical flow skewing the water balance, and the hypothesis that more

evaporation should occur on the pile slopes than the flat upper surfaces as a result of increased air circulation could not be confirmed or disproven. For future projects for which determination of evaporation is a primary research goal, it is recommended that surficial lysimeters be installed for a more accurate water balance.

The base-case whole-pile FAO-PM method slightly underestimated observed study-period evaporation for Pile 1, overestimated it for Pile 2, and significantly overestimated it for Pile 3. The FAO-PM model was successfully calibrated to observed evaporation by adjusting the depth of the soil layer susceptible to evaporation, Z_e , to 0.19 m for Pile 1 and to 0.03 m for Pile 2. Based on Pile 3 soil properties, in particular the broad particle size distribution, the calibration of Z_e to 0.01 m is considered unrealistic, and the FAO-PM method is therefore not successful for prediction of such low evaporation from waste rock.

One research question posed for this study was how we might improve the applicability of the FAO-PM method in waste rock settings. To address this question, the inclusion of an additional term, the coefficient of preferential flow (K_{PF}), which attributes a specified percentage of evaporable water from large precipitation events to deep percolation, is suggested. The inclusion of this term may be a more physically realistic approach than adjusting soil parameters outside of reasonable ranges of values. Further development of the K_{PF} approach is needed and is the logical next step in this research. Future work should include first the compilation of hydrological parameters for the proportion of preferential flow to matrix flow and the magnitude of threshold precipitation events that trigger preferential flow for several waste rock types, followed by calibration and validation of the additional term for waste rock at Antamina and other mine sites based on their climates.

One hypothesis of this study was that the FAO-PM evaporation method is most accurate in estimating evaporation from relatively fine-grained, homogeneous waste rock. While the base-case FAO-PM overestimated evaporation for this type of soil (Pile 2), the model can be calibrated to match calculated evaporation by applying a depth of soil susceptible to evaporation $Z_e = 0.03$ m. This value is lower than those suggested by Allen et al. (1998) for use in agricultural settings ($Z_e = 0.10-0.15$ m) but similar to the value determined for the crown of a similar waste-rock pile ($Z_e = 0.05$ m; Fretz, 2013).

The movement and evaporation of moisture from deeper within the pile must be considered when estimating evaporation using an analytical approach for coarser-grained waste rock. Other factors that complicate waste rock evaporation estimations, and subsequently, recharge to the bottom of a waste-rock pile, include the proportion of a dump that is occupied by slopes; orientation of the slopes in relation to wind, precipitation, and sun exposure; surficial and internal hydrology and preferential flow paths; and internal heat from exothermic reactions (sulfide oxidation).

6.3 Transition from neutral to acidic drainage

One objective of this study was to quantitatively describe the rapid shift from circumneutral (pH 7-8) to slightly more acidic (pH 6.4) drainage that occurred in Pile 2 effluent water during the 2010-2011 wet season. The shift resulted in increased Cu solute concentrations of more than an order of magnitude and Zn concentrations by a factor of three, and affected other solutes including a decrease in concentrations of oxyanion-forming Mo and As. The shift likely occurred as a result of depletion of carbonate phases, especially in the highly

reactive outer tipping phase of the pile. Seasonal flushing and variable residence times among flow paths likely contributed as well.

The waste rock in the outer tipping phase, which corresponds to Sub-lysimeter C and Field Barrel 2-3A is high in solid phase metal concentrations and sulfides, and very low in carbonates. Strikingly similar effluent water quality among Lysimeter D, Sub-lysimeter C, and Field Barrel 2-3A support the previously stated hypothesis that relatively small amounts of acidic water from highly reactive material may strongly influence overall outflow chemistry despite dilution with larger volumes of less acidic water.

Waste rock primary mineralogy contributes to the transition from neutral to acidic drainage and can complicate the interpretation of net buffering capacity. The only carbonate detected by XRD (minimum detection limit ~0.1 wt.%) in Pile 2 samples was siderite (FeCO₃), the dissolution of which releases iron which is then hydrolyzed. This produces acidity and counteracts the neutralization from carbonate dissolution. While XRD analysis performed for this study provides baseline knowledge of material mineralogy, it is recommended that future projects employ methods such as mineral liberation analysis (MLA) to better characterize the types and quantities of carbonates and sulfides in the system.

Another objective of this study was to determine the solid phase elemental and physical characteristics of a bright blue precipitate that began to form at Pile 2 effluent release points during the transition from neutral to acidic conditions. The precipitate was found to be predominantly amorphous Cu-sulfate with components of crystalline gypsum and malachite. The precipitate contained very high solid-phase metal concentrations. These results are

important in conjunction with the results from Chapter 5, which suggest that similar secondary minerals are likely forming inside of Pile 2.

6.4 Linking hydrology and geochemistry

One hypothesis for this research was that seasonal concentration and loading patterns for dissolved solutes are strongly controlled not only by solid-phase elemental, mineralogical, and physical characteristics of waste rock, but also by the hydrological flow patterns within waste rock that were described in Chapter 2. The findings of this study, which are outlined below, support that hypothesis.

Solute loadings are controlled mostly by flow volume and are almost always highest during Stage II, when flows are highest from about January through April. Seasonal concentration patterns are much more complex and vary with material type. For Piles 1 and 3, seasonal concentrations are controlled most strongly by dilution, resulting in high solute concentrations and low solute loads during the dry season, and low solute concentrations and high solute loads during the wet season. For Pile 2, flushing of accumulated solute through flow paths and seasonal pH changes from CO_2 degassing most strongly influence seasonal concentration patterns, leading to highest concentrations and loadings during the wet season and lowest concentrations and loadings during the dry season.

PHREEQC speciation analyses were completed in an attempt to answer the research question concerning additional mechanisms contributing to seasonal fluctuations in water chemistry. The results suggest that the precipitation and dissolution of secondary minerals strongly affect seasonal pH and solute concentration patterns in Pile 2, moderately affect seasonal concentration patterns in Pile 3, and minimally affect seasonal concentration patterns in

Pile 1. In all three piles, precipitation of secondary minerals may lead to attenuation of metals and metalloids, but also to persistent long term sources due to re-dissolution of these phases. Temporary sequestration of metals in carbonate phases, such as malachite or smithsonite, may also prolong the carbonate buffering after primary carbonates have been depleted.

Another observed hydrological mechanism contributing to seasonal fluctuations in water quality that relates back to one of the research questions for this topic is the decrease in moisture content during the dry season in Pile 2. The decreased moisture content leads to increased air permeability and CO_2 degassing to the atmosphere, which directly increases pore-water pH. Changes in pH, in turn, affect secondary mineral precipitation and sorption, contributing to seasonal fluctuations in concentration and loadings.

Sorption likely impacts the attenuation of Zn and Cu in all three piles, but does not strongly influence seasonal concentration patterns of those elements except for in Pile 2 when the pH fluctuates seasonally between about 5.5 and 7. Oxyanions are also likely controlled by sorption in all three piles, and seasonal concentrations of As, Mo, Sb, and Se tend to increase either during the first flush (Stage I) or to a lesser extent during peak flows (Stage II).

While this research illuminates many important links between hydrology and geochemistry of mine waste rock, future research possibilities regarding the topic remain abundant. For example, the effect of CO_2 degassing on internal and effluent pH is being examined in greater detail (Lorca, in progress). Additionally, further research is being conducted regarding secondary mineralization and its impact on metal release and attenuation, pH control, and as persistent sources of metals within waste-rock piles (Javadi, in progress). The passivation of primary carbonates by surficial secondary mineralization has been hypothesized to impact the buffering capacity of a system and is also being further explored (St. Arnault, in progress). On the technical level as a quality control check, a useful study may be to determine the effect of timing when measuring effluent water pH at the experimental piles, and the possible necessity of flow-through cells for those measurements.

Finally, despite the growing number of large-scale studies focusing on the hydrology and geochemistry of waste rock, scaling relationships between expensive and time-consuming large-scale experiments and less-expensive smaller-scale and laboratory experiments are still lacking. Several studies (e.g., Strömberg and Banwart, 1999; Wagner, 2004; Malmström et al., 2000; Hollings et al., 2001) show that laboratory experiments usually overestimate sulfide oxidation rates compared to field-scale studies. Development of accurate waste rock and/or meteorologically specific scaling relationships is a practical tool for environmental assessment. While the development of those relationships is not within the scope of this study, the 10-meter scale hydrological and geochemical relationships presented here will provide necessary parameters for future up-scaling hydrological and geochemical processes among the laboratory, field barrel, experimental pile, and full-dump scales.

6.5 Applications and significance

This study has developed a comprehensive dataset to be used directly by Antamina and other mines and in future reactive transport modeling to make waste dump effluent water quality predictions. The study is unique in the abundance and variety of data available, allowing for interpretation and integration of hydrological and geochemical processes from the pore-water scale to the field barrel scale to the experimental pile scale. The experimental set-up isolates

the effect of material type, which profoundly affects hydrological processes such as internal flow regimes and evaporation in addition to geochemical processes that lead to neutral and acidic conditions. Finally, the climate at Antamina, with distinct wet and dry seasons that dictate flow patterns, allows for a unique study of seasonal forcings and their effect on waste rock hydrology and aqueous geochemistry.

The findings are especially applicable to mines that have similar carbonate-hosted skarn ore bodies, are exposed to similar climatic conditions, or that may have waste rock effluent water that fluctuates between acidic and neutral drainage conditions. Some findings of this research will be used in estimation and calibration of parameters to be used in predictive models concerning the hydrogeology and geochemistry of waste rock. Additionally, the relationships between preferential and matrix flow presented in this research will help in development of proper mechanistic models for explaining fluctuations in solute concentrations and loadings released from different waste rock types.

This research presents a comprehensive and holistic conceptual framework where hydrological and geochemical components are analyzed together. The links between hydrological and geochemical processes in waste rock are extremely complex: they are highly site-dependent, and are dependent upon multiple interacting processes that are difficult to characterize in large domains and over long times. Accordingly, predictive efforts will likely continue to be based upon semi-empirical models that integrate sitespecific observations. Future work includes the up-scaling of laboratory and field barrels studies to the experimental pile and operational waste dump scales in order to determine the feasibility of predictive modeling in such complex systems. The increased understanding of the connections between hydrological and geochemical processes through this and similar

research provide better-defined inputs for that modeling, which may in turn decrease the uncertainty associated with long-term, multi-scale water quality predictions.

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Appendices

Appendix A Tracer study

The tracer study performed on the crowns of Piles 1, 2, and 3 during December 2010 is described in Chapters 1 and 2. The intensity of the tracer events were 8.5 mm/hour, 6.0 mm/hr, and 7.5 mm/hr for Piles 1, 2, and 3, respectively. For Antamina's climate, these intensities correspond to 7- to 8-year, 5-year, and 6- to 7-year storm events for Piles 1, 2, and 3, respectively (Figure A.1- Figure A.3). Tracer application distribution was moderate for the first test administered (Pile 1) and improved for Piles 2 and 3 (Figure A.4 to Figure A.6).

Same-scale bromide breakthrough curves are presented in Chapter 2 for the purpose of comparison among the three piles, and full-scale plots are presented in Figure A.7.

A.1 Temporal moment analysis: Flow-corrected time

The steady-state representation of transient flow through temporal moment analysis described in Eriksson et al. (1997) and referred to here as *flow corrected time* was employed in order to analyze the tracer results based on volume-normalized flow (i.e., considering each time unit to be a period in which a uniform amount of flow was released from a lysimeter). The method is described briefly below.

The parameter for which a uniform amount of flow is released from a lysimeter is τ , and in this study is comparable to days, but for clarity in the methods description in this appendix the units will be referred to here as 'flow-corrected time', or FCT units. The steady-state water flow (\tilde{Q} , liters) that corresponds to the flow-corrected time τ is defined as the total

volume of effluent water for the experimental time period (V_{tot} , liters) divided by the experimental time period (Υ , days).

$$\tilde{Q} \equiv \frac{V_{tot}}{\gamma}$$

Eq. A.1

The flow-corrected time τ (*FCTs*) is determined by the accumulated volume of water at time *t* (*V*(*t*), liters) according to the equation

$$\tau = \Upsilon \frac{V(t)}{V_{tot}}$$

Eq. A.2

where V(t) is determined using the measured flow of water at time t (Q(t), liters), according to the equation

$$V(t) = \int_0^t Q(t')dt'$$

Eq. A.3

and V_{tot} is determined using the measured flow for the entire experimental period as

$$V_{tot} = \int_0^{\gamma} Q(t) dt$$

Eq. A.4.

The 'daily' or FCT mass (*S*, mg) for a given depth (*z*, in this case the depth of the lysimeters, 10 m) and a given τ are determined using the effluent concentration (*c*, mg/l) at the same *z* and τ according to the equation

$$S(\tau, z) = c(\tau, z)\tilde{Q}$$

Eq. A.5.

The arrival time of the center of the mass of solute ($\bar{\tau}$, FCTs) is determined according to the equation

$$\bar{\tau} = \frac{\int_0^\infty \tau S(\tau, z) d\tau}{\int_0^\infty S(\tau, z) d\tau}$$

Eq. A.6.

Assuming conservative transport without diffusion into immobile water zones, $\bar{\tau}$ can also be expressed as

$$\bar{\tau} = \frac{z}{v} = \frac{z\theta_m^*A}{\tilde{Q}}$$

Eq. A.7

where *v* is the mean pore water velocity, *A* is the lysimeter cross-sectional area, and θ_m^* is an apparent mobile water content.

Under the assumption of conservative transport, the apparent mobile water content to total water content ratio, θ_m^*/θ , can be used to determine relative proportions of 'preferential' or

'mobile' flow (i.e., faster flow, likely analogous to fast preferential and fast matrix flow as defined by this dissertation) and 'immobile' (or comparatively immobile, that is, flowing at slower velocities, such as slower matrix flow). The closer the ratio is to 1, the higher the percentage of highly mobile or 'preferential flow', and the closer the ratio is to 0, the lower the percentage of less mobile or slow matrix flow.

The spreading of mass (σ_{τ}) around the mean arrival time ($\bar{\tau}$) can be determined by the equation

$$\sigma_{\tau} = \sqrt{\left(\frac{\int_{0}^{\infty} (\tau - \bar{\tau})^{2} S(\tau, z) d\tau}{\int_{0}^{\infty} S(\tau, z) d\tau}\right)}$$

Eq. A.8

and a relative spreading of mass $(CV\tau)$ around the mean arrival time $(\bar{\tau})$ can be determined by the equation

$$CV_{\tau} = \frac{\sigma_{\tau}}{\bar{\tau}}$$

Eq. A.9.





Figure A.1. Pile 1 intensity-duration-frequency (IDF) graph. From Golder (1999), provided by Antamina, adapted by Blackmore (unpublished data).



Figure A.2. Pile 2 intensity-duration-frequency (IDF) graph. From Golder (1999), provided by Antamina, adapted by Blackmore (unpublished data).



Figure A.3. Pile 3 intensity-duration-frequency (IDF) graph. From Golder (1999), provided by Antamina, adapted by Blackmore (unpublished data).

Pile 1 Tracer Test - Jan 19, 2010



Figure A.4. Pile 1 tracer distribution plot. From Blackmore, unpublished data.

Pile 3 Tracer Test - Jan 22, 2010



Figure A.5. Pile 2 tracer distribution plot. From Blackmore, unpublished data.



Figure A.6. Pile 3 tracer distribution plot. From Blackmore, unpublished data.



Figure A.7. Full-scale bromide breakthrough curves for all Lysimeters of Piles 1, 2, and 3.

Appendix B Particle size distributions (PSDs)

Particle size distributions were conducted by Golder Associates during the construction process according to method ASTM D 5519, and are described in Aranda (2009).

B.1 PSDs for all tipping phases

Ranges of the minimum and maximum percent passing for each measured particle size, as well as the average percent passing for each measured particle size can be found in Chapter 1 and Figure B.1. The PSD results from each tipping phase for each of the three piles are presented in Figure B.2 to Figure B.4. A PSD analysis was not completed for the outer tipping phase for Pile 1 (Field Barrel 1-3A).

B.2 Calculation of percent of material at a specified grain size diameter (D_S) , Uniformity Coefficient (C_u) , and Coefficient of Curvature (C_c)

The percent of material at a specified grain size diameter (D_S , e.g., $D_{10[mm]}$, $D_{20[mm]}$) was calculated algebraically through linear interpolation between known percentages of sieve sizes for each tipping phase (Table B.1 to Table B.3). Average D_S were calculated from each pile's average PSD curve. Uniformity coefficients (C_u) were calculated with the equation

$$C_u = D_{60}/D_{10}$$

Eq. B.1

Coefficients of curvature (C_c) were calculated with the equation

$$C_c = (D_{30})^2 / (D_{10} * D_{60})$$

Eq. B.2

Average C_u and C_c values were calculated as averages of the individual tipping phase C_u and C_c values (as opposed to the C_u and C_c of the pile average PSD curve) in order to best represent the average material by calculating ratios of D_S within tipping phases (Table B.4 to Table B.6).

B.3 Estimation of boulders in Pile 3, Tipping Phase III

A high percentage of Pile 3 Tipping Phase III material was boulders >1 m, but that size fraction was not included in the Golder Associates, Peru particle size analyses for that pile. The percentage of boulders in Pile 3 was therefore estimated using photographs and personal communication with Daniel Bay, who was on-site and responsible for Pile 3 construction. It is estimated that the boulders comprise about 12% of Tipping Phase III, or about 3% of the pile (Table B.7).

B.4 Tables

Table B.1. Pile 1 percent of material at a specified grain size diameter values (D_S) for each tipping phase and the average curve.

	D ₁₀	D ₂₀	D ₃₀	D ₄₀	D ₅₀	D ₆₀
Pile 1 Protective layer (Field Barrels 1-0A & 1-0B)	7.63	44.36	98.45	169.79	246.31	374.34
Pile 1 Tipping Phase I (Field Barrel 1-1A)	8.69	31.12	61.87	134.02	203.20	247.54
Pile 1 Tipping Phase II (Field Barrels 1-2A & 1-2B)	17.70	83.05	127.92	191.04	273.45	370.35
Pile 1 : Average Curve	11.58	41.68	100.24	163.82	233.24	311.34

Table B.2. Pile 2 percent of material at a specified grain size diameter values (D_S) for each tipping phase and the average curve.

	D ₁₀	D ₂₀	D ₃₀	D ₄₀	D ₅₀	D ₆₀
Pile 2 Protective layer						
(Field Barrel 2-0A)	2.19	8.77	16.40	26.79	42.23	57.67
Pile 2 Tipping Phase IA						
(Field Barrel 2-1A)	0.24	6.26	14.08	22.80	33.94	45.65
Pile 2 Tipping Phase IB						
(Field Barrel 2-1B)	0.03	0.20	2.14	6.17	11.26	18.90
Pile 2 Tipping Phase II						
(Field Barrel 2-2A)	0.11	0.55	3.10	6.42	11.26	18.25
Pile 2 Tipping Phase III						
(Field Barrel 2-3A)	0.13	0.60	3.39	7.12	13.32	23.88
Pile 2 : Average Curve	0.12	1.68	5.81	11.64	19.58	33.10

Table B.3. Pile 3 percent of material at a specified grain size diameter values (D_S) for each tipping phase

and the average curve.

	D ₁₀	D ₂₀	D ₃₀	D ₄₀	D ₅₀	D ₆₀
Pile 3 Protective layer						
(Field Barrel 3-0A)	2.74	11.91	23.64	41.36	59.69	81.08
Pile 3 Tipping Phase IA						
(Field Barrel 3-1A)	0.40	2.32	4.60	8.22	13.48	21.43
Pile 3 Tipping Phase II						
(Field Barrel 3-2A)	0.32	2.19	5.11	10.27	17.37	29.61
Pile 3 Tipping Phase III						
(Field Barrel 3-3A)	2.29	6.40	19.61	66.41	107.89	151.19
Pile 3 Tipping phase 4						
(Field Barrel 3-4A)	0.13	0.40	1.49	3.29	5.55	10.24
Pile 3: Average Curve	0.37	2.65	6.33	13.11	23.87	50.09

	Uniformity Coefficient C_u D_{60}/D_{10}	Coefficient of Curvature C_c $((D_{30})^2)/(D_{10}*D_{60})$
Pile 1 Protective layer		
(Field Barrels 1-0A & 1-0B)	49.05	3.39
Pile 1 Tipping Phase I		
(Field Barrel 1-1A)	28.47	1.78
Pile 1 Tipping Phase II		
(Field Barrels 1-2A & 1-2B)	20.92	2.50
Pile 1 : Average	32.81	2.56

Table B.4. Pile 1 tipping phase and average uniformity coefficients and coefficients of curvature.

Table B.5. Pile 2 tipping phase and average uniformity coefficients and coefficients of curvature.

	Uniformity Coefficient C _u	Coefficient of Curvature C _c
Pile 2 Protective layer		
(Field Barrel 2-0A)	26.36	2.13
Pile 2 Tipping Phase IA		
(Field Barrel 2-1A)	187.20	17.82
Pile 2 Tipping Phase IB		
(Field Barrel 2-1B)	640.95	8.20
Pile 2 Tipping Phase II		
(Field Barrel 2-2A)	169.66	4.91
Pile 2 Tipping Phase III		
(Field Barrel 2-3A)	188.79	3.80
Pile 2 : Average	242.59	7.37

Table B.6. Pile 3 tipping phase and average uniformity coefficients and coefficients of curvature.

	Uniformity Coefficient C _u	Coefficient of Curvature Cc
Pile 3 Protective layer		
(Field Barrel 3-0A)	29.63	2.52
Pile 3 Tipping Phase IA		
(Field Barrel 3-1A)	54.13	2.49
Pile 3 Tipping Phase II		
(Field Barrel 3-2A)	92.41	2.75
Pile 3 Tipping Phase III		
(Field Barrel 3-3A)	65.90	1.11
Pile 3 Tipping phase 4		
(Field Barrel 3-4A)	77.90	1.66
Pile 3: Average	63.99	2.11

 Table B.7. Original particle size data for Pile 3, Tipping Phase III (Sample M15) as reported by Golder

 Assoc. Peru, and revised data including about 12% boulders in that tipping phase.

Pile 3, Tipping Phase III (Sample M15)				
	Original data	Revised data		
Particle size (mm)	Percent Passing (%)	Percent Passing (%)		
2000	100	100.0		
914.4	100	88.0		
406.4	86.5	76.1		
254	77.7	68.4		
152.4	68.5	60.3		
76.2	48.5	42.7		
25.4	32.7	28.8		
19.05	29.3	25.8		
12.7	24.3	21.4		
9.525	21.9	19.3		
4.76	16.1	14.2		
0.595	8.1	7.1		
0.42	6.8	6.0		
0.149	4.1	3.6		
0.074	2.8	2.5		

B.5 Figures



Figure B.1. Piles 1-3 ranges and average particle size distributions.



Figure B.2. Pile 1 particle size distributions for each tipping phase.



Figure B.3. Pile 2 particle size distributions for each tipping phase.



Figure B.4. Pile 3 particle size distributions for each tipping phase.

Appendix C Measurement of saturated hydraulic conductivity by ring infiltrometer

In March and April, 2009, single ring infiltrometer tests were performed by Sharon Blackmore and Pablo Urrutia on Piles 1-3 to determine saturated hydraulic conductivity of the crowns of the piles. Eight to ten tests were performed on each pile to provide a good range of coverage and average values (Table C.1, Figure C.1).

C.1 Tables

 Table C.1. Saturated hydraulic conductivity from all locations and pile averages (modified from Blackmore, unpublished data).

	Vertical Saturated Hydraulic Conductivity (m/s)				
Position	Pile 1	Pile 2	Pile 3		
1	5.80E-06	1.66E-05	4.04E-06		
2	1.19E-04	4.78E-05	5.59E-07*		
3	1.16E-05	9.25E-06	1.16E-05		
4	3.71E-06	3.53E-06	2.21E-06		
5	2.96E-05	2.86E-05	8.17E-06		
6	1.66E-05	1.01E-05	4.83E-06		
7	1.69E-05	9.01E-06	1.31E-05		
8	1.13E-05	2.01E-07	5.13E-06		
9		8.65E-06	2.00E-07		
10		5.14E-08	2.18E-06		
Average	2.68E-05	1.34E-05	5.71E-06		
* Result is based on two measurem possible bentonite contamination.	ients as test was aba	ndoned due to absent	seepage and		

C.2 Figures



Figure C.1. Positions of single ring infiltrometer tests on Piles 1-3 (modified from Blackmore, unpublished data).

Appendix D Porosity

Porosity was measured by Golder Associates, Peru and/or at the University of British Columbia and is reported in Speidel (2011). Average porosity measurements for Piles 1, 2, and 3 are 0.28, 0.33, and 0.38, respectively.

Appendix E Flow estimation for tipping bucket data gaps

Gaps in the tipping bucket flow data occurred occasionally during the study period. The gaps were usually caused by bucket or electronic malfunction. Specific examples of causes that lead to data gaps include:

- moving parts getting stuck,
- components breaking off of the unit,
- connection wires disconnected from the datalogger, and
- temporary loss of power to the system.

General steps for estimating flow data are outlined below. Each missing data gap was evaluated on a case-by-case basis.

- 1. Determine what flow data is missing
- 2. Determine magnitude of comparison
 - a. use linear interpolation between missing points if missing data is less than one week (FINISHED)
 - b. use correlations with other lysimeters/time periods if missing data is more than one week (MOVE ON TO STEP 3)
- 3. Determine what flow that is available is most similar to the missing lysimeter flow
 - a. observe effluent flow graph patterns, including:

- i. same year and different years
- ii. same pile and different piles
- iii. same lysimeter and different lysimeters
- b. observe lysimeter flow in response to precipitation
- 4. If comparing two different lysimeters from the same time period, determine timing shift if necessary (i.e., if one lysimeter tends to respond sooner or later than the other lysimeter, and by how many days)
 - a. Compare spikes, determine time offset.
- 5. Use linear regression and the method of ordinary least squares to determine the volume correlation between lysimeters/time periods
 - a. Use correlations from within reasonable time frames and within similar flow periods
- 6. Apply correlation equation to missing data and note method/equation/time offset

For example, there is a relatively strong correlation between P2C and P2D flow. For a period when data was missing for P2C in April 2011, then, a two-day offset and numerical relationship to P2D was determined using the flow data from February and March of that year (Figure E.1).

E.1 Figures

	A	В	С	D	E	F	G	Н		J	К	L	
68	7-Mar-2011	3.98	5.29										
69	8-Mar-2011	4.59	5.65							TWODA	Y OFFSET		
70	9-Mar-2011	5.10	6.18							P2C = 0.9	052*P2D +	0.1755	
71	10-Mar-2011	5.85	6.38										
72	11-Mar-2011	6.22	6.10		7.00					y=0.90	52x + 0.1755		
73	12-Mar-2011	6.09	5.57							R ²	= 0.7594		
74	13-Mar-2011	6.06	5.74		6.00				<u> </u>				
75	14-Mar-2011	6.20	5.11		E 00								
76	15-Mar-2011	6.05	4.48	day l	5.00								
77	16-Mar-2011	5.74	5.44	È	4.00								
78	17-Mar-2011	5.38	5.05	5	·			5-4-F		 Seri 	es1		
79	18-Mar-2011	5.10	4.85	ő	3.00						nr (Corier1)	1	
80	19-Mar-2011	4.86	4.72							Line	ar (seriest)		
81	20-Mar-2011	4.76	4.54	2	2.00								
82	21-Mar-2011	4.79	4.48		1.00								
83	22-Mar-2011	4.76	4.36										
84	23-Mar-2011	4.70	4.24		0.00	1			1				
85	24-Mar-2011	4.44	4.15		0.00	2.00) 4.(00 E	5.00	8.00			
86	25-Mar-2011	4.31	4.17				P2D Flow	(mm/day)				<i>.</i>	
87	26-Mar-2011	4.15	4.36										
88	27-Mar-2011	3.85	4.33										
89	28-Mar-2011	3.72	4.21										
90	29-Mar-2011	3.65	4.10										
91	30-Mar-2011	3.81	4.05										
92	31-Mar-2011	3.92	4.17										

Figure E.1. Example of using linear regression and ordinary least squares analysis to determine a temporal and volumetric relationship between effluent flow for P2C and P2D.

Appendix F Mineralogy of Piles 2 and 3 material as observed by XRD and SEM

Results from X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM) with Energy Dispersive Spectroscopy (EDS) technologies indicate that, while the dominant expected minerals are present in all samples of each waste rock type in Piles 2 and 3, there is nonetheless significant heterogeneity within each respective waste rock type (Figure F.1 and Figure F.2). These heterogeneities include difference in type and abundance of sulfide minerals and carbonates, which can directly impact the quality of water flowing through mine waste dumps.

Additionally, XRD and SEM/EDS methods were used to determine the abundances of crystalline (Table F.1) and amorphous (Table F.2) phases in metal-rich solids that precipitated out of supersaturated effluent water from an experimental waste-rock pile (Figure F.3 and Figure F.4). The crystalline phases shifted over time, and included gypsum (CaSO₄·2H₂O), malachite (Cu₂CO₃(OH)₂), dioptase (CuSiO₃·H₂O), and rhodochrosite (MnCO₃). SEM/EDS analysis confirmed the association of Zn, Cu, and Si in the precipitate samples (Figure F.5). A similar precipitate formed from supersaturated effluent of a laboratory experiment with intrusive material 2-3A. That predominantly amorphous solid contained gypsum and jokokuite (MnSO₄·5H₂O) with Cu and Zn substitutions for Mn, and possible occurrences of szmikite and zincosite.

In addition to the XRD/SEM/EDS data given here, detailed results and analyses as well as raw Topas and EVA files are available in Supplementary Materials (contact: Roger Beckie or K. Ulrich Mayer, Department of Earth, Ocean, and Atmospheric Sciences, The University of British Columbia, Vancouver, BC, Canada).

F.1 Tables

Table F.1. Weight percent of crystalline minerals detected by XRD for blue precipitate samples collected from Pile 2 Lysimeter D in July (P2D_precip_jul2011) and August (P2D_precip_aug2011_i) of 2011, as well as a sample from a laboratory experiment comprised of effluent flow from a column of 2-3A material (2-3A_precip).

	P2D_precip_jul2011	P2D_precip_aug2011	2-3A_precip
Dioptase	20.3	N/D	N/D
Jokokuite	N/D	N/D	94.9
Gypsum	46.5	83.9	1.5
Malachite	30.0	15.8	N/D
Rhodochrosite	2.6	N/D	N/D
Quartz	0.6	0.3	N/D
Szmikite	N/D	N/D	3.0
Zincosite	N/D	N/D	0.6

Table F.2. Weight percent of both crystalline and amorphous minerals detected by XRD for a blue precipitate samples collected from Pile 2 Lysimeter D in August 2011 (P2D_precip_aug2011) to which a corundum spike was added and quartz contamination was accounted for in order to determine abundance of amorphous and crystalline material.

Mineral name	Mineral Formula	Abundance (wt %)
Gypsum	CaSO₄·2H₂O	22.0
Malachite	Cu ₂ CO ₃ (OH) ₂	4.2
Amorphous		73.8

F.2 Figures



Figure F.1. Compilation of waste rock and precipitate 2-3A XRD diffractograms.



Figure F.2. Examples of EDS mapping for Pile 2 solid phase waste rock samples.



Figure F.3. Rietveld refinement for samples P2D_precip_jul2011 (left) and P2D_precip_aug2011 prior to corundum spike right), showing a much cleaner diffractogram and better fit for the latter sample.



Figure F.4. Examples of EDS mapping for Pile 2 predominantly amorphous blue precipitate samples.



Figure F.5. Example of SEM element mapping for the blue precipitate sample P2D_precip_jul2011: A. Backscattered electron (BSE) image showing lighter-colored Cu-Zn silicate (dioptase) on top of darker-colored Ca sulphate (gypsum), as supported by the subsequent element maps

- B. Element map of S and Si
- C. Element map of Ca and Cu
- **D.** Element map of S and Zn

E. Element map of Mn showing low concentrations (exhibited by spotty nature of element map), but with highest occurrences associated with Cu-Zn silicates.

F. EDS spectrum of entire field of view for images A-E

Appendix G Soil water solution sampler (SWSS) chemistry

Data from the SWSS in Piles 2 and 3 are not abundant, but do provide insight into pore-water concentrations. Figure G.1 illustrates the spatial variability of solute concentrations within Pile 2, e.g., Mn concentrations from internal SWSS that span 5 orders of magnitude.



G.1 Figures

Figure G.1. Select solute concentrations for Pile 2 soil water solution samplers.

Appendix H Compiled PHREEQC speciation calculations

Thegraphical results of PHREEQC speciation calculations presented in Chapter 5 include only phases that have a saturation index greater than -2 and that may have the tendency to precipitate as secondary minerals at atmospheric temperatures and pressures. The complete results of the simulations (Figure H.1 to Figure H.11) include minerals that have consistently extremely low saturation indices (e.g., siderite) and minerals that will not tend to precipitate under atmospheric conditions (e.g., quartz and albite).

The database employed for PHREEQC simulations, 'Antamina_DB', can be found in Supplementary Materials (contact: Roger Beckie or K. Ulrich Mayer, Department of Earth, Ocean, and Atmospheric Sciences, The University of British Columbia, Vancouver, BC, Canada).



Figure H.1. PHREEQC speciation calculations for all Pile 1 oxides, hydroxides, and molybdates.



Figure H.2. PHREEQC speciation calculations for all Pile 1 carbonates.



Figure H.3 PHREEQC speciation calculations for all Pile 1 sulfates.



Figure H.4. PHREEQC speciation calculations for all Pile 1 silicates.


Figure H.5. PHREEQC speciation calculations for all Pile 2 oxides, hydroxides, and molybdates.



Figure H.6. PHREEQC speciation calculations for all Pile 2 carbonates.



Figure H.7. PHREEQC speciation calculations for all Pile 2 sulfates.



Figure H.8. PHREEQC speciation calculations for all Pile 2 silicates.



Figure H.9. PHREEQC speciation calculations for all Pile 3 oxides, hydroxides, and molybdates.



Figure H.10. PHREEQC speciation calculations for all Pile 3 carbonates.



Figure H.11. PHREEQC speciation calculations for all Pile 3 sulfates.



Figure H.12. PHREEQC speciation calculations for all Pile 3 silicates.

Appendix I Ambient and internal temperature measurements

Internal temperatures of Pile 1 are near ambient temperatures and fluctuate seasonally by one to two degrees Celsius (Figure I.1 and Figure I.2). Piles 2 and 3 internal temperatures are approximately 5 to 7 degrees higher than ambient temperatures and do not exhibit consistent seasonal fluctuations (Figure I.3and Figure I.4). The minor seasonal variations (Pile 1) and lack of seasonal variations (Piles 2 and 3) suggest that sulfide oxidation rates are relatively constant year round in all three piles.



I.1 Figures

Figure I.1. Daily ambient temperature at the experimental piles test site.



Figure I.2. Internal seasonal temperature variations for instrumentation Line 1 in Pile 1.



Figure I.3. Internal temperature measurements for instrumentation Line 1 in Pile 2. No distinct seasonal pattern is evident, suggesting near-constant sulfide oxidation rates seasonally.



Figure I.4. Internal temperature measurements for instrumentation Line 1 in Pile 3. No distinct seasonal pattern is evident, suggesting near-constant sulfide oxidation rates seasonally.

Appendix J Evidence of CO₂ degassing in Pile 2

It is hypothesized that seasonal pH changes in Pile 2 effluent water are largely controlled by seasonal CO_2 fluctuations, which are in turn controlled by higher moisture contents and lower air circulation in the wet season (Figure J.1). The supporting PHREEQC simulations based on pCO₂ input conditions of 10⁻³ and 10⁻² atm (Table J.1) suggest that CO₂ accumulation within the pile during the wet season can lead to pH fluctuations exceeding 0.5 pH-units (Table J.2). The simulation is also representative of pH increases that occur when effluent water exits the pile through outflow structures during the wet season, leading to rapid accumulation of solid phase precipitates (Chapter 4; Appendix F).

Pile 3 is similar to Pile 2 in its relatively finer particle size distribution, but seasonal fluctuations in CO_2 concentrations are not nearly as dramatic in the majority of Pile 3 gas sampling ports (Figure J.2), and it is hypothesized that seasonal CO_2 degassing is not a major control on Pile 3 pH.

J.1 Tables

Table J.1. Input file for PHREEQC simulations testing effect of CO2 degassing on pH.

```
SELECTED OUTPUT
   -file
                        carbonate_concepts_2.xls
   -reset
                       false
   -simulation
                       true
   -solution
                       true
   -ph
                        true
   -pe
                        true
   -alkalinity
                       true
   -charge_balance
                       true
   -percent_error
                        true
   -saturation_indices Calcite
# simulation of acid neutralization at a pCO2 = 1e-3 atm
SOLUTION 1
             25
   temp
             3
   рΗ
            4
   pe
   redox
            pe
   units
            mmol/kgw
   density 1
           0 charge
   S(6)
   -water 1 # kg
EQUILIBRIUM PHASES 1
   CO2(g) -3 10
Calcite 0 10
            0 0
   Gypsum
END
# simulation of acid neutralization at a pCO2 = 1e-2 atm
SOLUTION 2
             25
   temp
   рН
             3
            4
   pe
   redox
           pe
            mmol/kgw
   units
   density 1
   S(6)
            0 charge
   -water
            1 # kg
EQUILIBRIUM PHASES 1
   CO2(g) -2 10
   Calcite 0 10
   Gypsum
           0 0
SAVE SOLUTION 2
END
# simulation of CO2 degassing after Solution 2 leaves pile
USE SOLUTION 2
EQUILIBRIUM PHASES 1
   CO2(g) -3 10
```

Table J.2. Selected output for PHREEQC simulations suggesting that CO_2 degassing can have significant impact on seasonal pH fluctuations.

sim	soln	рН	ре	Alk	charge	pct_err	si_Calcite
1	1	3	4	-0.00103	0.001025	100	-999.999
1	1	7.86376	- 2.21068	0.001206	0.001025	30.2607	0
2	2	3	4	-0.00103	0.001025	100	-999.999
2	2	7.25499	- 1.60205	0.003012	0.001025	14.8193	0
3	2	8.23459	- 2.29753	0.003012	0.001025	15.1908	0.9512

J.2 Figures



Figure J.1. Pile 2 CO₂ concentrations change greatly between the wet and dry seasons, impacting seasonal pH fluctuations.



Figure J.2. The majority of Pile 3 CO₂ concentrations are less variable between the wet and dry seasons, resulting in less impact on seasonal pH fluctuations.

Appendix K The effects of secondary mineral precipitation and dissolution on pore water pH

An example of the effect of secondary mineral precipitation and dissolution on pore water pH is evidenced by a PHREEQC simulation of the presence of jarosite in variable-pH solutions, the results of which are described in Chapter 5, Section 5.5.2.2. The inputs include simulations at pH4, pH 5, and pH 6 (Table K.1). The results show the dominant Fe species (Table K.2) and that the major reaction at the three pH values is net-neutral

$$KFe^{3}(OH)_{6}(SO_{4})^{2} < = >K^{+} + 3Fe(OH)_{2}^{+} + 2SO_{4}^{2^{-}}$$

Eq. K.1.

At pH 4, the minor Fe species is Fe(OH)²⁺, and jarosite dissolution increases pH, while jarosite precipitation generates acidity:

$$KFe^{3}(OH)_{6}(SO_{4})^{2} + 3H^{+} < = >K^{+} + 3Fe(OH)^{2+} + 3H_{2}O + 2SO_{4}^{2-}$$

Eq. K.2

At pH 6, when the minor Fe species is $FeOH_3$ and jarosite tends to dissolve, the opposite occurs; jarosite dissolution generates acidity:

$$KFe^{3}(OH)_{6}(SO_{4})^{2} + 3H_{2}O < = >K^{+} + 3Fe(OH)_{3} + 3H^{+} + 2SO_{4}^{2-}$$

Eq. K.3

K.1 Tables

SOLU	TION 1	
t	temp	25
I	рН	4
I	pe	4
]	redox	ре
ı	units	mmol/kgw
C	density	1
2	S(6)	0 charge
I	Fe(3)	0.001
-	-water	1 # kg
end		
SOLU	TION 1	
1	temp	25
I	рН	5
I	pe	4
1	redox	pe
ι	units	mmol/kgw
(density	1
0	S(6)	0 charge
I	Fe(3)	0.001
-	-water	1 # kg
end		
SOLU	TION 1	
1	temp	25
I	рН	6
I	pe	4
1	redox	pe
ι	units	mmol/kgw
(density	1
0	S(6)	0 charge
I	Fe(3)	0.001
-	-water	1 # kg

Table K.1. PHREEQC input file for effects of jarosite dissolution-precipitation on pH.

Table K.2. PHREEQC selected output for jarosite precipitation-dissolution reaction, with molality and

log activities of key major and minor Fe species highlighted in yellow.

```
Input file: C:\Users\holly\Dropbox\Thesis\Chem chapter\Phreeqc\ppt diss pH control\Fe-
ph.pqi
 Output file: C:\Users\holly\Dropbox\Thesis\Chem chapter\Phreeqc\ppt diss pH control\Fe-
ph.pqo
Database file: C:\Users\holly\Dropbox\Thesis\Chem chapter\Phreeqc\Antamina DB.dat
_____
Reading data base.
      SOLUTION MASTER SPECIES
      SOLUTION SPECIES
      PHASES
      EXCHANGE MASTER SPECIES
      EXCHANGE_SPECIES
      SURFACE MASTER SPECIES
      SURFACE SPECIES
      RATES
      END
      ____
             _____
Reading input data for simulation 1.
        _____
      DATABASE C:\Users\holly\Dropbox\Thesis\Chem chapter\Phreeqc\Antamina DB.dat
      SOLUTION 1
          temp
                    25
          рΗ
                    4
          pe
                   4
          redox pe
          units
                    mmol/kgw
          density 1
                 0 charge
0.001
          S(6)
          Fe(3)
          water
                   1 # kg
      end
          _____
Beginning of initial solution calculations.
 _____
Initial solution 1.
-----Solution composition-----
      Elements
                       Molality
                                      Moles
      Fe(3)
                      1.000e-006 1.000e-006
-----Description of solution-----

        pH
        4.000

        pe
        =
        4.000

        Activity of water
        =
        1.000

                        Ionic strength = 5.128e-005
                     Mass of water (kg) = 1.000e+000
                Total alkalinity (eq/kg) = -1.011e-004
                  Total carbon (mol/kg) = 0.000e+000
                     Total CO2 (mol/kg) = 0.000e+000
                Temperature (deg C) = 25.00
Electrical balance (eq) = 1.021e-004
 Percent error, 100*(Cat-|An|)/(Cat+|An|) = 100.00
                             Iterations =
                                            3
```

Total H = 1.110125e+002 Total 0 = 5.550622e+001-----Distribution of species-----Log Log Log mole V Molality Activity Molality Activity Gamma cm3/mol Species 1.008e-0041.000e-004-3.996-4.000-0.0041.009e-0101.001e-010-9.996-10.000-0.0045.551e+0011.000e+0001.744-0.0000.000 0.00 H+ OH-(0) 1.744 H2.0 18.07 1.000e-006 Fe(3) Fe (OH) 2+7.599e-0077.536e-007FeOH+22.353e-0072.276e-007Fe+33.799e-0093.525e-009 -6.123 -0.004 -6.643 -0.014 -6.119 (0)-6.628 (0) -8.420 -8.453 -0.033 (0)
 Fe (OH) 3
 9.708e-010
 9.708e-010
 -9.013
 -9.013
 0.000

 Fe2 (OH) 2+4
 1.593e-012
 1.394e-012
 -11.798
 -11.856
 -0.058

 Fe (OH) 4 8.928e-015
 8.854e-015
 -14.049
 -14.053
 -0.004

 Fe3 (OH) 4+5
 2.703e-016
 2.195e-016
 -15.568
 -15.659
 -0.090
 (0) (0) (0)(0) 1.416e-019 H(0) H2 7.079e-020 7.079e-020 -19.150 -19.150 0.000 (0) 0(0)0.000e+000 02 0.000e+000 0.000e+000 -54.080 -54.080 0.000 (0) -----Saturation indices-----SI log IAP log K(298 K, 1 atm) Phase -1.34 3.55 4.89 Fe(OH)3 4.55 3.55 -1.00 FeOOH Fe(OH)3(a) Goethite -16.00 -19.15 -3.15 H2 -1.51 -0.00 1.51 H20 H2(q)
 -1.51
 -0.00
 1.51
 H2O

 11.10
 7.09
 -4.01
 Fe2O3

 0.71
 7.09
 6.39
 Fe2O3

 -51.19
 -54.08
 -2.89
 O2
 H2O(g) Hematite Maghemite 02 (g) End of simulation. _____ _____ Reading input data for simulation 2. _____ SOLUTION 1 25 temp 5 рН 4 pe redox pe mmol/kgw units density 1 S(6) 0 charge 0.001 Fe(3) water 1 # kg end _____ Beginning of initial solution calculations. Initial solution 1. -----Solution composition-----Elements Molality Moles 1.000e-006 1.000e-006 Fe(3) -----Description of solution----рн = 5.000

Activi Ion Mass of Total alkalin Total carb Total c Total C Temperat Electrical b Percent error, 100*(Cat- An)	pe ty of water ic strength water (kg) ity (eq/kg) on (mol/kg) 02 (mol/kg) 02 (mol/kg) ure (deg C) alance (eq) /(Cat+ An) Iterations Total H Total O	$\begin{array}{rcrr} = & 4.00\\ = & 1.000\\ = & 5.552\\ = & 1.000\\ = & -1.004\\ = & 0.000\\ = & 0.000\\ = & 25.00\\ = & 1.104\\ = & 99.98\\ = & 3\\ = & 1.1101\\ = & 5.5506\end{array}$	00 10 10 10 10 10 10 10 10 10			
Di	stribution	of species				
Species Molality	Activity	Log Molality	Log Activity	Log Gamma	mole V cm3/mol	
H+ 1.003e-005 OH- 1.004e-009 H2O 5.551e+001	1.000e-005 1.001e-009 1.000e+000	-4.999 -8.998 1.744	-5.000 -9.000 -0.000	-0.001 -0.001 0.000	0.00 (0) 18.07	
Fe(3) 1.000e-006 Fe(0H)2+ 9.585e-007 Fe0U(2) 2.010e-000	9.558e-007	-6.018	-6.020	-0.001	(0)	
Fe(OH)2 2.919e-008 Fe(OH)3 1.231e-008 Fe+3 4.583e-011 Fe(OH)4- 1.126e-012 Fe2(OH)2+4 2.344e-014 Fe3(OH)4+5 4.798e-018	2.00/e-008 1.231e-008 4.471e-011 1.123e-012 2.243e-014 4.478e-018	-7.535 -7.910 -10.339 -11.948 -13.630 -17.319	-7.910 -7.910 -10.350 -11.950 -13.649 -17.349	-0.005 0.000 -0.011 -0.001 -0.019 -0.030	(0) (0) (0) (0) (0)	
H(0) 1.416e-021 H2 7.079e-022	7.079e-022	-21.150	-21.150	0.000	(0)	
O(0) 0.000e+000 O2 0.000e+000	0.000e+000	-50.080	-50.080	0.000	(0)	
	Saturation	indices				
Phase SI	log IAP	log K(29	8 K, 1 atı	n)		
Fe (OH) 3 (a) -0.24 Goethite 5.65 H2 (g) -18.00 H2O (g) -1.51 Hematite 13.31 Maghemite 2.91 O2 (g) -47.19	4.65 4.65 -21.15 -0.00 9.30 9.30 -50.08	4.89 F -1.00 F -3.15 H 1.51 H -4.01 F 6.39 F -2.89 O	e (OH) 3 eOOH 2 20 e2O3 e2O3 2			
End of simulation.						
Reading input data for simulat	ion 3.					
SOLUTION 1 temp 25 pH 6 pe 4 redox pe units mmol/kgw density 1 S(6) 0 charge Fe(3) 0.001 water 1 # kg						
Beginning of initial solution	calculation	s. 				
Initial solution 1.						

Elements	Mola	ality	Moles			
Fe(3)	1.0000	e-006 1.0	00e-006			
	De	scription	of soluti	on		
ercent error, 1	Activi Ion Mass of Total alkalin Total carb Total carb Total C Temperat Electrical b 00*(Cat- An)	ty of wate ic strengt water (kg ity (eq/kg O2 (mol/kg Ure (deg C alance (eq /(Cat+ An Iteration Total Total	$\begin{array}{rcl} p H &=& 6 \\ p e &=& 4 \\ e r &=& 1 \\ h &=& 9 \\ p &=& 1 \\ 0 &=& 1 \\ 0 &=& 1 \\ 0 &=& 0 \\ 0 \\ p &=& 0 \\ 0 \\ 0 \\ p &=& 0 \\ 0 \\ 0 \\ p &=& 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 $	000 000 28e-007 00e+000 99e-007 00e+000 00e+000 00 80e-006 93 0124e+002 0622e+001		
	DI	SULIDULIOI	I OI SPECI	g Lo	d Fod	mole V
Species	Molality	Activity	y Molalit	y Activit	y Gamma	cm3/mol
Н+ ОН- Н2О	1.001e-006 1.002e-008 5.551e+001	1.000e-006 1.001e-008 1.000e+000	6 -6.00 8 -7.99 0 1.74	0 -6.00 9 -8.00 4 -0.00	0 -0.000 0 -0.000 0 0.000	0.00 (0) 18.07
(3) 1.00	0e-006	<u> </u>	-6.05	4 -6 05	4 _0 000	(0)
Fe (OH) 3	1.137e-007	1.137e-007	-6.94	4 -6.94	4 0.000	(0)
FeOH+2	2.677e-009	2.665e-009	-8.57	2 -8.57	4 -0.002	(0)
Fe (OH) 4-	1.038e-010	1.037e-010) -9.98	4 -9.98	4 -0.000	(0)
Fe2 (OH) 2+4	1.947e-016	1.912e-016	5 -12.30	1 -15.71	9 -0.008	(0)
Fe3 (OH) 4+5	3.627e-020	3.525e-020	-19.44	0 -19.45	3 -0.012	(0)
0) 1.41 H2	6e-023 7.079e-024	7.079e-024	-23.15	0 -23.15	0 0.000	(0)
0) 0.00 02	0e+000 0.000e+000	0.000e+000	-46.08	0 -46.08	0 0.000	(0)
		Saturation	n indices-			
Dhaca	C T	log TAD		0.00 TZ 1	2+m)	
Phase	21	IOG IAP	IOG K(.	298 K, I	alli)	
Fe(OH)3(a)	0.72	5.62	4.89	Fe(OH)3		
Goethite	6.62	5.62	-1.00	FeOOH		
H2O (a)	-20.00	-23.13	-3.13	п2 H2O		
Hematite	15.24	11.23	-4.01	Fe203		
Maghemite	4.85	11.23	6.39	Fe203		
O2 (g)	-43.19	-46.08	-2.89	02		
d of simulation	-					
	-					
ading input dat	a for simulat	ion 4.				
	· 					

Appendix L The effects of water mixing at the base of the piles on secondary mineralization and pH

The substantial mineralogical heterogeneity of Pile 2 materials can lead to localized areas of high reactivity and metal release into the aqueous phase (Chapters 4 and 5). The mixing of high-concentration, low-pH water with less-concentrated water can have a significant impact on the precipitation and dissolution of secondary minerals that would not occur if mixing did not take place. To highlight the effects of mixing of water draining from distinct tipping phases in Pile 2, a PHREEQC simulation that mixes effluent water from individual field barrels was conducted. The saturation indices of Cu-, Zn-, and Mn- sulfates, oxides, and carbonates consistently increase to supersaturation levels with the addition of variable amounts of lower-pH, higher concentration 2-3A effluent water to less-concentrated, higher-pH water from the other tipping phases (Figure L.1 to Figure L.4). Secondary mineralization therefore plays a major role in the release and attenuation of these metals not only temporally but also spatially within the waste-rock piles.



Figure L.1. Solubility and pH effects of mixing high-concentration, low-pH 2-3A effluent water with 2-0A effluent water.



Figure L.2. Solubility and pH effects of mixing high-concentration, low-pH 2-3A effluent water with 2-1A effluent water.



Figure L.3. Solubility and pH effects of mixing high-concentration, low-pH 2-3A effluent water with 2-2A effluent water.



Figure L.4. Solubility and pH effects of mixing high-concentration, low-pH 2-3A effluent water with 2-2B effluent water.