Minewall Stations and Mass Loadings at an Epithermal High Sulfidation Deposit – What, No Scaling?

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ABSTRACT

A geochemical study was completed to determine in-situ loading rates from pit wall alteration types on a mass per unit area basis using Minewall wash stations. Surface water quality samples were also collected to determine the aqueous geochemical signature from acid rock drainage and metal leaching of the open pit and waste rock dumps. Secondary mineral precipitates were collected and analyzed to provide insight into metal controls. The study provided information for use in predictive water quality modeling of current and future pit and waste rock dump water quality.

Study results show that pit and waste rock dump water quality can be described as a Ca-Fe-Al-H-SO_4 system in an advanced state of pyrite oxidation and acid sulfate flushing. Surface water quality samples indicate there is a noticeable dry-wet cycle that stores and releases secondary acidic minerals of wide ranging solubilities. X-Ray Diffraction analyses identified alunite(?), calcite, gypsum, chalcanthite, paracoquimbite, coquimbite, ferricopiapite, zincocopiapite, bronchantite, antlerite, and posnjakite that can potentially store and release a host of major and trace ions.

Minewall loading rates are up to 100 to 1000 times higher than humidity cell loading rates on a mass per mass basis, and likely originating from both primary mineral weathering (sulfide oxidation) and secondary mineral dissolution. It is likely that the degree of secondary mineral storage and release changes throughout the year in response to dry- (storage) wet-season (release), compared to primary mineral weathering loading contributions. Implications of these Minewall station loading rates are that they do not require scaling factors for use in water quality modeling to avoid effectively underestimating modeling estimates.

Keywords: Minewall, epithermal, modeling, loading rates, water quality

INTRODUCTION

The ore deposit of interest is an economic Au-Ag high sulfidation epithermal type. The mine is an open pit heap leach operation and has been operating since the late 1990s. The mine classifies material in terms of alteration types summarized in Table 1 and Figure 1.

Table 1 Pit surface areas at end of mining

Final pit exposure surface areas				
Alteration	**Code**	**m^2**	**km^2**	**%**
Colluvium	CO	7,308	0.007	0.37
Argillic	AR	1,158,343	1.2	59
Quartz Alunite	QA	603,192	0.60	31
Vuggy Silica	VS	27,794	0.028	1.4
Siliceous Clay	SA	136,332	0.14	7.0
no information	-	24,080	0.024	1.2
Total		**1,957,048**	**2.0**	**100**

Notes: Argillic composed of argillic oxide (28.5%) and argillic sulfide (71.5%)

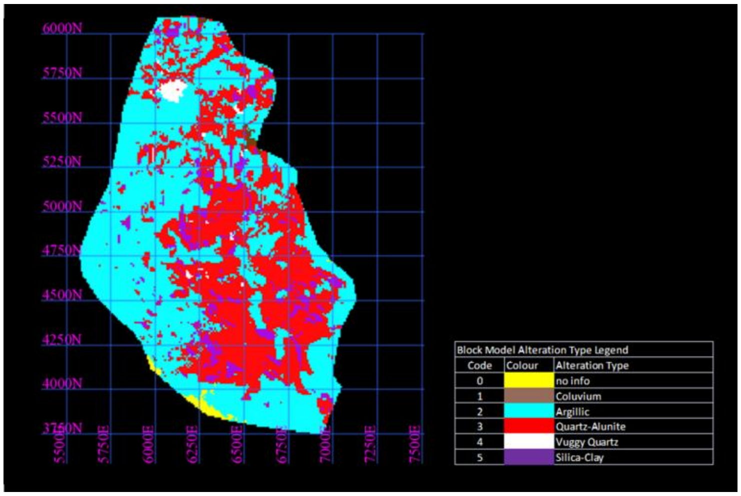

Figure 1 Pit alteration surface areas at the end of mining produced in Surpac

Table 2 summarizes the paragenetic minerals identified relevant to ARD-ML as sources of acidity and metal loadings to waste rock materials contact water quality. These minerals are termed as primary minerals in this study.

Table 2 Selected paragenetic minerals important to ARD-ML processes

Selected paragenetic minerals	Ideal formula
Alunite	$KAl_3(SO_4)_2(OH)_6$
Pyrite	FeS_2
Sphalerite	$(Zn,Fe)S$
Bismuthinite-stibnite	$Bi_2S_3 – Sb_2S_3$
Enargite	Cu_3AsS_4
Galena	PbS
Tennantite	$(Cu,Fe)_{12}As_4S_{13}$
Covellite	CuS
Native sulfur	S
Schwertmannite	$Fe^{3+}{}_{16}O_{16}(OH)_{12}(SO_4)_2$
Lepidocrocite	$FeO(OH)$
Goethite	$FeO(OH)$

The objectives of this study were to:

- Quantify site specific *in situ* loading rates of the various alterations types found on the open pit wall on a unit area basis [i.e., mass / (area * time)]
- Characterize surface water quality sampled directly downstream of the major mine components including pit walls and waste rock dumps
- Identify and quantify the secondary minerals controlling metal solubility, and
- Suggest modeling approaches to estimate closure water quality for mitigation purposes.

METHODOLOGY

International industry standard methods were employed throughout the desktop, laboratory and field scale studies consistent with MEND (2009) guidelines, the GARD Guide (INAP 2009) and Morin and Hutt (1997). Three types of sampling were carried out: surface waters, solid-phase secondary mineral precipitates and mine wall station leachate sampling within and directly downstream of the waste rock dumps (WRD) and pit walls. Analytical testing for the aqueous-phase was carried out at Certimin S.A., Lima (formerly CIMM) while solid-phase analyses were carried out at Mineral Services in North Vancouver, British Columbia, Canada.

Surface Waters

Surface water samples were collected within and directly downstream of the waste rock dumps and pits. The following parameters were measured or analyzed: pH (lab and field), electrical conductivity (lab and field), lab REDOX, acidity, sulfate, dissolved oxygen, alkalinity (carbonate, bicarbonate), cyanide (total, WAD), nitrogen (nitrate, nitrite, ammonia), fluoride, chloride, phosphate-phosphorus, total suspended solids, total dissolved solids, turbidity, and a 54 total and dissolved metals suite. Samples were collected in the field, split for total and dissolved metals analyses, preserved with standard high purity nitric acid after passed through standard 0.45 μm filters. Holding times were typically 24-48 hrs.

Secondary Mineralogy

Secondary mineral precipitates were identified in the field and collected for advanced mineralogical analyses. The objectives of the analyses was to identity and quantify the secondary weathering phases and associated metals of interest including Al, Fe, S, As, Cd, Cu, Pb, Sb, Zn and Hg. The mineralogical analyses consisted of X-Ray Diffraction with Rietveld-refinement, optical petrography, and scanning electron microscopy.

Thermodynamic Modeling

The geochemical thermodynamic modeling software Geochemist's Workbench (GWB) was used to model surface waters to determine potential secondary mineral controls on water quality (Bethke, 2008). Note that the data base thermo_minteq.dat was used for all modeling runs.

Minewall Stations

Established methodologies (Castendyk and Eary, 2009) for the prediction of closure pit lake water quality include mass-water balance approaches in parallel with thermodynamic geochemical modeling and water balance calculations. A prerequisite includes the quantification of elemental loading rates, typically sourced from standard humidity cells or larger-scale field kinetic tests (MEND, 2009) on a mass per unit mass basis over time [e.g., mg/(kg * week)]). Note that field based approaches are preferred for predictive water quality assessments as they include secondary mineral solubility controls under site-specific conditions of aged materials at advanced oxidation conditions (i.e., microbially mediated with pyrite oxidation by Fe^{3+}). Conversely, laboratory humidity cells are designed to estimate primary oxidation rates using a high liquid-to-solid leachate ratio (MEND, 2009) and are often the only source of elemental loading rate data available for predictive water quality modeling but require scaling from laboratory conditions to expected site-specific field conditions.

Another approach is the quantification of loadings rates on a mass per unit surface area basis [e.g., mg/(m^2*week)]. This later method, referred to as the Minewall approach, is a site-specific method and has been used successfully to bracket loading rates without the use of scaling factors (Morwijk Enterprises, 1995; Morin and Hutt, 2004). The method is particularly useful for active mines where reactive pit wall material is exposed and available for relatively easy leachate sampling. The method is designed for pit lake water quality predictions required for mine closure assessments.

Five Minewall stations were constructed on the main alteration types. Photo 1 shows an example station after construction. Between sampling events, a cover was placed over the station to allow:

- Mineral reactions to proceed aided only by humidity as the sole source of water, and

- Secondary minerals to precipitate and prevent flushing or hydraulic disturbance.

It is expected that the reactivity of a particular alteration type varies at different scales (mm to meters) and temporally as new materials is exposed on pit wall, however the size of the Minewall window (~1m), good understanding of typical alteration mineralogy and selection in the field results in reasonable representative sampling. Site-specific field-based calculations of material loading rates and reaction progress over time was subsequently generated.

Photo 1 Typical Minewall station prior to leachate collection (left) and with cover between sampling events (right). Note that the upper horizontal structure of the Minewall measures ~50cm for scale.

Minewall stations were sampled weekly for the first month and then monthly for eight months thereafter between November 7, 2011 and July 7, 2012. Sampling consists of gently flushing one litre of distilled water over the face of the exposed material and collecting the leachate in a clean HDPE sample bottle for analyses. Approximately 0.75 L of leachate was collected per sampling event. The following parameters were measured or analyzed: pH (lab), electrical conductivity (lab), REDOX, acidity, alkalinity, sulfate, and a 52 element total and dissolved suite. Full Minewall construction and sampling methodology can be found in Morin and Hutt (2004). Samples were collected in the field, split for total and dissolved metals analyses, preserved with standard high purity nitric acid after passed through standard 0.45 μm filters. Holding times were typically 24-48 hrs.

RESULTS AND DISCUSSION

Surface Water Quality (WQ)

These waste materials are highly acid generating; similar to other deposits types around the world, such as Pueblo Viejo, Dominican Republic and Summitville, Colorado. Waste rock dump and pit wall contact waters can be described by the Ca-Fe-Al-H-SO_4 system (Figure 1). The measured acidity over time indicates that there is a noticeable increase as the wet season begins, typically October or November. The mechanism for this temporal difference is due to the dissolution and flushing of soluble secondary acidic minerals, which have precipitated in the preceding dry season via evapo-concentration. This is a common climate driven process observed at other acidic mine sites controlling WQ (Nordstrom and Alpers, 1999). Such waters are often characterized by a Ficklin plot where the acidic system results in high dissolved trace metal concentrations, and in this case is an excellent predictive tool to determine bulk trace metal concentrations Figure 2. The pH shows a narrow acidic range less than pH 3.0 and can be considered to have high metals and high acidity originating from epithermal high sulfidation quartz alunite acid sulfate mine components (Plumlee et al, 1999).

Note that water treatment at site includes HDS + RO technology to meet national WQ regulations for users downstream. ARD has been calculated to continue and persist for several decades to hundreds of years after closure.

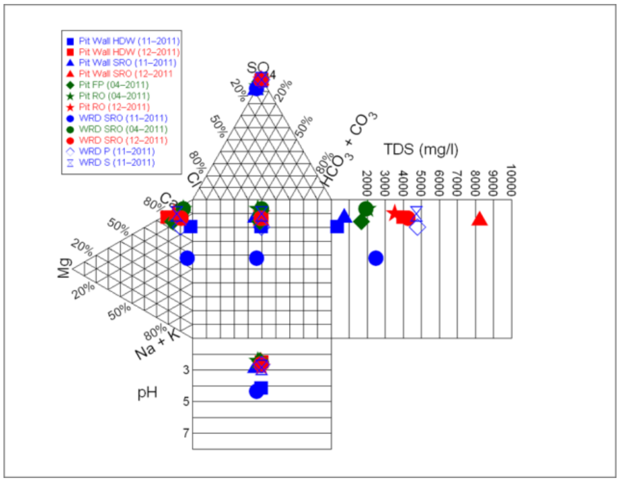

Figure 1 Durov diagram of waste rock dump and pit wall contact waters

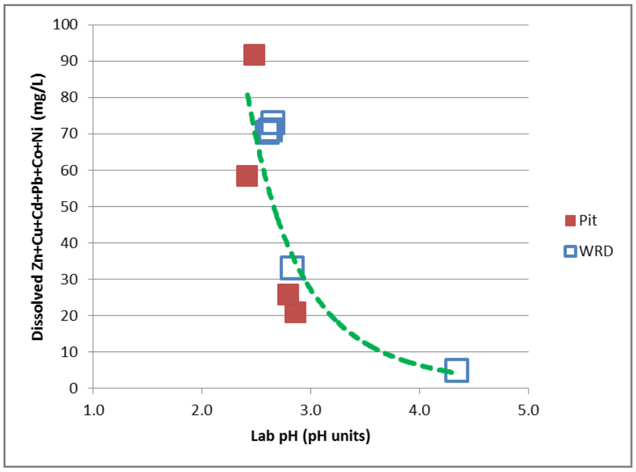

Figure 2 Ficklin Plot of waste rock dump and pit wall contact waters.

Thermodynamic Modeling

Sulfide oxidation and acid sulfate dissolution at Pierina are the main geochemical process impacting WQ. The paragenetic sequence of secondary Fe-SO4 minerals after pyrite oxidation has been documented by Bandy (1938), Buurman (1975) and Nordstrom and Alpers (1999) and is summarized by Jambor et al. (2000; Table 1). The mineral evolution can be regarded as an initial precipitation of hydrated Fe-SO4 minerals followed by progressive (de)hydration as the mineral crystal lattice matures. In an open system, such as WRDs and pits, the (de)hydration cycle will typically follow the seasonal climate trends (precipitation and evaporation). However, the entire or partial suite of hydrates may be present as moisture content or vapour pressure varies at the micro-scale within/on the WRD and pit wall materials.

Table 1 Paragenetic Secondary Mineral Sequence after Pyrite Oxidation (modified from Jambor et al, 2000)

Stage	Mineral	Formula
Early	Pyrite	FeS_2
	Melanterite	$FeSO_4{\cdot}7H_2O$
	Siderotil	$FeSO_4{\cdot}5H_2O$
	Rozenite	$FeSO_4{\cdot}4H_2O$
	Szmolnokite	$FeSO_4{\cdot}H_2O$
	Copiapite	$Fe^{2+}Fe^{3+}_4(SO_4)_6(OH)_2{\cdot}20H_2O$
	Romerite	$Fe^{2+}Fe^{3+}_2(SO_4)_4{\cdot}14H_2O$
	Coquimbite	$Fe^{3+}_2(SO_4)_3{\cdot}9H_2O$
	Kornelite	$Fe^{3+}_2(SO_4)_3{\cdot}7H_2O$
	Rhomboclase	$(H_3O)Fe^{3+}(SO_4)_2{\cdot}3H_2O$
	Parabuttlerite/Voltaite	$K_2Fe^{2+}_5Fe^{3+}_4(SO_4)_2{\cdot}18H_2O$
Late	Jarosite/Halotrichite/Bilinite	$Fe^{2+}(Al,Fe^{3+})_2(SO_4)_4{\cdot}22H_2O$

Results of thermodynamic modeling of WRD and pit WQ are presented in Figure 3 through Figure 6. Modeling indicates dissolved Ca, K, Al and SO_4 may be controlled in the form of gypsum ($CaSO_4{\cdot}2H_2O$) and alunite precipitation [$(K, Na)_2Al_6(SO_4)_4(OH)_{12}$]. Additional potential controls on dissolved Cu and SO_4 include bronchanite [$Cu_4SO_4(OH)_6$] and antlerite [$Cu_3SO_4(OH)_4$], however the pH of the system would have to approach neutral conditions for bronchanite stability.

Other secondary minerals that may be theoretically controlling WRD and pit WQ are ferrihydrite [$Fe(OH)_3$], K-jarosite [$Fe^{2+}(Al,Fe^{3+})_2(SO_4)_4{\cdot}22H_2O$] and melanterite ($FeSO_4{\cdot}7H_2O$). Ferrihydrite is important as it is a common host for metal sorption in the aqueous systems (Dzombak and Morel, 1990). The latter two minerals are important as they bracket an important and common family of hydrated Fe-SO_4 minerals found in acid environments (Nordstrom and Alpers, 1999 and Jamieson et al, 2005) and may be additional controls on trace metals such as Zn.

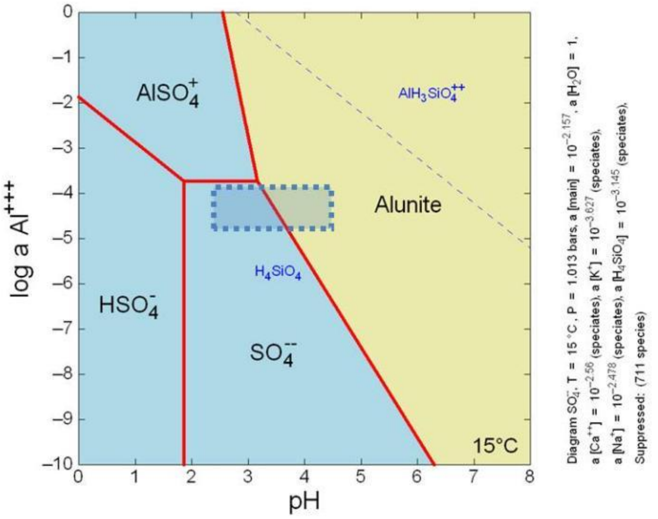

Figure 3 Log Activity of Al vs. pH Diagram (dashed box indicates WRD and pit waters)

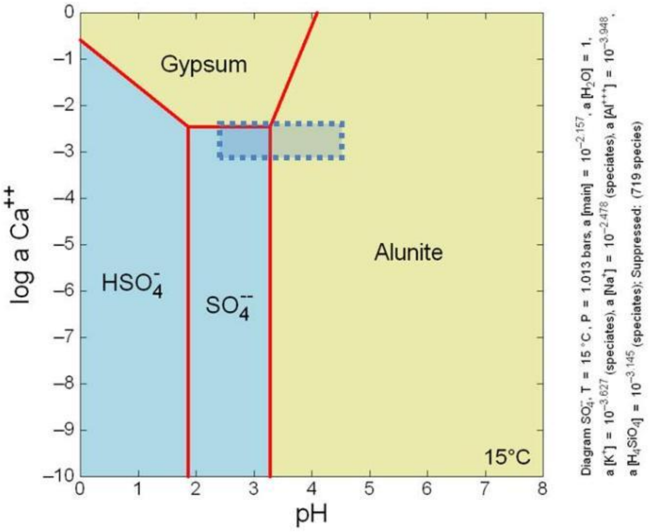

Figure 4 Log Activity of Ca vs. pH Diagram (dashed box indicates WRD and pit waters)

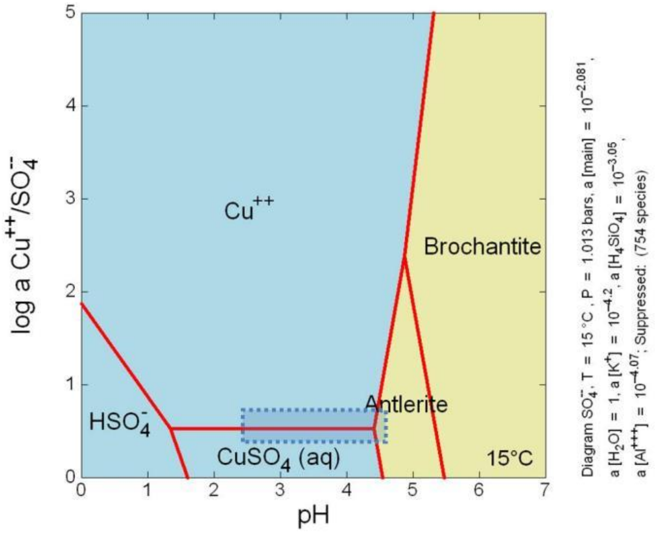

Figure 5 Log Activity of Cu/SO_4 vs. pH Diagram (dashed box indicates WRD and pit waters)

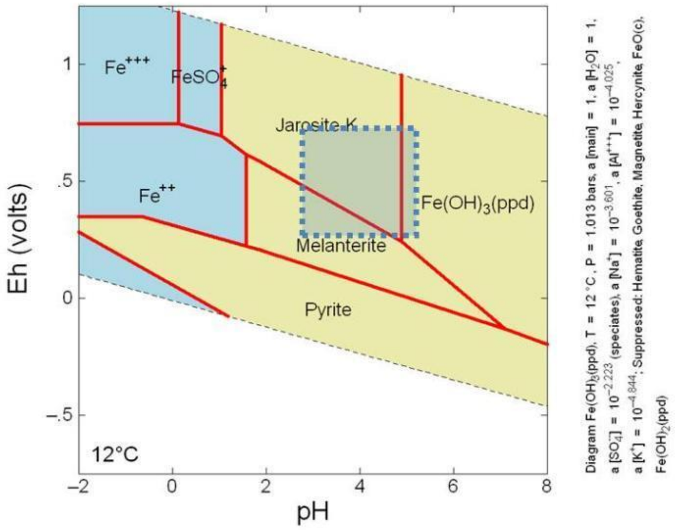

Figure 6 Eh-pH Diagram for the Fe-S-K System (dashed box indicates WRD and pit waters)

Secondary Mineralogy

Secondary mineral precipitates can be found at the centimetre to 10s of meter scale. Six of ten samples collected showed distinct morphological differences or were from distinct environmental locations (i.e., WRD and pit vs. Leach Pad) and were submitted for mineralogical analyses.

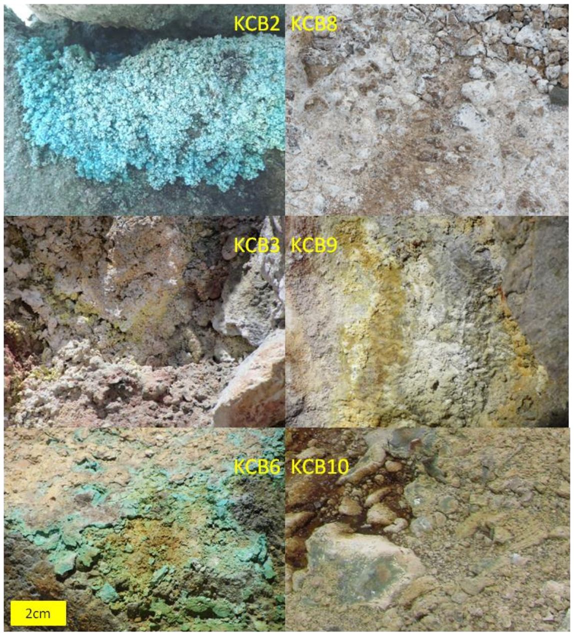

Figure 7 Secondary mineral sample locations

Table 2 summarizes the secondary minerals identified by XRD with Rietveld refinement. Note that primary alunite is present in several distinct morphologies and is ubiquitous. Furthermore, alunite is kinetically slow to precipitate at standard temperature and pressure likely requiring high ionic strengths in solution to overcome this barrier (Alpers et al, 1994). However, alunite has been observed in low P&T digenetic environments (Wray, 2011; Prietzel and Mayer, 2005; Goldbery, 1980 and Goldbery, 1978). The formation of alunite can be described as a result of the alteration of K-rich clays, such as kaolinte and/or illite in acidic environments. Although sample collection focussed on secondary minerals, "entrainment" of primary alunite in sample collection cannot be ruled out.

An unexpected result of the XRD analysis was the presence of calcite in the 6KCB sample. Calcite is extremely soluble in acidic conditions, such as those found within the pit and WRD environments. Analytical misinterpretation has been ruled out as this mineral was identified petrographically on several occasions. Carbonate is typically found as rims on lithic fragments and is thought to be either from the original paragenetic sequence or less likely, as a secondary precipitate forming at ambient conditions in the pit. In addition, calcite may be present at the core of particles, either through original paragenetic mineral encapsulation or subsequent secondary mineral armouring and unavailable for reactions. Neither of these possibilities can be ruled out at this time, and may be moot as there is nil buffering capacity evident in the highly acidic pit and WRD aqueous environment. However, the identification of bronchanite via XRD coupled with the theoretical thermodynamic modeling provides supporting evidence and a potential geochemical pathway for slightly acidic to near-neutral pH micro-environments. However, the pH of the pit on a macro-scale remains highly acidic.

Calcium, Cu, Fe, Zn and S attenuating mechanisms are evident through ideal crystal lattice structure formulas. This is especially important for the Cu-SO_4 phases where Cu contributes as much as 4 moles to the weight of the ideal minerals found at station 6KCB. Additional important trace elements associated by either substitution/co-precipitation into the lattice or sorption onto the mineral include Cu, Co, Mn, S, Al, Si, Na, Pb, Mn. Note that no micro/nano mineralogical techniques were done to investigate these mechanisms and quantify concentrations.

Table 2 Secondary minerals identified by XRD with Rietveld refinement.

Selected Minerals	Ideal Formula	2KCB	3KCB	6KCB	8KCB	9KCB	10KCB
				Weight %			
Pyrite	FeS_2	2.6		4.2		5.7	3
Covellite?	CuS				0.2		
Alunite	$K_2Al_6(SO_4)_4(OH)_{12}$	6.9	6.3	7.6	1.2	9.8	1.4
Gypsum	$CaSO_4 \cdot 2H_2O$	0.5		35.3	1.1	19.5	13.5
Chalcanthite	$CuSO_4 \cdot 5H_2O$	78.1					
Paracoquimbite	$Fe_2(SO_4)_3 \cdot 9H_2O$		28.7 (Al, Si, Na)				
Coquimbite	$Fe_2(SO_4)_3 \cdot 9H_2O$		2.2				
Ferricopiapite	$Fe^{2+}_{0.66}Fe^{3+}_4(SO_4)_6O(OH) \cdot 20H_2O$		47.2 (Al, Si)				
Zincocopiapite	$ZnFe_4(SO_4)_6O(OH) \cdot 18H_2O$					11.7	
Calcite	$CaCO_3$			7.0(Cu, Co, Mn, S, Al, Si, Na)	0.5		
Bronchantite	$Cu_4(SO_4)(OH)_6$			14.1 (Al, Si, Fe)			
Antlerite	$Cu_3(SO_4)(OH)_4$			9.2 (Al, Si, Fe)			
Posnjakite?	$Cu_4(SO_4)(OH)_6 \cdot H_2O$			0.6 (Al, Si, Fe)			
Amorphous (SEM)	(Fe, Mn, Pb) - (hydr)oxide Fe – (hydr)oxide with As, Zn, P, Al						

Notes: Elements in parentheses identified in/on mineral structure by SEM.

Secondary minerals are both sinks and sources of the above mentioned elements. They are sinks as the dry season approaches and pit and WRD waters experience evapo-concentration and secondary mineral precipitation. Conversely, secondary minerals are sources of elemental loadings to surface waters as the wet season approaches and minerals dissolve due to their moderate to high solubility.

Mass Loadings per Unit Area

Minewall loading rates (Figure 8 to Figure 10), based on unit surface areas, were compared with humidity cell loading rates and show *in situ* field rates are potentially 100-1000 times higher than lab-based rates. This agrees with an extensive comparison of Minewall and humidity cell data done by Morin and Hutt (2004). The Minewall loading rates are believed to be originating from both primary mineral weathering rates (pyrite oxidation) as well as secondary mineral dissolution. The relative magnitude of each was not determined; however, it is likely that secondary dissolution contributions oscillate throughout the year being greater during the onset of the wet season compared to primary minerals weathering loading contributions. The humidity cells contained drill core reject (80% passing <2 mm) that was acid generating (Figure 8) and show initial high first flushes, but much lower than Minewall station average acid loading rates. Note that humidity cell material particles are assumed to have cubic surface areas as a reasonably conservative estimate (as opposed to a sphere) for each mesh size particle analysis and respective surface area calculations.

The above observations have important scaling implications to modeling. Scaling is defined as the factors used to estimate the climatic and physical factors in the field that require accounting for when loading rates are derived from laboratory-based kinetic experiments (e.g., humidity cells). Minewall stations are designed to produce site-specific in situ loading rates, meaning that climate and physical scaling factor products are equal to one. The Minewall station leachates are thus assumed to be at quasi-equilibrium (Morin and Hutt, 2007), meaning that the following factors are at a scale large enough not to require additional adjustments:

Mass – generally it is difficult to convert exposed Minewall station material to a mass basis, as the depth/thickness of mass contributing to active leaching cannot be accurately estimated. For example, if we assume a uniform 2.7 t/m^3 density of the minerals exposed at the QA Minewall station and either a 0.002 m or 0.01 m active leaching depth, the resulting calculations would yield 0.46 kg and 2.3 kg of active mass contributing to leaching, respectively. Field observations indicate that an estimated volume of <10% to 15% of the total flushing solution (~1 L) is initially taken up (i.e., sponge effect) by the wall material. Therefore, field observations would suggest that the depth of the active mineral layer is on the order of millimetres instead of cm. This estimate varies for the different alteration types (i.e., the AR material has a relatively higher sponge effect than the QA material), however the absolute differences between alteration types is not believed to impact concepts or interpretations materially. Note that inundation of large proportions of pit wall areas (i.e., pit lake formation) can result in water penetrating the wall to a significant depth as the pit lake develops and perhaps nullifying the small-scale observations at the Minewall station. Another important observation is that the ARG material shows continually increasing dissolved constituents and is likely associated with its friable nature. The advanced hydrothermal alteration inherent in the ARG material and subsequent chemical weathering at ambient conditions degrades this material physically into a fine-grained "muck" quickly after initial mining exposure. The potential suspended solids content is in the 1 g/m^2 to 10 g/m^2 range for all alteration types.

Area – at the Minewall station, the scale is believed to represent the alteration type average per unit area. In other words, alteration surface area in one part of the pit is equal to alteration surface area in another part of the pit (i.e., no scaling roughness factors according to fractures).

Surface Area Roughness – surface area roughness and/or fracturing is estimated to control loading rate estimates on a mass per unit area by 2-3 factors at most. This will not affect selection of base cases or upper bound loading rates for predictive WQ modeling.

Solid:Liquid ratio – over a one week period in April and November 2011, 5 L and 2 L of precipitation would have fallen on an average Minewall station surface area of 0.11 m^2, assuming the Minewall surface was planar. In reality, the Minewall stations are inclined and if we assume a slope of 1:2.5 the resulting planar area of the average Minewall station would capture 2.2 L and 0.8 L for the month of April and November, respectively. In practicality, this is considered the same as the 1 L flushing and 0.75 L collection volumes during Minewall station sampling in the first month.

Reaction rates – reaction rates are assumed to be optimal (i.e., pH <3.5 and advanced enough that Fe^{3+} is the primary electron acceptor in pyrite oxidation likely mediated by microbial activity as shown in Equations 1). Note that no Fe speciation or microbial identification was carried out in this study; however, the low pH, high dissolved Fe, SO_4 and acidity in WQ samples and age of the pit wall material suggests this assumption is valid.

$$Fe^{2+}{}_{(aq)} + 0.25O_{2(aq)} + H^{+}{}_{(aq)} \rightarrow Fe^{3+}{}_{(aq)} + 0.5H_2O_{(l)}$$

$$FeS_{2(s)} + 14Fe^{3+}{}_{(aq)} + 8H_2O_{(l)} \rightarrow 15Fe^{2+}{}_{(aq)} + 2SO_4^{2-}{}_{(aq)} + 16H^{+}{}_{(aq)}$$

Equations 1 Ferrous Oxidation (upper) and Advanced Pyrite Oxidation (lower)

Conversely, humidity cell scaling factors typically -scale down loading rates for grain size based on the fact that the humidity cell is testing 80% <2 mm and is often assumed to typically represent 5% to 25% of the waste and pit wall grain size. Additionally, this is only one of several scaling factors that are applied to loading rates (Morin, 2013) translating into a typical factor product of 0.1-0.001. This effectively decreases the applied loadings rates and could underestimate WQ predictions. Note that the humidity cells operated for 25 and 60 weeks to near stable rates. The comparison between lab and field data strongly suggests the Minewall station data should be used for future pit inundation, flushing and pit lake predictions for closure WQ and mitigation assessments.

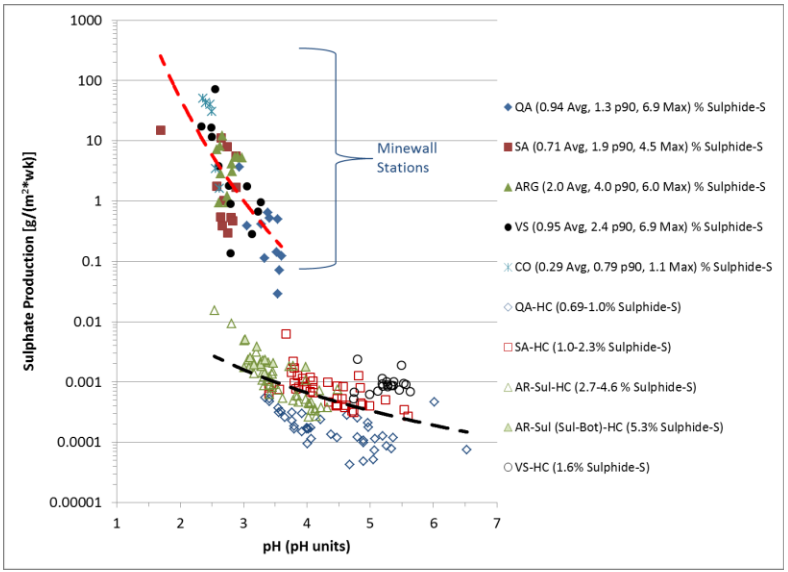

Figure 8 Minewall station and humidity cell leachate acidity loading rates versus pH.

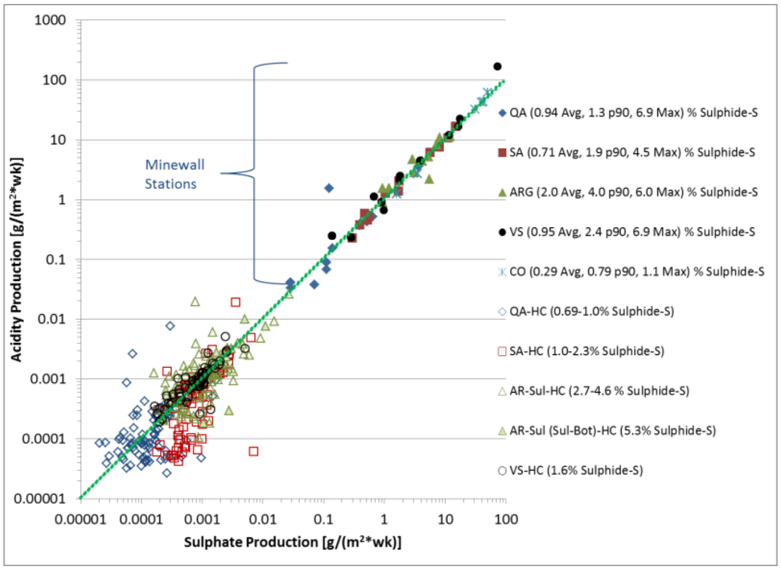

Figure 9 Minewall station and humidity cell leachate acidity versus sulfate loading rates.

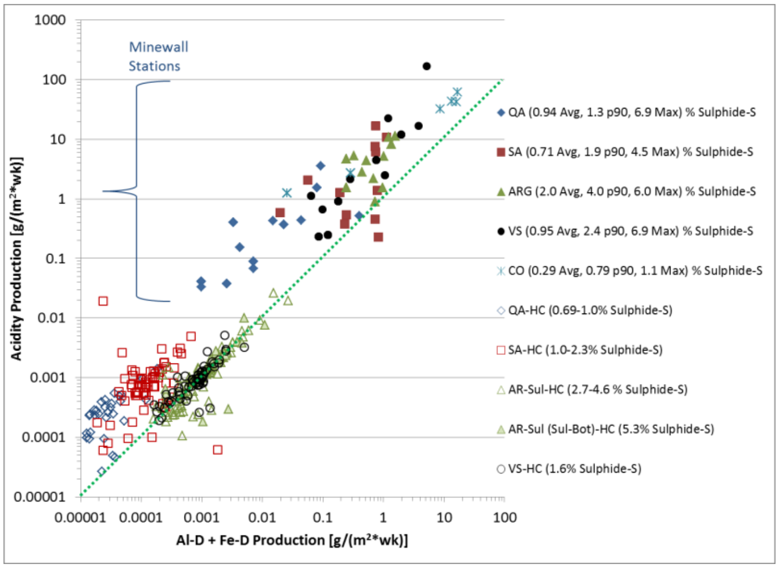

Figure 10 Minewall station and humidity cell leachate acidity versus Al-D + Fe-D loading rates.

CONCLUSION

Epithermal high sulfidation acid sulfate geology produces leachate water high in metal and acidity, consistent with other deposits of the same type. Field leaching studies were initiated on representative alteration types on aged pit walls at the meter scale known as Minewalls. Loading rates are up to 100 to 1000 times higher than humidity cell loading rates on a mass per unit area basis with both primary and secondary minerals contributing to loadings on a seasonal basis. Minerals of interest included pyrite, calcite, chalcanthite, paracoquimbite, coquimbite, ferricopiapite, zincocopiapite, bronchantite, antlerite, and posnjakite and possibly alunite. Minewall station loading rates do not require scaling factors for use in water quality modeling and will avoid effectively underestimating estimates.

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