Characterization of ARD Neutralization Sludges: Effect of ARD Influent Chemistry on Sludge Composition

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Abstract
As part of a project funded by the Mine Environment Neutral Drainage Program (MEND) and several industrial partners, ARD neutralization sludges generated via lime addition from seven sites across Canada were examined by high resolution microscopy, including Scanning Electron Microscopy (SEM), and Scanning Transmission Electron Microscopy (STEM). The primary objectives were to resolve the nature of the metal(loid) phase associations, and to define the links between ARD influent/effluent chemistry, treatment process and sludge composition. In all cases, metal-bearing phases were amorphous or poorly crystalline and variable in composition (relatively pure to highly heterogeneous). Metal-host phases were sludge specific, and included relatively pure Fe-oxyhydroxide, amorphous Mg-Al-(Fe) hydroxysulfate as well as amorphous metal (e.g., Cu) hydroxides. The data indicate that the nature of metal(loid) phase associations is strongly dependent on ARD influent chemistry, with the relative proportions of Fe, Mg, Al and sulfate being dominant variables. Compositional zoning in sludge particles was evident for high-density sludges (HDS), consistent with dissolution and re-precipitation reactions predicted to occur in response to sludge recycling in the HDS process. Implications for sludge chemical stability and management are discussed.

Key Words: ARD, high density sludge, SEM, TEM, XAS, lime treatment.

Introduction
Lime addition is a common treatment method for managing acid rock drainage (ARD), whereby an increase in pH promotes the precipitation of metals from solution as voluminous sludges that must be separated from the waste stream. Neutralization sludges represent a significant waste product from mining and metallurgical operations. Within Canada alone, it is estimated that approximately 7 x 10^6 m^3 of lime-treatment sludges are generated on an annual basis (MEND, 1997). Given that neutralization sludges represent significant repositories of metal-rich material, an understanding of their chemical stability in various depositional settings (ponds, open pits, co-disposal with waste rock, tailings, etc.) is a prerequisite for effective environmental management. In particular, trace-element associations within lime neutralization sludges must be understood to allow for Eh and pH dependent solubility predictions.

Due to the extremely fine-grained and often amorphous (*i.e.*, non crystalline) character of sludge solids, the composition of these materials has been difficult to elucidate. Traditional methods such as X-Ray Diffraction (XRD) and optical microscopy have proved ineffective since amorphous materials are not detected by XRD and since optical microscopy does not provide sufficient spatial resolution to fully differentiate trace element associations. Early conceptions that metals precipitate solely as their respective hydroxides (*e.g.*, $Cu(OH)_2$, $Zn(OH)_2$) during the neutralization process are now known to be overly simplified and largely incorrect. Instead, it is now known that metals may be removed from solution through several pathways in addition to hydroxide formation, including coprecipitation with hydrous ferric oxides (*e.g.*, FeOOH), Mn-oxyhydroxides (MnOOH), Al hydroxides ($Al(OH)_3$), and other mixed Fe-Mg-Al-hydroxy sulfates (Webster et al., 1998; MEND, 2005; Loomer et al., 2007a,b). The current lack of definition of trace element associations in sludge materials is considered a significant information gap in the industry (MEND, 2005).

In order to provide further insight into characterization and management of ARD neutralization sludges, a combination of high-resolution microscopy methods and effluent chemical analysis was utilized to characterize the controls governing metal sequestration. Specific objectives included the following: 1) to elucidate the trace metal associations (phase relationships) in sludge materials; 2) to assess the links between the sludge trace metal associations and ARD influent chemistry; and 3) provide a basis from which to assess sludge chemical stability in various depositional environments.

Methods

Samples of ARD influent, treated effluent, and sludge solids were donated by several mines across Canada (Figure 1), including the Equity Mine (Goldcorp Canada), Geco Mine (Xstrata Zinc), Brunswick Mine (Xstrata Zinc), Britannia Mine (EPCOR Utilities Inc. and B.C. Ministry of Forests, Lands and Natural Resource Operations), Samatosum Mine (Inmet), Sullivan Mine (Teck) and Chisel North Mine (Hudson Bay Mining and Smelting). Background information with respect to commodities, deposit type and ARD treatment process at the mines is provided in Table 1.

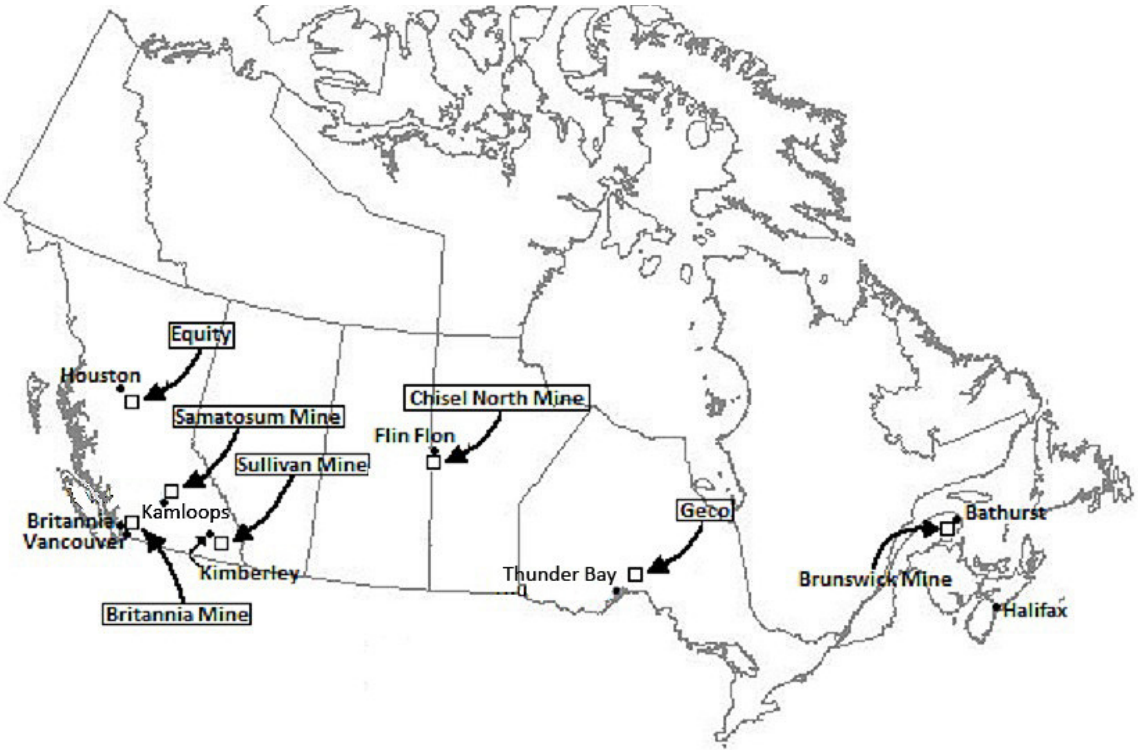

Figure 1. Location of the mines across Canada that participated in the ARD neutralization sludge characterization program.

Table 1. Background information on participating mines with respect to commodities, deposit type and treatment process.

	Mine						
	Equity	Geco	Britannia	Brunswick	Chisel North	Samatosum	Sullivan
Commodities	Au-Ag-Cu	Cu-Zn	Cu (Zn-Pb-Ag)	Pb-Zn-Cu-Ag	Cu-Zn	Ag-Cu-Pb-Zn-Au	Pb-Zn-Ag-Fe
Deposit Type	Intrusion-related hydrothermal	VMS	Massive Sulfide	VMS	VMS	Stockwork system	SedEx
Treatment Process	HDS	HDS	HDS	HDS	HDS	HDS	HDS

VMS = volcanic massive sulfide; HDS = high density sludge; SedEx = Sedimentary exhalative deposit

Influent and effluent water sample collection from the treatment plants was timed to coincide with sludge sample collection. Influent and effluent waters were sampled on multiple days before and after sludge collection to both: 1) assess variability in the influent and effluent streams; and 2) to ensure that the process waters were representative of the sludges generated. Overall, all influent and effluent waters showed a high level of consistency over the daily time scales of sample collection. Waters were analyzed for a full suite of physical and chemical parameters.

Sludge materials were analyzed by total elemental analysis, X-Ray Diffraction (XRD), optical microscopy, scanning electron microscopy (SEM), and (scanning) transmission electron microscopy (STEM) as described in Martin et al. (2011). Optical images were collected using the Leitz Laborlux 11 Pol petrographic microscope. For SEM, samples were analysed using a JEOL JSM6400 Scanning Electron Microscope equipped with an EDAX Genesis Energy Dispersive X-ray Spectroscopy system (EDS) operated at a 20 keV accelerating voltage. Back scattered electron (BSE) images, point EDS analyses, and 2-dimensional elemental maps were collected. STEM microscopic analysis was performed using a JEOL 2011 instrument for imaging, selected-area electron diffraction (SAED) and qualitative EDS analyses. STEM imaging was conducted using a Gatan Annular Dark Field (ADF) detector. Chemical composition in STEM mode was determined using an EDAX Genesis EDS System; point EDS analyses and 2-dimensional elemental maps were collected. When applicable, mineralogical identification from SAED patterns was conducted using Crystal Maker 2.0 software.

Results and Discussion

Influent and effluent water quality

Equity Mine

Equity Mine ARD influent was dominated by SO_4^{2-}>Mg>Al>Fe>Ca>F. With respect to cations, the combined molar concentration of Mg+Al was greater than four times the concentration of Fe. Zn (~120 mg/L) and Cu (~60 mg/L) represent the dominant trace elements in the ARD feed. Of the major cations, Al and Fe were removed completely during treatment while Mg was reduced in concentration by ~60% (Figure 2). Through the treatment process the pH increased from 2.6 to 7.0. The composition of the clarifier outflow (e.g., treated effluent) was dominated by SO_4^{2-}, Ca, Mg, Mn, Na and Sr, with the majority of trace elements at values below the limits of analytical detection. Sulfate concentrations were reduced

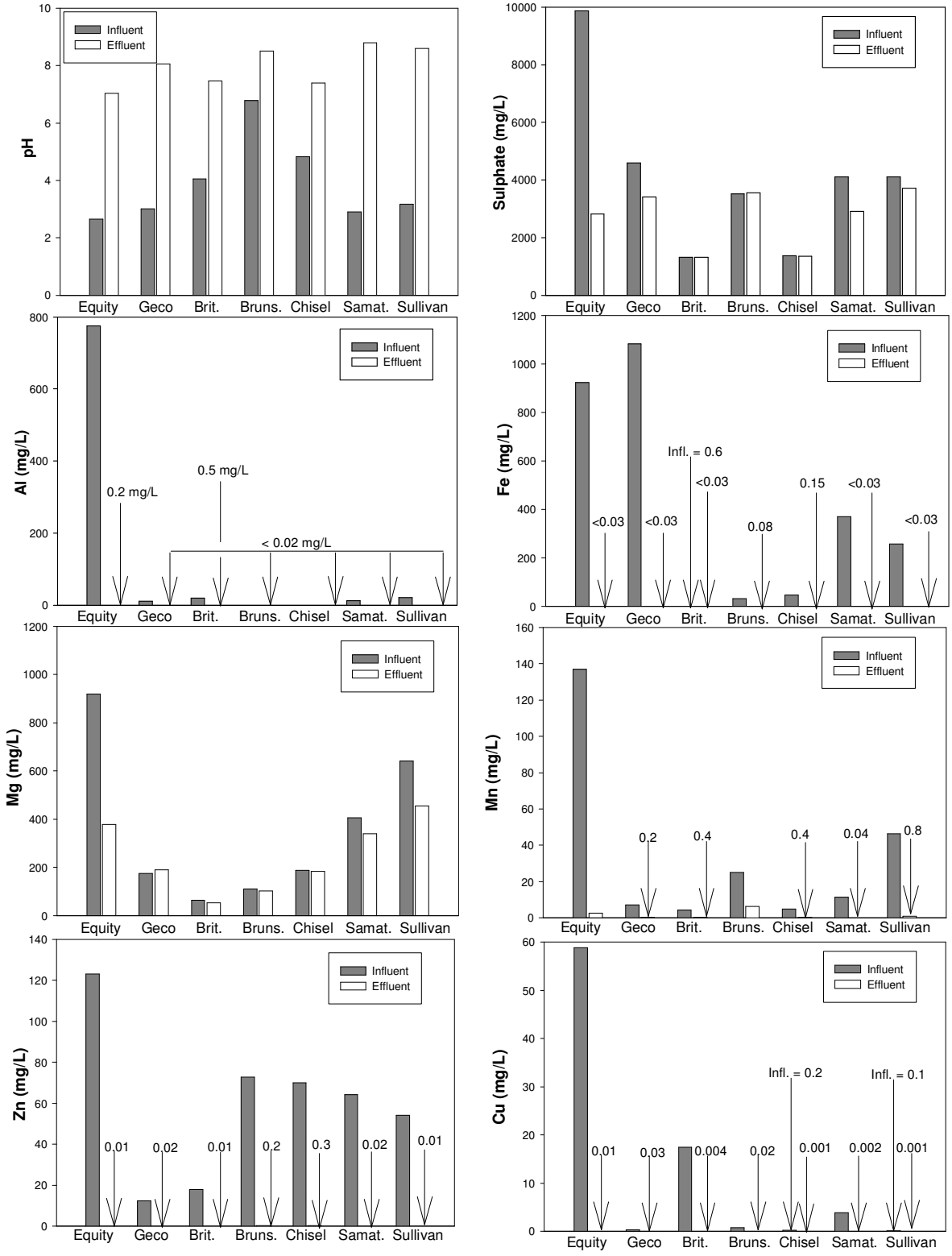

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Figure 2. Influent (raw ARD) and effluent (post HDS lime treatment) water quality for Equity Mine, Geco Mine, Britannia Mine (Brit.), Brunswick Mine (Bruns.), Chisel North Mine (Chisel), Samatosum Mine (Samat.) and Sullivan Mine. All labeled values with arrows represent effluent values unless indicated. All values for dissolved species.

considerably during the treatment process from ~9,000 mg/L in the influent to ~2,800 mg/L in the outflow. Saturation indices calculated using PHREEQC (Parkhurst and Appelo, 1999) indicate that the treated effluent was near saturation with respect to gypsum and fluorite.

Geco Mine

The Geco ARD solute inventory was dominated by SO_4^{2-}>Fe>>Ca≅Mg (Figure 2). Based on molar proportions, the average concentration of Fe was greater than the combined contribution from Ca and Mg. Zn (~12 mg/L), and to a lesser degree Cu (~0.3 mg/L) and Cd (~0.04 mg/L), represent the dominant trace elements in Geco ARD. Concentrations of these elements were reduced in the outflow by an average of greater than 90% relative to the composition of the feed water while pH increased from 3.0 to 8.1. Sulfate concentrations decreased only marginally through the HDS process (4,590 mg/L to 3,400 mg/L). An increase in Mg concentration in the treated effluent likely reflects the dissolution of Mg-bearing lime. Saturation indices indicate that the Geco effluent was slightly supersaturated with respect to gypsum, fluorite, calcite, ferrihydrite, barite, and gibbsite ($Al(OH)_3$).

Britannia Mine

The Britannia Mine ARD influent was dominated by SO_4^{2-}>Ca>Mg>Al >Cu>Zn (Figure 2). The dominant trace elements in Britannia Mine ARD were Cu (~18 mg/L) and Zn (~18 mg/L), with concentrations being reduced to <10 ppb through the HDS process. Through the treatment process pH increased from 4.0 to 7.5. The composition of the clarifier outflow was dominated by SO_4^{2-}, Ca and Mg. SO_4^{2-} showed a negligible change in concentration through the treatment circuit. Saturation indices indicate that the effluent solution was supersaturated with respect to goethite, ferrihydrite, barite and gibbsite, and nearly saturated with respect to gypsum, calcite, fluorite, and quartz.

Brunswick Mine

Brunswick Mine ARD influent composition was dominated by Na>SO_4^{2-}>Mg>Ca>Cl. Zn (~70 mg/L) represents the dominant trace element of concern in ARD feed waters (Figure 2). SO_4^{2-}, Na, Ca, and Mg represented the main solutes in the clarifier outflow with most trace elements at values below the limits of analytical detection. While the pH increased from 6.8 to 8.5, concentrations of SO_4^{2-}, Mg, and Ca were not appreciably affected by the treatment. Solubility calculations indicate that the effluent solution was supersaturated with respect to calcite, goethite, ferrihydrite, barite, and gibbsite, and approached the limits of saturation for gypsum and quartz.

Chisel North Mine

Chisel North Mine ARD was dominated by Cl>Na>Ca>SO_4^{2-}>Mg. Zn (~65 mg/L) represents the dominant trace element of concern in ARD feed waters. Through the treatment process, the pH of the influent water increased from ~4.8 to 7.4, with the concentrations of Zn being reduced to 0.3 mg/L. Dominant solutes in the clarifier outflow include SO_4^{2-}, Ca, Mg, and Na, all of which showed negligible changes in concentration through the HDS process. Calculated saturation indices indicate that the effluent solution was supersaturated with respect to goethite, ferrihydrite, barite and gibbsite, and approached saturation for gypsum, fluorite, and quartz.

Samatosum Mine

Samatosum Mine ARD influent was dominated by SO_4^{2-}>Mg>Ca>Fe (Figure 2). With respect to cations, the molar concentration of Mg was nearly twice that of Ca. Zn (~64 mg/L) represents the dominant trace element in ARD feed waters. The composition of the clarifier outflow was dominated by SO_4^{2-}, Ca, and Mg with SO_4^{2-} concentrations showing a significant decrease through the treatment process (~4,100 mg/L to 2,900 mg/L). Through the treatment process pH increased from 2.9 to 8.8 through the treatment process. Solubility calculations indicate that the effluent solution was supersaturated with respect to gypsum, calcite, goethite, ferrihydrite and barite.

Sullivan Mine
Sullivan Mine ARD was dominated by SO_4^{2-}>Mg>Ca>Fe. With respect to cations, the Mg concentration was more than three times that of Ca. Zn (54 mg/L) represents the most abundant trace element in the ARD feed. Through the treatment process, the pH of the influent water increased from ~3.2 to 8.6, with soluble Zn levels reduced to <0.01 mg/L. Of the major cations, Al and Fe were removed completely while Mg was reduced in concentration by ~30%. The composition of the clarifier outflow was dominated by SO_4^{2-}, Ca, and Mg. A minor reduction in sulfate concentration (~10%) was observed through the process (~ 4100 to 3700 mg/L) while the pH increased from 3.2 to 8.6. Saturation indices indicated the effluent was supersaturated with respect to gypsum, calcite, goethite, ferrihydrite, barite, and gibbsite.

Solid phase characterization
Equity Mine
The Equity Mine sludge was composed primarily of Ca, S, Fe, Al, and Mg (14, 12, 4.3, 4.0, and 2.5 wt. %, respectively) (Figure 3). Gypsum, Al oxyhydroxide, Fe-Al oxyhydroxide, calcite and apatite are the main sludge phases based on SEM imaging of composition and morphology. SEM and STEM analyses indicate that the main Zn-bearing phase is an amorphous Mg-Al-(Fe) hydroxysulfate (Figure 4). Other elements detected in the Mg-Al-(Fe) hydroxysulfate phase included Cu, As and Pb (EDS spectra shown in Table 4). SAED analysis conducted on the Mg-Al-(Fe) hydroxysulfate did not produce any discernible diffraction patterns, suggesting that this phase is amorphous. Qualitative assessment of the SEM images indicates the Mg-Al-(Fe) hydroxysulfate particles range from <1 μm to approximately 15 μm in size. STEM analysis also illustrates that while Ca may be an important component of the bulk sludge, it is not a major component of the metal-bearing Al-(Fe) hydroxysulfate phase. Larger grains of the Mg-Al-(Fe) hydroxysulfate show compositional zoning in concentric layers alternating between Mg+Al-rich (Fe-poor) and Fe-rich, which can be attributed to dissolution and re-precipitation reactions that occur during sludge recycling in the HDS process (Figure 4).

Geco Mine
The Geco HDS sample is composed primarily of Fe, Ca and S (26, 10, and 7 wt. %, respectively) with lower concentrations of Al, Mg, and Si (<1 wt. % combined) (Figure 3). The Fe content of the Geco HDS is the highest of all sludges analyzed, while the Mg concentration is the lowest. Phases identified by SEM include dominant gypsum, Fe-oxyhydroxide, Al-hydroxide and lime/calcite (Figure 4). Zn and Cu in the Geco sludge sample are predominantly associated with the Fe-dominant hydroxide (EDS spectra shown in Figure 4). High resolution EDS collected during STEM indicates that the Fe oxyhydroxide phase is essentially pure with only minor amounts of other constituents (Mg, Al and SO_4^{2-}). SAED analysis of the Fe oxyhydroxide suggests that this phase is poorly crystalline to amorphous (SAED pattern shown in Figure 4).

Britannia Mine
The Britannia HDS is composed primarily of Ca, Al, Zn and Cu (13, 6, 5 and 5 wt. %, respectively) with Mg in lower proportions (3 wt. %) (Figure 3). The Cu content measured in the Britannia sludge represents the highest of all the nine sludge samples analyzed while the Fe concentration is the lowest. The predominant metals of interest are Cu and Zn, which are present as fine-grained fibrous aggregates of Cu-Zn oxyhydroxide that include significant but variable Mg, Al and Si (Figure 4). STEM spectra indicate variable metal content in the Cu hydroxide (Figure 4). Other phases identified by SEM include a calcium-rich phase, likely calcite or Mg-calcite as revealed by XRD. The Fe content of the sample is generally low, but Fe-oxyhydroxides tend to form small clusters in the middle of the Cu-oxyhydroxide aggregates. The results of SAED analysis indicate that the Cu-oxyhydroxide phase is mostly amorphous.

Brunswick Mine
The Brunswick HDS is composed primarily of Ca and Fe (16 and 11 wt. %, respectively), with Mn and Zn also present in abundance (Figure 3). High resolution microscopy revealed the presence of two major

phases: 1) a calcium-rich phase (likely calcite, as supported by XRD analysis); and, 2) an Fe-Mn-Zn-rich oxyhydroxide phase. STEM elemental maps demonstrate that Zn is dominantly associated with the Fe-Mn-Zn-rich oxyhydroxide phase. EDS spectra demonstrate that the Fe-Mn-Zn-rich oxyhydroxide phase is fine-grained, fibrous and heterogeneous in its elemental proportions. Other elements consistently detected in the oxyhydroxide phases include Si, S, Cl, Mg and trace amounts of Al and Cu. Analysis of large (>20 µm), relatively pure calcite grains shows that Zn and calcite are not associated. Consistent with amorphous or nanocrystalline material, the Fe-Mn-Zn oxyhydroxide generated diffuse and spotty ring diffraction patterns when analyzed by SAED.

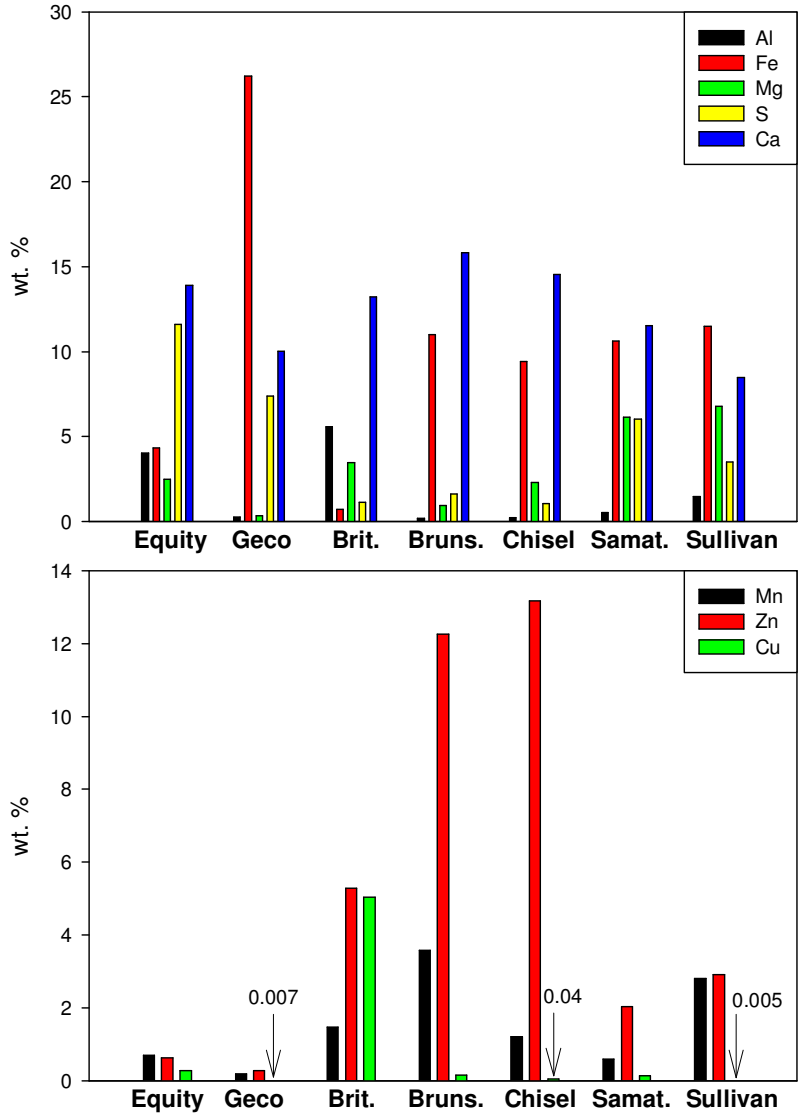

Figure 3. Solid phase elemental abundance for high density sludges for Equity Mine, Geco Mine, Britannia Mine (Brit.), Brunswick Mine (Bruns.), Chisel North Mine (Chisel), Samatosum Mine (Samat.) and Sullivan Mine.

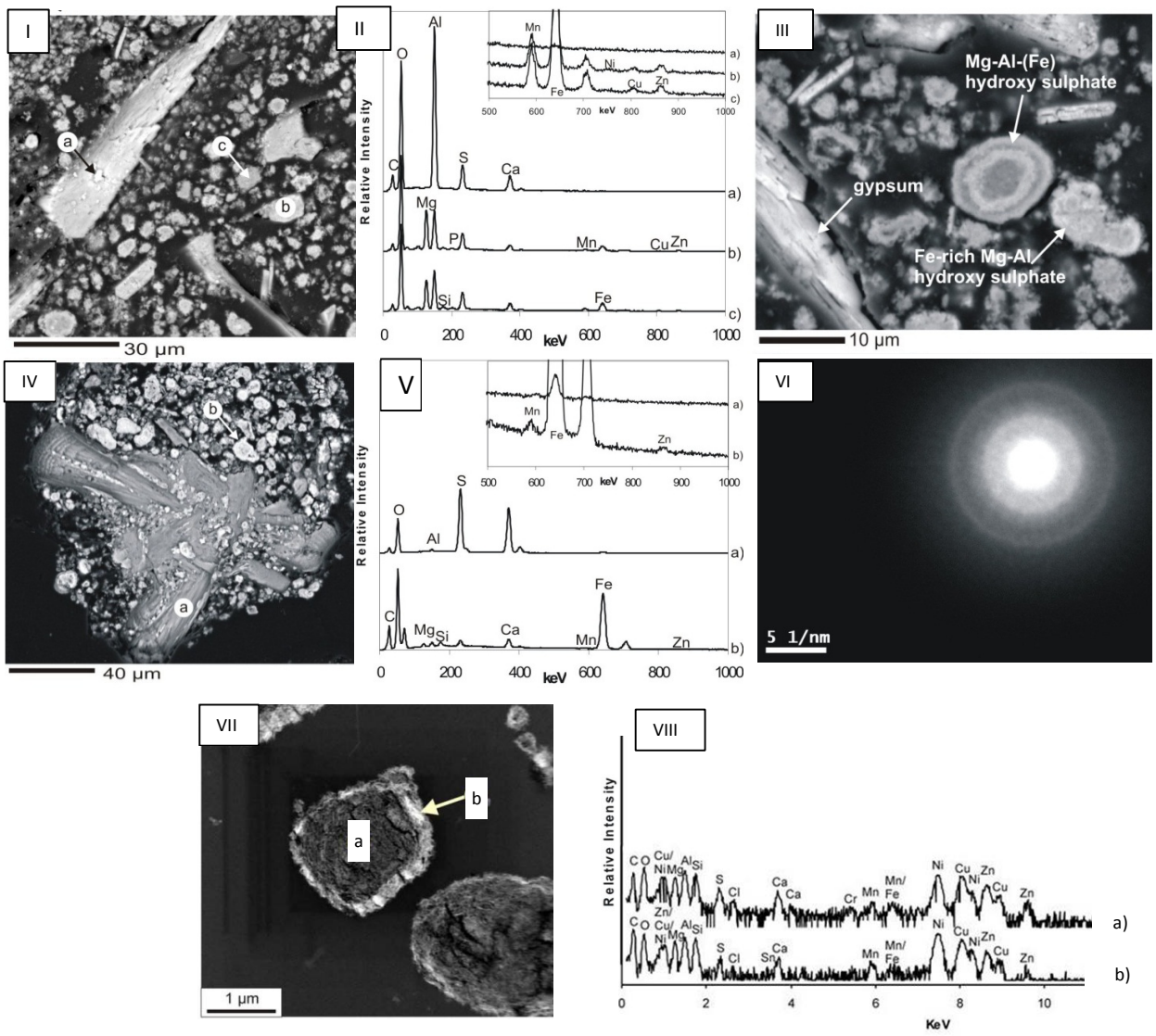

Figure 4: (I) SEM back scattered electron (BSE) image of Equity sludge and (II) associated Energy Dispersion Spectra (EDS) of gypsum + Al hydroxide (point a) and metal-bearing Mg-Al-(Fe)-hydroxysulfate (points b& c). (III) SEM BSE image of Equity sludge showing compositional zoning of Mg-Al-(Fe)-hydroxysulfate. (IV) SEM BSE image of Geco sludge and (V) associated EDS spectra of gypsum (point a) and metal-bearing Fe-oxide (point b). (VI) Selected area electron diffraction (SAED) pattern of Geco Fe-oxide (point b) showing broad diffusive rings, indicative of poorly crystalline material. (VII) STEM high angular dark field image of the Britannia Cu hydroxide showing compositional zonation; and (VIII) EDS spectra of Cu hydroxide showing variable metal content of particle interior (point a) and particle exterior (point b).

Chisel North

The Chisel North HDS sample is composed primarily of Ca and Fe (15 and 9 wt. %, respectively) with Mg present in lower proportions (2.3 wt. %) (Figure 3). SEM analysis suggests that two major mineral phases are present: 1) a calcium-rich phase (likely calcite, as supported by XRD analysis); and, 2) a Zn-Fe-Mn oxyhydroxide phase. Mg, Si, S, Ca and trace amounts of Al were consistently detected in the Zn-Fe-Mn oxyhydroxide. The predominant metal of interest in sludge materials is Zn, which is associated with the Zn-Fe-Mn oxyhydroxide. Trace levels of Cu and S are commonly associated with the Zn-Fe-Mn

oxyhydroxide. The results of SAED indicate that the Zn-Fe-Mn oxyhydroxide is amorphous or nanocystalline, and occurs as fine-grained, fibrous particles.

Samatosum Mine
The Samatosum HDS is composed primarily of Ca, Fe, Mg, and S (12, 11, 6.1, and 6.0 wt. %, respectively) (Figure 3). Five major phases in the sample are apparent from the SEM data: 1) a calcium-rich phase - likely calcite as indicated by XRD; 2) Al-silicate; 3) gypsum (identified by XRD); 4) relatively-pure Fe oxyhydroxide; and, 5) a Zn-bearing Mg- and Fe-rich oxyhydroxide phase. STEM analyses indicated that Zn is primarily associated with the Mg-Fe-rich phase. Al, Si, P, S, Cl, Ca and Mn were also consistently detected in the Mg-Fe phase. The results of SAED indicate that Mg-Fe oxyhydroxide is amorphous or nanocystalline, forming fine-grained and fibrous zones within the sludge matrix.

Sullivan Mine
The Sullivan HDS sample is composed primarily of Fe, Ca, and Mg (11, 8.5, and 6.8 wt. %, respectively) (Figure 3). SEM analysis indicates that there are three major mineral phases present: 1) a calcium-rich phase, likely calcite (as indicated by XRD); 2) gypsum (identified by XRD); and, 3) a Zn-bearing Mg- and Fe-rich oxyhydroxide. The predominant metal of interest in the Sullivan HDS is Zn, which is associated with the Mg-Fe oxyhydroxide. Al, Si, P, S, Cl, Ca, Mn and Cu were also consistently detected in the Mg-Fe phase. The results of SAED indicate that the Mg-Fe oxyhydroxide is amorphous or nanocystalline, occurs as fine-grained fibrous particles, and is heterogeneous in composition.

Solubility considerations for prediction of sludge type
The results of high-resolution microscopy on seven HDS samples has yielded five dominant metal-bearing phases: 1) Mg-Al-(Fe) hydroxysulfate (Equity); 2) Fe oxyhydroxide (Geco); 3) Cu-Zn hydroxide (Britannia); 4) Zn-Fe-Mn hydroxide (Brunswick and Chisel North); and, 5) Fe-Mg hydroxide (Samatosum and Sullivan) (summarized in Table 2). The results of the analysis also suggest that the nature of the metal-hosting phase can be linked to the composition of ARD feed waters, and specifically, the relative proportions of the major phase-forming elements (S, Al, Fe, Mg, Mn). The dominance of Fe, Al and Mg in the Equity HDS, for example, is consistent with the high concentrations of these elements in the ARD influent (Figure 2). The Equity HDS is also the only example of a dominant metal-bearing hydroxysulfate phase. This agrees with the high sulfate concentration in the ARD feed, and the marked reduction in sulfate concentration through the treatment process. In the Equity example, the pH-dependent solubility of sulfate is governed through associations with Al and Mg, which are also present in high concentrations in the ARD influent. For all other mines, which show much lower values for Al and Mg, sulfate concentration is not appreciably changed through the HDS process (Figure 2).

Mg is also a significant component of the Zn-bearing phases in the Samatosum and Sullivan (Fe-Mg-hydroxide) HDS samples, for which Mg concentrations in ARD were 405 and 641 mg/L, respectively (Figure 2). Like the Equity example, Mg shows a significant decrease in concentration between the influent and effluent samples at Samatosum and Sullivan (Figure 2). In contrast, Mg behaves conservatively at Geco, Britannia, Chisel North and Brunswick where Mg concentrations in ARD are considerably lower (64 to 188 mg/L). Such observations suggest the pH-dependent solubility of Mg is minimally influenced at these lower Mg concentrations.

The precipitation of Fe exhibits slightly more complex solubility controls. Fe is a significant component of the Zn-bearing sludge phase in six of the seven samples, precipitating with four different phases. Given the pH dependent solubility of ferrous Fe, near complete removal of Fe is expected in all HDS systems (Figure 2). The Geco ARD exhibits the highest Fe concentrations (1082 mg/L) and the Zn-bearing phase that forms in the neutralization process is a relatively pure Fe-oxyhydroxide. In this regard, the formation of a relatively pure Fe phase can be linked to the high concentration in the ARD feed, and relatively low

levels of other ions (e.g., Mg, Al), thereby minimizing competition from other competing metal phases (Aubé and Zinck, 1999). Although the Equity ARD exhibits comparable Fe content, competition by other phase-forming elements (e.g., Al, Mg, and S) does not allow the formation of a pure Fe oxyhydroxide. Fe is also relevant for the Samatosum, Sullivan, Chisel and Brunswick HDS samples, with ARD influent values ranging from 32 to 370 mg/L.

Of the samples analyzed, only the Britannia HDS did not show appreciable Fe in the metal-hosting phase. This can be attributed to the very low Fe content <0.6 mg/L) in the ARD feed at this site. In this regard, the predominance of a metal-bearing Cu-Zn-hydroxide at Britannia can be linked to the high concentrations of both Cu and Zn, in concert with the very low values for other phase-forming elements (S, Al, Fe, Mg, and Mn) (Figure 2).

Mn was also found to be a significant component in the metal bearing phases for Brunswick and Chisel North (Fe-Mn-hydroxide). In the case of Mn, the importance for the Brunswick and Chisel North sludge samples appears to relate to the higher proportion of Mn in comparison to other phase-forming elements (e.g., Al, Mg).

Table 2. Summary of dominant parameters in ARD influent, solid-phase elemental abundance in HDS samples, and dominant metal-bearing phase for sludge samples.

	Mine						
	Equity	Geco	Britannia	Brunswick	Chisel North	Samatosum	Sullivan
Dominant parameters in Influent	SO_4^{2-}, Al, Mg, Fe	SO_4^{2-}, Fe, Mg	SO_4^{2-}, Mg, Zn, Cu	SO_4^{2-}, Mg, Zn	SO_4^{2-}, Mg, Zn	SO_4^{2-}, Mg, Fe	SO_4^{2-}, Mg, Fe
Dominant solid-phase elements	Ca, S, Fe, Al, Mg	Fe, Ca, S	Ca, Al, Mg	Ca, Fe	Ca, Fe, Mg	Ca, Fe, Mg, S	Fe, Ca, Mg
Metal-hosting phase	Mg-Al-(Fe) hydroxysulphate	Fe-oxyhydroxide	Cu-Zn-hydroxide	Zn-Fe-Mn hydroxide	Zn-Fe-Mn hydroxide	Fe-Mg hydroxide	Fe-Mg hydroxide

Overall, the analysis provided herein provides a potential framework from which to define the metal-bearing phase or "sludge type", given a specific ARD influent composition. This is highlighted in the ternary plots in Figure 5, which show the location of the various sludge phases as a function of the relative proportions of Mg-Fe-Al and Fe-Cu-Zn. Such a framework could be applied in the pre-mine development phase to highlight potential environmental liabilities associated with sludge storage in various depositional environments (discrete impoundments, pit lakes, co-disposal with tailings, etc.). Currently, there is not sufficient information available from which to assess the chemical stability of the various metal-bearing phases identified in this study. Specifically, in order for a potential framework to be applied successfully, sludge chemical stability as a function of varying pH and Eh conditions must be established. For example, while aerobic Eh values are predicted in the treatment circuits, suboxic Eh conditions are predicted upon final placement in zones where saturated conditions are likely to develop. Such topics are proposed to be examined in the future through lab-scale and/or field scale studies.

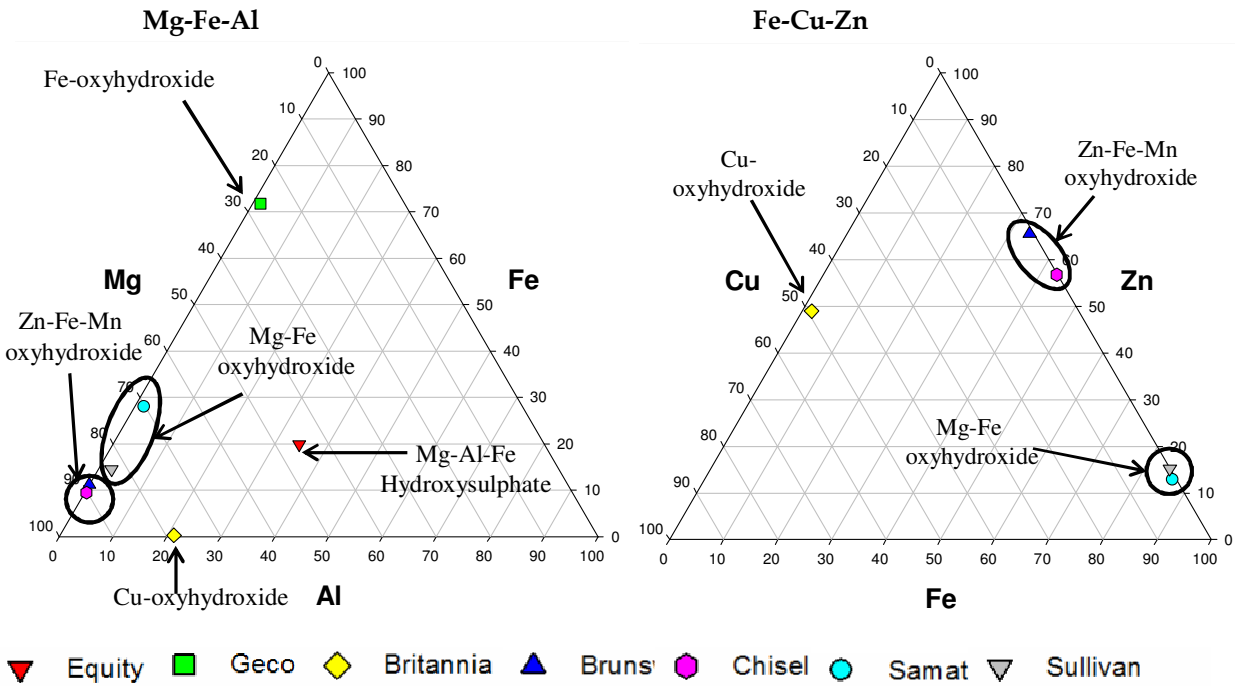

Figure 4. Ternary diagrams showing relative molar proportions of Mg-Fe-Al (left) and Fe-Cu-Zn (right) in ARD influent, and associated metal-bearing phases.

Conclusions

In all HDS samples, metal-bearing phases were amorphous (or poorly crystalline) and variable in composition (relatively pure to heterogeneous). Five dominant metal-bearing phases were identified: 1) Mg-Al-(Fe) hydroxysulfate (Equity); 2) Fe oxyhydroxide (Geco); 3) Cu-Zn hydroxide (Britannia); 4) Zn-Fe-Mn hydroxide (Brunswick and Chisel North); and, 5) Fe-Mg hydroxide (Samatosum and Sullivan). The nature of the metal-bearing phases is largely governed by the composition of the ARD influent, with the relative proportions of S, Fe, Al, Mg, and Mn being particularly relevant. Such relationships present the possibility of predicting sludge type based on ARD composition. Different metal-hosting phases can be expected to show contrasting chemical stabilities with respect to pH and Eh conditions. Therefore, the results highlight the need to understand the controls governing long-term chemical stability of sludge phases in various depositional settings.

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