

Assessing weathering in field cell experiments using quantitative mineralogy and sequential leaching

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Abstract

The objective of this study was to characterize the weathering behavior of select samples from the non acid producing waste rock materials at the Antamina mine using field cell tests and laboratory scale sequential extraction tests. Field cell results have indicated the release of metals, particularly arsenic and zinc, under neutral pH conditions. Sequential extraction and mineralogical characterization tests have demonstrated that carbonate dissolution under acidic conditions may be a significant source of leached metals. Comparison of field cell and sequential extraction tests demonstrated that solid phase metal content and leachate metal concentration are not necessarily correlated: a high metal content in the solid phase does not imply high concentrations in the leachate, and conversely, relatively low levels of metal in the solid phase can result in significant metal release. The observed field cell behavior can be explained by differences in the mineralogical forms of the metals.

Introduction

The Antamina mine, located in Ancash, Peru is one of the world's largest copper producers processing 104 thousand tonnes of ore and generating approximately 340 thousand tonnes of waste rock, daily. Waste rock management is therefore a fundamental environmental issue that requires planning, monitoring and care. At present, effluent from the more reactive waste dump is routed to the tailings pond from which no active discharge occurs and seepage is pumped back during the dry season. Drainage from the less reactive dump passes through a wetland where attenuation of metals occurs. Both effluent and in-stream discharge limits are easily met.

Antamina continues to focus its development and understanding on all areas of acid and neutral rock drainage and metal leaching; the Antamina mine has embarked on an integrated research project in collaboration with Teck Metals Applied Research and Technology group and the University of British Columbia, with additional funding and support from the National Sciences and Engineering Research Council of Canada. The aim of this project is to improve the understanding of hydrologic and geochemical processes which determine long-term waste rock weathering behavior thereby providing information that can be used in waste handling and storage and planning for long-term monitoring during the operations and closure phases of the mine life cycle.

While numerous studies on waste rock leaching under acidic conditions have been carried out and reported in the literature, only a few studies examining waste rock leaching under neutral or alkaline conditions have been reported. One of the major goals of this particular study is to examine the behavior of select samples from the carbonate-hosted sulfide waste rock material, as found at Antamina, under circum-neutral drainage conditions.

The study was comprised of three separate components:

- field cell tests whose primary objective was to monitor and assess the long-term leaching behavior of waste rock materials by measuring changes in leachate pH, and sulfate, arsenic, copper, molybdenum, and zinc concentrations.
- mineralogical characterization tests employing standard techniques such as particle size analysis and ICP analysis to determine mass distribution, total metal content and metal distribution;

state-of-the-art Mineral Liberation Analyzer (MLA) tests to determine modal mineralogy, mineral association and mineral liberation.

- sequential extraction tests to assess metal leaching potential from specific solid phase mineralogical fractions under increasingly acidic conditions.

Materials and Methods

One of the first on-site initiatives to qualitatively assess waste rock metal leaching potential was the development of a waste rock classification system based on the solid phase contents of arsenic, zinc and sulfide, resulting in three distinct waste rock classes as summarized in Table 1. It should be noted that the exoskarn, endoskarn and intrusive rock are the most reactive waste material types and are not the focus of this study. This study looks at the hornfels, marble and limestone rock groups within all three waste classes which represent approximately just under half of the waste rock mined at Antamina.

Table 1: Waste rock classification criteria

| Class | Reactivity | Description | As (mg/kg) | Zn (mg/kg) | Visual Sulfide Content |
|-------|-------------------|--|------------|------------|------------------------|
| A | Reactive | Mineralized/oxidized rock (including endoskarn, exoskarn, intrusive) and hornfels, marbles, limestones with high zinc, arsenic and sulfide | >400 | >1500 | >3% |
| B | Slightly reactive | Hornfels, marbles, and limestones with moderate zinc. | <400 | 700-1500 | <3% |
| C | Not reactive | Hornfels, marbles, and limestones with low zinc and arsenic, low sulfide | <400 | <700 | <3% |

Shortly after the development of the waste rock classification system, a comprehensive field cell testing program was developed to provide an ongoing assessment of the long-term acid and neutral rock drainage and metal leaching potential of the major ore, waste rock and tailings types (Golder, 2010). Some of the field cells containing hornfels, marble and limestone were soon observed to contain anomalous metal concentrations in the leachate. In some instances, a sample with low solid phase metal content would exhibit high leachate metal content; while in others, a sample with a high solid phase metal content would exhibit low leachate metal content. Some of these samples were selected for further study in order to understand how the waste rock classification system could be improved to account for these anomalous samples.

All of the test work was conducted on waste rock materials that had been used in the field cell testing program initiated in 2002 and in the University of British Columbia (UBC) field cell testing program. In the case of the UBC field tests, the waste rock materials used were the same as those used in the construction of the waste rock test piles.

Field Cell Studies

Each field cell consisted of a 208 litre (55 gallon) drum fitted with a PVC sample outlet and a bottom drainage layer of silica sand over a geotextile material. The drums were filled with waste rock samples and left open to atmosphere. Leachate samples from the field cells were collected at regular intervals during the wet season and analyzed for elemental content, alkalinity, acidity, turbidity, conductivity and pH (Aranda, 2010). This discussion will focus solely on the parameters of leachate pH and sulfate concentration, as well as arsenic and zinc concentration, in order to assess their efficacy as classification criteria. A detailed description of the field cell construction may be found in C. Aranda's M.A.Sc thesis entitled "Assessment of Waste Rock Weathering Characteristics of the Antamina Mine Based on Field Cell Experiments."

Sample Characterization and Mineralogical Analyses

The waste rock samples used in this study are described in Table 2; sample lithology was determined by visual characterization in the Antamina Geology Department and the subsequent class designation was determined by ICP analysis and the current waste rock classification guidelines. In addition, Table 2 also contains observations of field cell arsenic and zinc leaching behavior (Golder, 2011). A comparison of the sample classification to its observed leaching behavior demonstrates poor correlation between assigned (based on classification criteria) and observed sample reactivity.

Table 2: Waste rock samples

| Sample ID | Lithology | Class ¹ | Observed Field Cell Behavior |
|-----------|-----------|--------------------|---|
| Cell-21 | Marble | C | High leachate arsenic concentrations |
| Cell-24 | Marble | B | High leachate arsenic concentrations |
| Tucush-1 | Hornfels | B | High leachate concentrations of zinc and copper |
| Tucush-3 | Hornfels | A | Low leachate zinc concentrations |
| Tucush-4 | Limestone | C | High leachate zinc concentrations |

¹by Antamina geology

Particle size analysis testing was conducted on all samples both before and after sequential extraction using ASTM protocol C-136. Representative sub-samples of the sized fractions from the head sample and the leached residue were sent to the ALS Minerals lab in North Vancouver for chemical analysis by ICP. Select waste rock samples were sent to Teck's Applied Research and Technology (ART) group in Trail, where modal mineralogy, mineral liberation and mineral associations were determined using MLA.

Sequential Extraction Studies

In order to further characterize the geochemical behavior of the waste rock material, sequential extraction tests were conducted on the samples listed in Table 2. The objectives of this test work were the following:

- to assess the solubility of specific mineralogical phases under reaction conditions ranging from neutral to increasingly acidic. These extraction steps use more or less selective reagents to successively solubilize specific mineralogical fractions thought to be responsible for trace metal release. The reaction conditions are also intended to roughly simulate weathering conditions on site.
- to interpret the concentration data and trends of select parameters.
- to interpret the observed field cell leaching behavior using data from the sequential extraction tests.
- to improve upon the current waste rock classification criteria.

Sequential extraction is a qualitative procedure used to identify a specific solid phase mineral group (e.g. carbonate, iron oxide, sulfide) or form (e.g. soluble, exchangeable, sorbed) that a metal is associated with. In determining the solid phase speciation of a particular metal, it becomes possible to make inferences about its behavior in the environment, particularly in response to changes in parameters such as Eh and pH. A typical reaction sequence successively targets the following metals:

- soluble and exchangeable
- bound to carbonates
- in manganese oxyhydroxides, amorphous and well crystallized iron oxyhydroxides
- in sulfides
- in the residual fraction (usually aluminosilicates)

The sequential extraction procedure used in this study, and summarized in Appendix 1, was based on the original protocol devised by Tessier et al. (1979) and subsequently modified by others (Yoshida, 2001) to test coarse and larger samples (1.5 to 3 kg).

Results and Discussion

Field Cells

Leachates from the various field cell samples were monitored with respect to changes in leachate pH, and sulfate, arsenic and zinc concentration over a period of seven years (monitoring is still ongoing and will continue for the foreseeable future). As shown in Figure 1.a, during the last rainy season (from October 2010 to March 2011), the pH for all waste rock samples varied from a low of 7.72 to a high of 9.12. This fluctuation can be explained by the dissolution of carbonate in order to buffer acidic drainage produced by sulfide oxidation. The samples exhibiting the highest pH are Cell 21 (originally categorized as a Class C marble) and Tucush-4 (originally categorized as a Class C limestone). In both cases, the samples contain well in excess of 10% carbonate.

All samples demonstrated the general trend of maximum sulfate concentrations at the start of the rainy season (Figure 1.b) decreasing to minimum sulfate concentrations at the end of the rainy season. This observation suggests the flushing of soluble oxidation products, accumulated during the dry season, at the onset of the rainy season. The highest sulfate concentrations were observed for the Cell 21 and Tucush-1 (Class B hornfels), while the lowest concentration was observed for Tucush-4. The presence of sulfate is an indication of sulfide oxidation, all of this occurring in samples previously thought to be unreactive or of limited reactivity.

While it is difficult to infer much about the arsenic leaching behavior of the Tucush-1, Tucush-3, and Tucush-4 samples, due to an absence of data and clustered sampling intervals, the leaching behavior of Cell 21 and Cell 24 (Class B marble) indicates very high levels of arsenic that are slowly decreasing to stabilize at concentrations of approximately 1.0 mg/L and 0.09 mg/L respectively.

Preliminary analysis of the field cell data indicates that arsenic and zinc sulfide oxidation is occurring in the samples. High leachate concentrations of these metals, combined with fluctuations in pH and flushing of sulfate at the onset of the rainy season are evidence of sulfide mineral oxidation, which solubilizes metals, produces sulfate and generates localized acidity. The acidity is buffered through carbonate dissolution, accounting for the observed fluctuations on pH, and followed by the precipitation of soluble sulfates (e.g. gypsum and iron sulfates), which are dissolved and flushed from the field cells at the beginning of the rainy season.

Field cell results also demonstrate that there is poor correlation between solid phase elemental content measured by ICP analysis and the observed leaching behavior. High levels of solid phase zinc in Tucush-3 do not translate to high levels of zinc in the field cell leachates; and low levels of solid phase zinc in Tucush-4 do not translate to low levels of zinc in the field cell leachates.

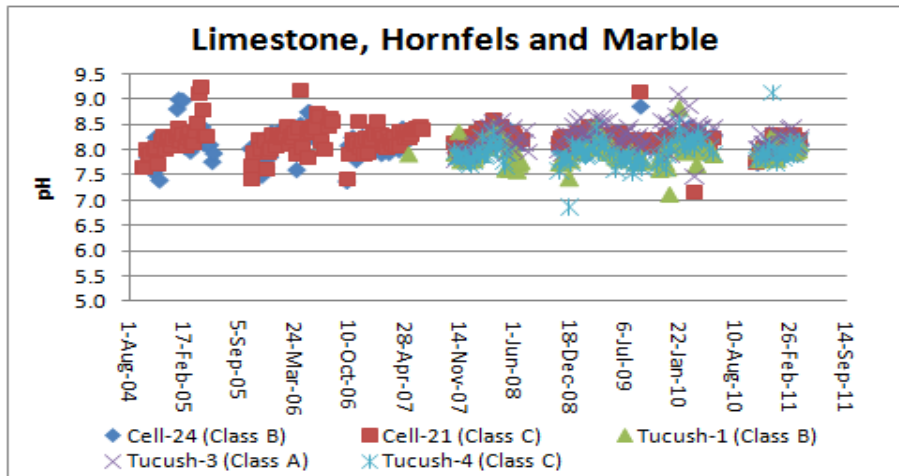


Figure 1.a: Change of pH versus time

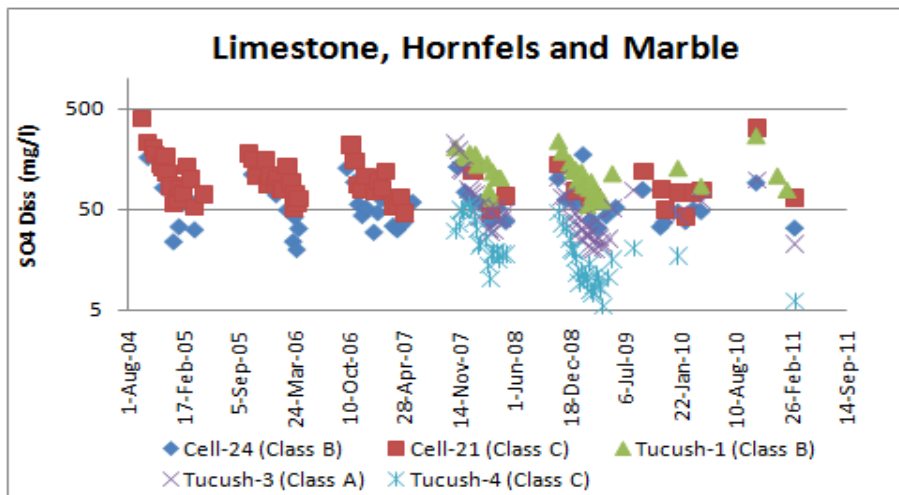


Figure 1.b: Sulfate concentration versus time

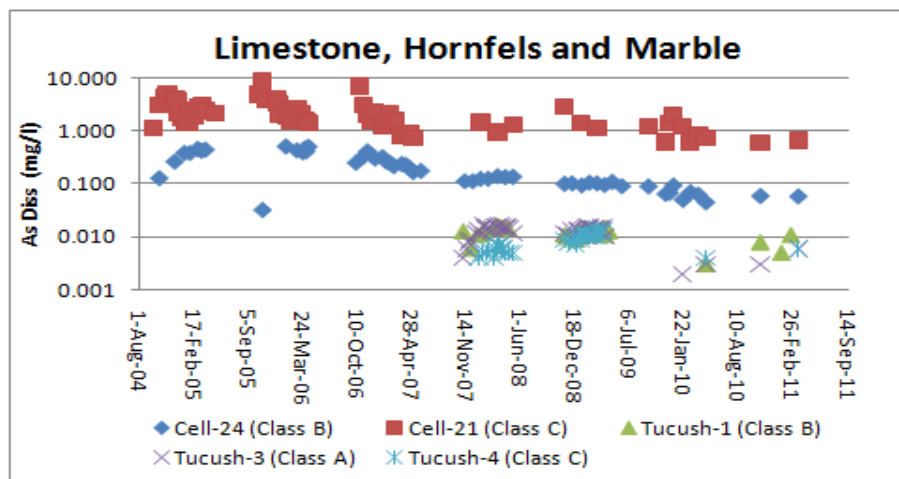


Figure 1.c: Arsenic concentration versus time

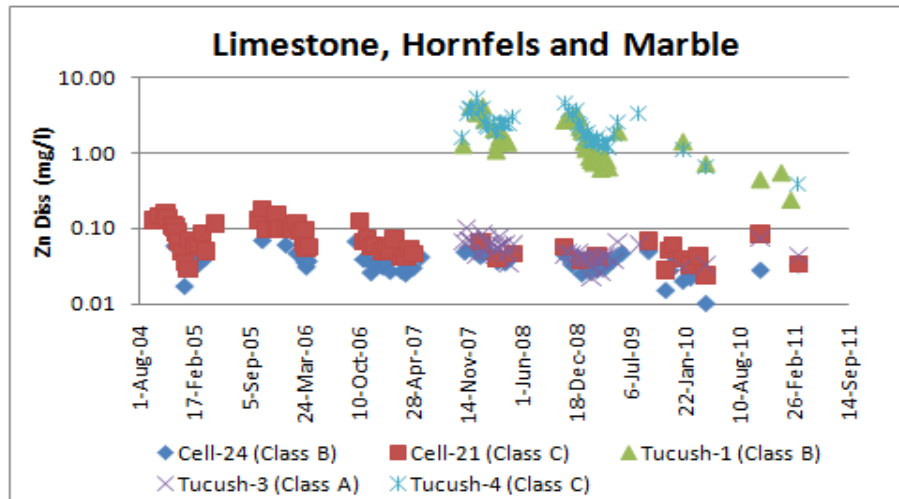


Figure 1.d: Zinc concentration versus time

Chemical Composition and Mineralogy of Waste Rock Samples

The solid phase elemental concentrations of arsenic, zinc and sulfur in all waste rock samples were determined by ICP analysis and have been summarized in Table 3. The MLA results for the modal mineralogy of the waste rock samples have been summarized in Appendix 2. In addition, selected MLA results for each of the waste rock samples have been summarized in Tables 4 through 6.

Sulfides were identified as the primary source of sulfur in the waste rock samples (Appendix 2). All samples contained either minor (1 – 10%) or trace (<1%) amounts of pyrite and pyrrhotite, with the exception of Tucush-4, which contained major (>10%) amounts of pyrite. Additional sulfide minerals identified by MLA were bornite, galena, sphalerite, chalcopyrite, stibnite, watanabeite, molybdenite, and enargite. Cell 21, Cell 24 and Tucush-1 contained primarily trace quantities of these sulfides, while Tucush-4 contained minor quantities of sphalerite. Roughly 70% of the sulfide mineralization in the Tucush-3 sample was present in minor quantities.

All samples contained major quantities of carbonate, and only trace quantities of siderite and dolomite, identifying calcite as the primary source of acid neutralization. Sulfates were also identified in all of the waste rock samples, but were present in trace quantities only.

Table 3: Solid phase composition of waste rock samples

| Sample ID | Lithology | Class ¹ | Zn mg/kg | As mg/kg | S % |
|-----------|-----------|--------------------|-------------|-------------|--------|
| Cell-21 | Marble | C | 5400 | 92 | 0.41 |
| Cell-24 | Marble | B | 200 | 26 | 0.46 |
| Tucush-1 | Hornfels | B | n/a | n/a | n/a |
| Tucush-3 | Hornfels | A | 13100 | 785 | 2.32 |
| Tucush-4 | Limestone | C | 34.9 | 50 | 1.22 |

¹ by Antamina geology

Table 4: Arsenic minerals (%) locked in binary or higher for Cell-21 and Cell-24

| Sample ID | Cell-21 | | | | | | SUM |
|---------------|---------------|-------------|---------------|--------------|-----------|-------------|--------|
| μm | Liberated (%) | Sulfide (%) | Carbonate (%) | Silicate (%) | Other (%) | Ternary (%) | |
| +50800 | 18.62 | 1.38 | 6.87 | 71.01 | 0.01 | 2.12 | 100.01 |
| -12700 | 30.12 | 1.78 | 20.14 | 35.64 | 0.33 | 11.98 | 99.99 |

| Sample ID | Cell-24 | | | | | | SUM |
|---------------|---------------|-------------|---------------|--------------|-----------|-------------|--------|
| μm | Liberated (%) | Sulfide (%) | Carbonate (%) | Silicate (%) | Other (%) | Ternary (%) | |
| +50800 | 67.22 | 1.30 | 12.17 | 7.68 | 0.02 | 11.61 | 100.00 |
| -12700 | 38.56 | 1.66 | 30.23 | 17.56 | 0.03 | 11.96 | 100.00 |
| -12700 (Dup) | 35.64 | 1.51 | 34.67 | 17.97 | 0.00 | 10.21 | 100.00 |

Cell 21

MLA analysis identified enargite and watanabeite as the primary sources of arsenic in this sample. The majority of arsenic minerals in both the coarse (+50.8 mm) and the fine (- 12.7 mm) size fractions are locked within binary or ternary mineral assemblages; 71% of the arsenic in the coarse fraction and 36% of the arsenic in the fine fraction is associated with relatively inert silicates, rendering it non-reactive on the basis of both liberation and mineral solubility. However, 19% of the arsenic in the coarse and 31% of the arsenic in the fines is liberated and therefore available for chemical reaction. On the basis of increasing surface area with decreasing particle size, the liberated arsenic in the fine fraction would oxidize more rapidly than the arsenic in the coarse fraction. One would expect to initially see high levels of arsenic in the leachate that eventually taper off to a more constant level exhibiting a gradual decrease in arsenic concentration. This behavior would be due to the oxidation of arsenic minerals in the coarse fraction, whose rate would be limited by the smaller surface area available for reaction. Figure 1.c exhibits just such a trend for the Cell 21 field cell material.

Significant quantities of arsenic sulfides are locked in the carbonate phase, with 7% in the coarse and 21% in the fine. Carbonates in the fine fraction could also be a potential source of arsenic under acidic conditions. The dissolution of carbonate to buffer the acidity produced by sulfide oxidation would lead to the liberation of additional arsenic sulfide mineralization. Almost 2% of the arsenic in the fines is associated with other sulfides creating the possibility of sulfide oxidation due to galvanic interactions. Under these conditions, when two sulfides are in direct contact with one another, the sulfide with the lower rest potential will act as the anode and the sulfide with the higher rest potential will act as the cathode (Price, 2009). The anode is oxidized and the cathode is reduced with electrons being transferred from anode to cathode. Some common sulfide minerals and their rest potentials have been summarized in Appendix 3.

Although initially designated as a Class C marble on the basis of solid phase chemical analysis, the high percentage of liberated arsenic in the fines, as well as the high percentage of arsenic locked in the carbonates in the fine would explain the observed field cell leaching behavior.

Cell 24

Originally designated a Class B marble, indicating that it should be only slightly reactive, this sample exhibited high field cell concentrations of arsenic in the leachate. This behavior can be explained by the presence of 68% and 39% (Table 4) of liberated arsenic sulfides, in the form of enargite and watanabeite, in the coarse and fine fractions respectively. Even though solid phase chemical analysis identified the presence of only 26 mg/kg of arsenic, a significant quantity in the fines is either fully liberated or associated with carbonates (approximately 31%). Carbonate dissolution in response to sulfide oxidation would expose

some, or perhaps all, of this locked sulfide, rendering it available for reaction. Similar observations can be made for the coarse fraction, although only 13% of the arsenic sulfides are associated with carbonates. In the case of the coarse fraction, particle size effects would significantly limit the rate of carbonate dissolution; assuming no surface passivation of the carbonate surface due to adsorption or precipitation reactions, the arsenic sulfides locked within this fraction will most likely remain so.

Both fractions also contain arsenic sulfides associated with other sulfides, once again creating the potential for galvanic interactions in which the enargite would be oxidized by the sulfide with the higher rest potential. It is also worth noting that in this sample decreasing particle size did not correspond to increasing arsenic mineral liberation as with Cell 21 waste rock material, implying different grain sizes (and potentially different host minerals) in the coarse and fine fractions.

Tucush-1

This sample was originally designated a Class B hornfels on the basis of lithology and chemical analysis, however field cell results indicate high levels of zinc and copper in the leachate. The primary zinc sulfide identified by MLA was sphalerite, which is concentrated in the larger particle sizes as summarized in Table 5; the coarse to middling size fractions (+297 μm) contained 85% of the zinc mineralization. Almost 70% of the zinc mineralization in this sample is fully liberated, with 59% occurring in the coarse fraction (+297 μm) and the remaining 11% occurring in the fine fraction (-600 μm).

Table 5: Zinc minerals (%) locked in binary or higher for Tucush-1

| Sample ID μm | Tucush-1 | | | | | | SUM |
|----------------------------|---------------|-------------|---------------|--------------|-----------|-------------|--------|
| | Liberated (%) | Sulfide (%) | Carbonate (%) | Silicate (%) | Other (%) | Ternary (%) | |
| 25400 | 6.20 | 1.93 | 1.48 | 2.08 | 0.01 | 0.64 | 12.34 |
| 25400 Dup | 7.84 | 0.24 | 1.60 | 2.03 | 0.13 | 0.50 | 12.34 |
| 4800 | 0.90 | 0.01 | 0.18 | 0.12 | 0.00 | 0.18 | 1.39 |
| 1200 | 37.71 | 0.35 | 5.13 | 3.36 | 0.00 | 2.75 | 49.30 |
| 600 | 5.99 | 0.01 | 1.10 | 0.87 | 0.00 | 0.75 | 8.72 |
| 297 | 2.16 | 0.48 | 0.33 | 0.23 | 0.06 | 0.50 | 3.76 |
| 105 | 0.16 | 0.02 | 0.06 | 0.28 | 0.01 | 0.15 | 0.68 |
| 53 | 2.38 | 0.35 | 0.47 | 0.76 | 0.03 | 1.03 | 5.02 |
| -53 | 5.69 | 0.02 | 0.37 | 0.24 | 0.00 | 0.13 | 6.45 |
| SUM | 69.03 | 3.41 | 10.72 | 9.97 | 0.24 | 6.63 | 100.00 |

Silicates account for 10% of the zinc mineralization in this sample, and ternary mineral assemblages and other minerals account for 7% and 1% respectively. Zinc minerals locked in the silicates will most likely remain unreactive. These minerals usually dissolve only at very low pH, after the complete dissolution of carbonate and Fe and Mn oxyhydroxides; even then their rate of dissolution is extremely slow relative to carbonates and oxyhydroxides.

The high zinc leachate concentration may be explained by the following:

- 4% of the zinc mineralization is associated with sulfide minerals, with almost 1% of this mineralization in the fine fraction (-600 μm), indicating galvanic interactions as a potential source of sulfide oxidation and subsequent metal leaching.
- carbonates account for 11% of all zinc mineralization; roughly 1.5% of this mineralization is in the fines. Carbonate dissolution from the fine fraction (-600 μm) under acidic conditions will increase zinc mineral liberation, thereby acting as a source for the release of additional zinc cations to solution.

- 11% of the zinc mineralization is liberated and in the fine fraction (-600 μm); the larger surface area available for reaction makes these zinc minerals more reactive than those in the coarser fractions.

Based on the MLA results, one would expect to see relatively rapid oxidation of the zinc sulfides in the fines, followed by carbonate dissolution and subsequent oxidation of newly liberated or exposed zinc sulfides. These reactions in the fines would be contemporaneous with the oxidation of liberated zinc sulfides in the coarser fractions, which would proceed at a slower rate due to the smaller surface area relative to particle diameter. In terms of field cell behavior, this would be reflected by high initial zinc concentrations, followed by an increase due to carbonate dissolution, followed by a decrease to an “equilibrium” concentration indicating ongoing oxidation of the liberated zinc sulfides in the coarser fractions. The concentration trend plotted in Figure 1.d could be explained by such a reaction sequence.

Tucush-3

Tucush-3 was originally designated a Class A hornfels, indicating a high potential for long-term leaching of arsenic and zinc. Field cell results however exhibit only very low concentrations of zinc in the leachate. The results of MLA analysis for this sample have been summarized in Table 6, where it can be seen that roughly 68% of the zinc mineralization, primarily in the form of sphalerite, is concentrated in the coarse fraction (+297 μm). This fraction also contains 31% zinc sulfides that are fully liberated and available for reaction.

Only 6% of the zinc sulfides are associated with the carbonates, and these are distributed throughout all of the size fractions. This indicates a limited potential for oxidation and zinc leaching due to carbonate dissolution. The remaining zinc sulfides are associated with silicates and ternary mineral assemblages, at 28% and 12% respectively.

Table 6: Zinc minerals (%) locked in binary or higher for Tucush-3 and Tucush-4

| Sample ID | Tucush-3 | | | | | | SUM |
|-----------|---------------|-------------|---------------|--------------|-----------|-------------|-------|
| | Liberated (%) | Sulfide (%) | Carbonate (%) | Silicate (%) | Other (%) | Ternary (%) | |
| 25400 | 10.18 | 0.08 | 0.77 | 6.66 | 0.15 | 2.75 | 20.59 |
| 4800 | 12.12 | 0.23 | 2.91 | 13.62 | 0.01 | 2.35 | 31.24 |
| 1200 | 4.54 | 0.14 | 0.24 | 0.45 | 0.00 | 0.22 | 5.59 |
| 600 | 4.20 | 0.49 | 0.71 | 3.03 | 0.00 | 1.61 | 10.04 |
| 297 | 5.34 | 0.16 | 0.26 | 1.07 | 0.01 | 1.44 | 8.28 |
| 105 | 4.23 | 0.45 | 0.26 | 1.16 | 0.08 | 0.99 | 7.17 |
| 53 | 2.86 | 0.22 | 0.18 | 0.54 | 0.02 | 0.66 | 4.48 |
| 53 Dup | 2.62 | 0.36 | 0.24 | 0.70 | 0.10 | 0.82 | 4.84 |
| -53 | 6.61 | 0.23 | 0.23 | 0.33 | 0.05 | 0.31 | 7.76 |
| SUM | 52.70 | 2.36 | 5.80 | 27.56 | 0.42 | 11.15 | 99.99 |

| Sample ID | Tucush-4 | | | | | | SUM |
|-----------|---------------|-------------|---------------|--------------|-----------|-------------|-------|
| | Liberated (%) | Sulfide (%) | Carbonate (%) | Silicate (%) | Other (%) | Ternary (%) | |
| 50800 | 5.79 | 0.07 | 10.55 | 2.96 | 0.02 | 3.28 | 22.76 |
| 25400 | 10.61 | 0.00 | 3.35 | 6.43 | 0.04 | 3.89 | 24.32 |
| 4800 | 0.65 | 0.00 | 0.08 | 0.70 | 0.00 | 0.29 | 1.72 |
| 1200 | 13.86 | 0.64 | 1.67 | 1.82 | 0.40 | 3.07 | 21.46 |
| 600 | 4.65 | 0.01 | 4.77 | 1.21 | 0.00 | 0.84 | 11.48 |
| 297 | 0.79 | 0.09 | 0.20 | 0.36 | 0.00 | 1.50 | 2.94 |
| 105 | 1.61 | 0.01 | 0.32 | 0.48 | 0.02 | 1.03 | 3.47 |
| 53 | 2.64 | 0.15 | 0.24 | 0.80 | 0.05 | 0.70 | 4.58 |
| -53 | 5.88 | 0.10 | 0.29 | 0.80 | 0.02 | 0.25 | 7.34 |
| SUM | 46.48 | 1.07 | 21.47 | 15.56 | 0.55 | 14.85 | 99.98 |

The low zinc concentrations in the field cells may be explained by the following:

- the bulk of the zinc minerals are concentrated in the coarse size fractions. Although there is a significant quantity of liberated zinc sulfide in this fraction, the small surface area relative to particle diameter will result in slow but sustained release of zinc metal cations to solution.
- only 6% of the zinc sulfides are associated with the carbonates; with 5% in the coarser fractions (+297 μm) and the remaining 1% in the fines (-600 μm). Therefore dissolution of carbonate minerals under acidic conditions would not release significant amounts of additional zinc cations to solution.

With 22% of the zinc sulfides liberated and in the fines (-600 μm), one would expect this material to exhibit relatively high initial zinc concentrations. Carbonate dissolution in the fines, followed by the oxidation of freshly exposed zinc sulfides should result in another concentration maximum. The trend should then be a gradual decrease in concentration and finally stabilizing to an “equilibrium” value indicating the depletion of all zinc sulfides in the fines and the continuing oxidation of liberated zinc sulfides in the coarse.

A comparison to the plotted data in Figure 1.d does show some elements of this behavior, but the initial zinc concentration is relatively low in comparison to the other samples. In addition, there is a maximum zinc concentration at the onset of the previous rainy season which is similar to the initial concentration measured at the onset of the 2007 rainy season. Such field cell leaching behavior would not be explained in the proposed scenario. MLA analysis shows that this sample contains minor (1 – 10%) amounts of five sulfides: sphalerite (the primary source of zinc), pyrite, pyrrhotite, chalcopyrite and galena. Additionally, 3% of the sphalerite is associated with other sulfides, therefore galvanic interactions may account for some of the observed field cell behavior. Those sulfides with the lower rest potentials will be oxidized first (Kwong, 2003), generally in the following order:

pyrrhotite → sphalerite → galena → chalcopyrite → pyrite

These galvanic interactions and the specific sulfide mineral associations (i.e. which sulfide minerals are in contact with one another) will determine the sequence in which the sulfides are oxidized. In this particular sample, the increasing zinc concentration could be accounted for by the presence of competing galvanic interactions. Under these conditions sphalerite oxidation would only occur once those sulfides with the lowest rest potentials, in this case pyrrhotite, were depleted. Subsequent sphalerite oxidation could then occur by the following mechanisms:

- increasing liberation of sphalerite due to the oxidative dissolution of associated pyrrhotite; greater exposed surface area; oxidation by oxygen
- galvanic interactions between sphalerite and either galena, chalcopyrite or pyrite; oxidation of sphalerite
- a combination of the above

Tucush-4

Based on its solid phase zinc content of 200 mg/kg, this waste rock sample was originally designated as a Class C limestone. However, field cell behavior has shown high concentrations of zinc in the leachate. As with the Tucush-3 sample, the majority of the zinc mineralization, primarily sphalerite, occurs in the coarse to middling size fractions; 82% of the zinc sulfides are in the +297 μm size fraction (Table 6). 36% of the zinc sulfides in this fraction are fully liberated, although the rate and extent of sulfide oxidation and subsequent zinc solubilization is likely limited by the small surface area relative to particle diameter of the materials in this fraction.

Only 1% of the zinc sulfides are associated with other sulfides, and these tend to be in the coarser (+297 μm) size fractions; galvanic interactions may play a role in the oxidation of zinc sulfides, however these reactions would likely be limited by the small surface area relative to particle diameter of these fractions. Of the remaining zinc minerals 22% are associated with carbonates, 16% are associated with silicates, 15% are associated with ternary mineral assemblages, and 1% is associated with other minerals.

The high concentration of zinc observed in the field cell leachate may be explained by the following:

- 22% of the zinc mineralization is fully liberated. Although 17% is concentrated in the three coarsest size fractions, an additional 14% is in the 1.2 mm middling fraction. While not as reactive as the fines, this fraction may nevertheless be a significant source of dissolved zinc.
- although MLA identified the presence of several sulfide minerals, with the exceptions of pyrite and galena, these minerals were all present in trace quantities only. The sample contained more than 10% pyrite and 1 – 10% galena. Both pyrite and galena, in the form of binary or ternary mineral assemblages with sphalerite, would promote the oxidation of sphalerite.
- 11% of the zinc mineralization is liberated and in the fine fraction (-600 μm); the larger surface area available for reaction makes these zinc minerals more reactive than those in the coarser fraction.

Comparison to the field cell trends plotted in Figure 1.d validates this interpretation of the MLA data.

Sequential Leaching

The sequential extraction results for arsenic and zinc for each of the waste rock samples have been summarized in Table 7.

Table 7: Results of sequential extractions

| Sample ID | Cell 21 | | Cell 24 | | Tucush-1 | | Tucush-3 | | Tucush-4 | |
|--------------|--------------|---------------|--------------|---------------|--------------|---------------|--------------|---------------|--------------|---------------|
| | [As] mg/L | %As | [As] mg/L | %As | [Zn] mg/L | %Zn | [Zn] mg/L | %Zn | [Zn] mg/L | %Zn |
| L1 | 0.13 | 14.60 | 0.01 | 1.07 | 0.00 | 0.00 | 0.35 | 2.55 | 3.16 | 20.84 |
| L2 | 0.05 | 5.61 | 0.04 | 3.92 | 0.61 | 17.33 | 1.28 | 9.34 | 4.15 | 27.37 |
| L3 | 0.30 | 32.38 | 0.16 | 14.84 | 2.25 | 63.92 | 3.72 | 27.13 | 1.37 | 9.04 |
| L4 | 0.14 | 15.04 | 0.39 | 37.47 | 0.00 | 0.00 | 0.77 | 5.62 | 1.45 | 9.56 |
| L5 | 0.30 | 32.38 | 0.45 | 42.70 | 0.66 | 18.75 | 7.59 | 55.36 | 5.03 | 33.18 |
| Sum | 0.91 | 100.00 | 1.05 | 100.00 | 3.52 | 100.00 | 13.71 | 100.00 | 15.16 | 100.00 |
| % Extraction | 1.6 | | 7.2 | | n/a | | 0.5 | | 29.7 | |

Cell 21 and Cell 24

The total arsenic extraction from Cell 21 and Cell 24 was 1.6% and 7.2% respectively (Table 7). These results are validated by the MLA data summarized in Table 4, which demonstrates that although both samples contain roughly the same quantity of liberated arsenic sulfides in the fines, Cell 24 has almost twice the amount of carbonate-associated arsenic sulfides in the fines, accounting for the greater overall extraction of arsenic from this sample.

MLA data for both samples also indicated that sulfides and silicates were a significant source of arsenic mineralization. This is borne out by the results of the sequential leach tests in which the sulfide fraction and the residual fraction are major sources of arsenic (Table 7 and Figure 2.a). While the sulfide fraction will leach arsenic under oxidizing conditions, the silicate fraction will only start leaching at low pH.

In the case of Cell 21, the exchangeable fraction and the oxyhydroxide fraction were also identified as significant sources of arsenic at 15% and 33% respectively. The arsenic in these fractions is either weakly sorbed to mineral surfaces or specifically adsorbed to mineral surfaces and can leach under circum-neutral conditions. The majority of the arsenic in Cell 24 was from the sulfide and residual fraction, at 38% and 43% respectively. An additional 15% was from the oxyhydroxide fraction, indicating the potential for arsenic leaching at neutral and alkaline pH, conditions under which the anion exchange capacity of oxyhydroxides is reduced and the solubility of anionic arsenic is increased (Price, 2009).

Tucush-1, Tucush-3 and Tucush-4

The sequential extraction of the Tucush-1 sample identified the carbonate, oxyhydroxide and residual fraction as sources of leachable arsenic. While there may have been zinc associated with the exchangeable and sulfide fractions, it was below detection limit. Although MLA analysis (Table 5) indicated the presence of significant quantities of liberated zinc sulfides, they were primarily concentrated in the coarse fractions. This may explain the absence of any significant quantity of leachable zinc from the sulfide fraction of the sequential leach.

The sequential leaching results obtained for Tucush-3 are validated by both the field cell observations and the MLA data which indicated that the Class A hornfels would not likely be reactive with respect to zinc leaching. Only 0.5% of the total zinc was leached under sequential extraction conditions, with 28% of the leachable zinc in the oxyhydroxide fraction, only 6% in the sulfide fraction, and 56% in the residual fraction. The MLA data summarized in Table 6 identified that most of the zinc sulfides were either liberated and concentrated in the coarse or locked in the silicates. This may explain the small percentage of leachable zinc extracted from the sulfide fraction; particle size effects would limit the extent of sulfide oxidation.

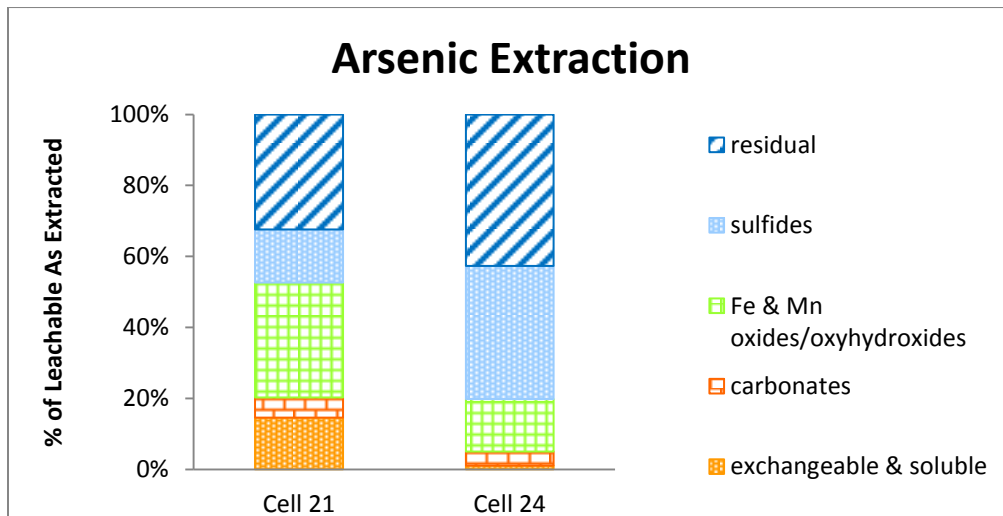


Figure 2.a: Arsenic extraction from Cell 21 and Cell 24

All five fractions in the sequential extraction of the Tucush-4 sample were demonstrated to be sources of leachable zinc: 21% from the exchangeable fraction, 28% from the carbonates, 9% from the oxyhydroxides, 10% from the sulfides, and 34% from the residual fraction. A total of 29.7% of the total zinc was leached from the sample. The MLA data summarized in Table 6 indicated that the majority of the liberated sulfide minerals were concentrated in the coarse fraction. This is borne out by the sequential leach results, in which only 10% of the leachable zinc came from the sulfides. This was likely due to particle size effects. The presence of leachable zinc in the exchangeable and carbonate fractions indicates the potential for zinc leaching under neutral and circum-neutral pH conditions and also serves to explain some of the observed field cell leaching behavior.

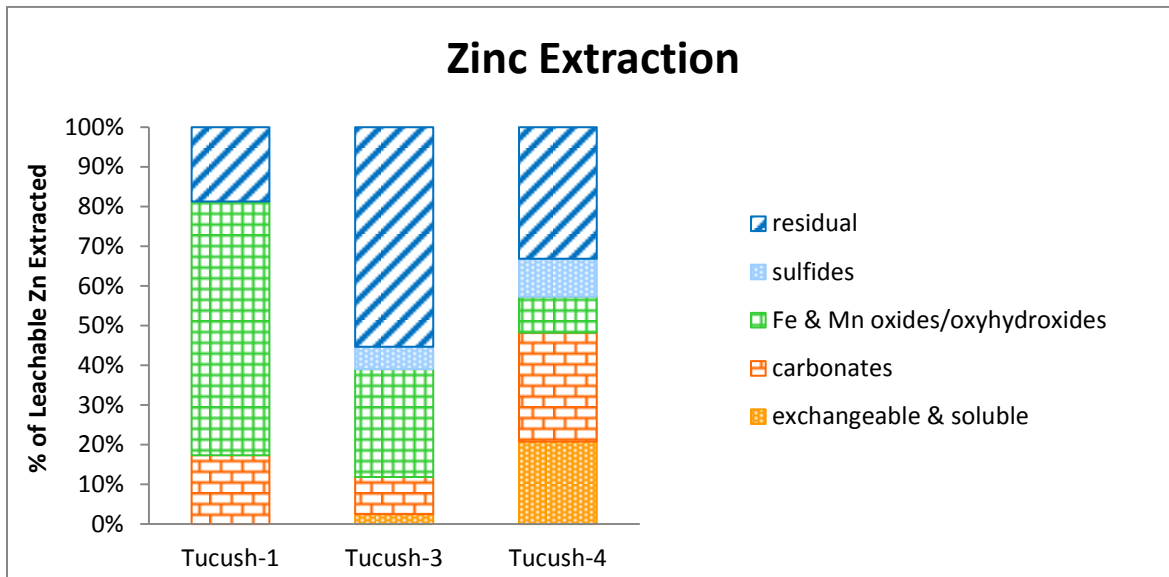


Figure 2.b: Zinc extraction from Tucush-1, Tucush-3 and Tucush-4

Conclusions

The Antamina mine is investigating opportunities to refine its waste rock classification system; studies such as this, based on the hornfels, marble and limestone waste rock lithologies, provide additional information that can be used in operational decision-making processes. The objective of this study was to characterize the selected samples, using mineralogical techniques and sequential extraction, in order to investigate their leaching potential under varying reaction conditions and to explain leaching behavior in the field cells. The main conclusions are summarized below:

- field cell tests were useful in assessing long-term arsenic and zinc leaching potential under site conditions
- the current classification system for marble, hornfels and limestone could be improved with the inclusion of sequential extraction data; for operational purposes, the inclusion of MLA data alone would suffice, however a practical way to incorporate it, so as not to impede the mining efficiency would need to be investigated.
- information on metal distribution, modal mineralogy and mineral association can be used to explain results obtained from both the field cells and sequential extraction
 - mineral associations can affect leaching if the associated mineral is likely to dissolve under acidic conditions resulting in the exposure of previously locked sulfides
 - mineral associations with relatively inert minerals are likely to render the sulfide effectively unreactive

- in the case of sulfide-sulfide associations, galvanic interactions may serve to activate or passivate sulfide oxidation, depending on the rest potentials of the associated minerals
- particle size effects (as related to particle surface area) are important in assessing sample reactivity i.e. fully liberated sulfides in the coarse fractions are less reactive than those in the fine fractions
- sequential extraction tests are useful in identifying the solid phase source of various metals, particularly the carbonate and oxyhydroxide phases which leach readily under circum-neutral or mildly acidic conditions.

References

- Aranda, C., 2010. *Assessment of Waste Rock Weathering Characteristics at the Antamina Mine Based on Field Cells Experiments*. Thesis (M.A.Sc). University of British Columbia
- Brown, D., R. Verburg, H. Letient, and C. Aranda. 2006. Geochemical Characterization and Water Quality Prediction at the Antamina Mine. Paper presented at the 7th ICARD, March 26-30, 2006.
- Golder Associates, 2010. *Waste Rock and Tailings Geochemistry – Field Cell Monitoring December 2002 to May 2009*. 28 January, 2010
- Golder Associates, 2011. *Waste Rock Classification*. 4 February, 2011.
- Kabwe, L., *Sequential Extractions of Trace Metals from Waste Rock Samples from Antamina Mine – Summary Final Progress Report, Part 1*. 30 August, 2010.
- Kwong, Y.T.J., G.W. Swerhone, and J.R. Lawrence. 2003. Galvanic Sulphide Oxidation as a Metal-Leaching Mechanism and its Implications. *Geochemistry, Environment, Analysis*, 3: 337-343
- Price, W.A., 2009. *Prediction Manual for Drainage Chemistry from Sulphidic Geologic Materials. MEND Report 1.20.1*. Smithers, BC: Natural Resources Canada
- Tessier, A., P.G.C. Campbell, and M. Bisson. 1979. Sequential Extraction Procedure for the Speciation of Particulate Trace Metals. *Analytical Chemistry*, 51 (7), 844-851.
- Yoshida, M., H. Kallali, F. Ayari, and M. Cheberli. 2001. Sequential Leaches of Trace Elements from Top Soil and Lacustrine Sediments in Sebkhath Sejoumi Basin near Municipal Solid Waste Landfill of Henchir El Yahoudia, South of Tunis City. *Water, Waste, and Environment Research*, Volume 2, 131-149.

Appendix 1
Sequential Extraction Procedure

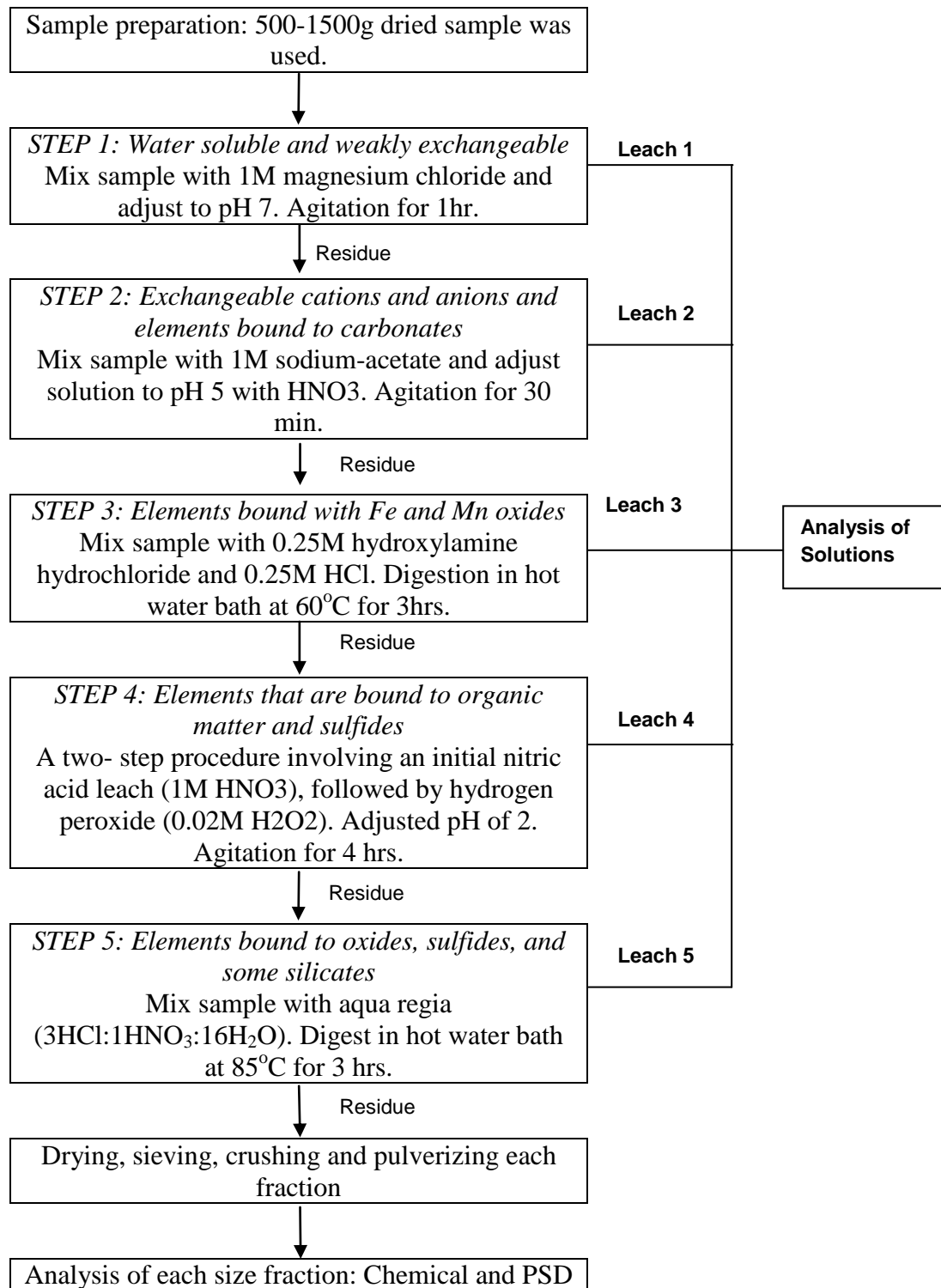


Figure A1: Modified five-step sequential extraction procedure

Appendix 2

Waste Rock Sample Mineralogy

Table A2: Mineralogy of waste rock samples

| Category | Mineral | Formula | Cell-24 (Marble) | Cell-21 (Marble) | Tucush-1 (Hornfels) | Tucush-3 (Hornfels) | Tucush-4 (Limestone) |
|------------|-----------------|---|------------------|------------------|---------------------|---------------------|----------------------|
| Sulfides | Bornite | Cu ₅ FeS ₄ | Trace | Trace | Trace | Trace | Trace |
| | Galena | PbS | Trace | Trace | Trace | Minor | Minor |
| | Sphalerite | (Zn,Fe)S | Trace | Trace | Trace | Minor | Trace |
| | Chalcopyrite | CuFeS ₂ | Trace | Trace | Trace | Minor | Trace |
| | Pyrrhotite | Fe(1-x)S | Minor | Minor | Trace | Minor | Trace |
| | Stibnite | Sb ₂ S ₃ | Trace | Trace | Trace | Trace | Trace |
| | Watanabeite | Cu ₄ (As,Sb) ₂ S ₅ | Trace | Trace | Trace | Minor | Trace |
| | Pyrite | FeS ₂ | Trace | Trace | Trace | Minor | Major |
| | Molybdenite | MoS ₂ | Trace | Trace | Trace | Trace | Trace |
| | Enargite | Cu ₃ AsS ₄ | Trace | Trace | Trace | Trace | Trace |
| Carbonates | Calcite | CaCO ₃ | Major | Major | Major | Major | Major |
| | Siderite | FeCO ₃ | Trace | Trace | Trace | Trace | Trace |
| | Dolomite | Ca,Mg(CO ₃) ₂ | Trace | Trace | Trace | Minor | Trace |
| Silicates | Biotite | K(Mg,Fe) ₃ AlSi ₃ O ₁₀ (F,OH) ₂ | Trace | Trace | Minor | Minor | Minor |
| | Chlorite | ClO ₂ | Trace | Trace | Trace | Trace | Minor |
| | K_Feldspar | K,NaAlSi ₃ O ₈ -CaAl ₂ Si ₂ O ₈ | Minor | Minor | Minor | Major | Minor |
| | Kaolinite | Al ₂ Si ₂ O ₅ (OH) ₄ | Trace | Trace | Trace | Trace | Trace |
| | Muscovite | (KF) ₂ (Al ₂ O ₃) ₃ (SiO ₂) ₆ .H ₂ O | Trace | Trace | Trace | Minor | Trace |
| | Plagioclase | NaAlSi ₃ O ₈ -CaAl ₂ Si ₂ O ₈ | Minor | Minor | Major | Major | Major |
| | Pyroxene | | Major | Major | Minor | Minor | Minor |
| | Quartz | SiO ₂ | Trace | Minor | Minor | Major | Major |
| | Talc | Mg ₃ Si ₄ O ₁₀ (OH) ₂ | Non- | Non- | Trace | Trace | Trace |
| | Mica | | Minor | Minor | Minor | Major | Minor |
| | Titanite | CaTiSiO ₅ | Trace | Trace | Trace | Trace | Trace |
| | Wollastonite | Ca(SiO ₃) | Trace | Minor | Minor | Minor | Minor |
| | Others | | Minor | Major | Major | Major | Major |
| Phosphate | | | Trace | Trace | Trace | Trace | Trace |
| Sulfates | FeOxyhydroxides | | Trace | Trace | Trace | Trace | Trace |
| | FeSulfate | FeSO ₄ | Trace | Trace | Trace | Trace | Trace |
| | Barite | BaSO ₄ | Trace | Trace | Trace | Trace | Trace |
| | Gypsum | CaSO ₄ .2H ₂ O | Trace | Trace | Trace | Trace | Trace |

Note: Qualitative ranges of mineral percentages based on the results of modal mineralogy performed on all size fractions in each sample. “Major”: Results of modal mineralogy indicate that mineral present in quantities greater than 10%. “Minor”: Results of modal mineralogy indicate that mineral present in quantities between 1 and 10%. “Trace”: Results of modal mineralogy indicate that mineral present in quantities less than 1%.

Appendix 3
Sulfide Rest Potentials

Table A3: Sulfide Mineral Rest Potentials (adapted from Kwong et al.,

| Sulfide Mineral | Formula | Rest Potential (in Volts versus SHE*) |
|------------------------|-----------------------|--|
| pyrite | FeS ₂ | 0.63 |
| chalcopyrite | CuFeS ₂ | 0.52 |
| chalcocite | Cu ₂ S | 0.44 |
| covellite | CuS | 0.42 |
| galena | PbS | 0.28 |
| sphalerite | ZnS | -0.24 |
| pyrrhotite | Fe _(1-x) S | -0.28 |