Mineralogical Characterization of Sulfidic Waste Rock at the Antamina Mine

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Abstract

The primary objective of this study is to characterize the long-term weathering behaviour of carbonate hosted sulfide waste rock material with high neutralization capacity. The focus of this study was on marble and hornfels waste rock types at the Antamina mine, which account for almost half of the waste rock material generated on site. Solid phase arsenic and zinc contents, along with some consideration for sulfide and visible oxide content, are currently used to classify the waste rock into the categories of reactive, slightly reactive and unreactive.

Results obtained from ongoing field cell studies have identified some anomalous samples which exhibit metal release, particularly arsenic and zinc, under neutral pH conditions, contrary to their initial classification. Sequential extraction and mineralogical characterization tests have demonstrated that carbonate dissolution under acidic conditions may be a significant source of leached metals. Additionally, 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.

Key words: neutral drainage, weathering, field cells, Mineral Liberation Analyzer, sequential extraction

Introduction

The Antamina mine, located in Ancash, Peru is one of the world's largest copper producers processing 104,000 tonnes of ore and generating approximately 340,000 tonnes of waste rock daily. Antamina has embarked on an integrated research project in collaboration with Teck's 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, fewer 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 portion of the waste rock material 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 such as particle size analysis and ICP analysis to determine mass distribution, total metal content and metal distribution; automated scanning electron microscopy using a Mineral Liberation Analyzer (MLA) 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.

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. Exoskarn, endoskarn and intrusive rock are the most reactive waste rock types at Antamina and are not the focus of this study; the focus is on the hornfels, marble and limestone rock groups, which combined represent just under half of all of the waste rock mined on site.

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 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.

Materials and Methods

Field Cell Studies

The field cells used in this study consisted of 208 litre (55 gallon) drums, each of which were fitted with a PVC sample outlet and contained a bottom drainage layer of silica sand over a geotextile material. After filling the drums with waste rock samples, they were left open to the atmosphere; leachate samples from the field cells were collected at regular intervals during the rainy season and then analyzed for elemental content, alkalinity, acidity, turbidity, conductivity and pH (Aranda 2010). The following discussion will focus only on leachate pH and sulfate, arsenic and zinc concentrations.

Sample Characterization and Mineralogical Analyses

The waste rock samples used in this study, and described in Table 2, were chosen on the basis of their anomalous behaviour. Initially, sample lithology was determined by visual characterization in the Antamina Geology Department; subsequent classification into the categories of reactive, slightly reactive or unreactive was determined by ICP analysis and the current waste rock classification guidelines (Table 1). Table 2 also contains observations of field cell arsenic and zinc leaching behaviour (Golder 2011). A comparison of the sample classification to its observed field cell leaching behaviour demonstrates poor correlation between assigned (based on classification criteria) and observed sample reactivity.

Particle size distributions were determined for all samples, both before and after sequential extraction testing, 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. Additional samples were sent to Teck's Applied Research and Technology (ART) Group in Trail BC, where modal mineralogy, mineral liberation and mineral associations were determined using MLA.

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

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Sequential Extraction Studies

Sequential extractions were carried out on all of the waste rock samples listed in Table 2. The objectives of this test work were the following:

- to assess the solubility of specific mineralsunder the conditions ranging from neutral to increasingly acidic. These extraction steps use more or less selective reagents to successively solubilize specific mineral 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 observed field cell leaching behavior
- to suggest improvements to the current waste rock classification guidelines

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 was based on the original protocol devised by Tessier *et al.*(1979) and subsequently modified by others (Yoshida*et al.* 2001) to test coarse and larger samples (1.5 to 3 kg).

Results and Discussion

Field Cells

During the last rainy season (from October 2010 to March 2011) the pH for all waste rock samples varied from a low of 7.7 to a high of 9.1, as shown in Figure 1.a. Seasonal trends show a pH minimum at the onset of the rainy season, increasing to a maximum at the end of the rainy season. An inverse trend was observed for sulfate concentrations; all samples demonstrated the general trend of maximum sulfate concentrations at the start of the rainy season, as shown in Figure 1.b, decreasing to minimum sulfate

concentrations at the end of the rainy season. This observation suggests flushing of soluble oxidation products, accumulated during the dry season, at the onset of the rainy season.

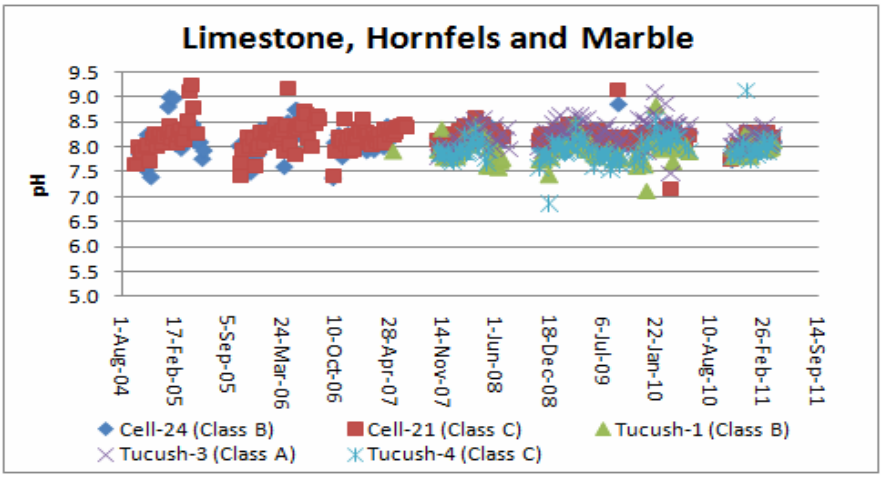

Figure 1.a: Change of pH versus time

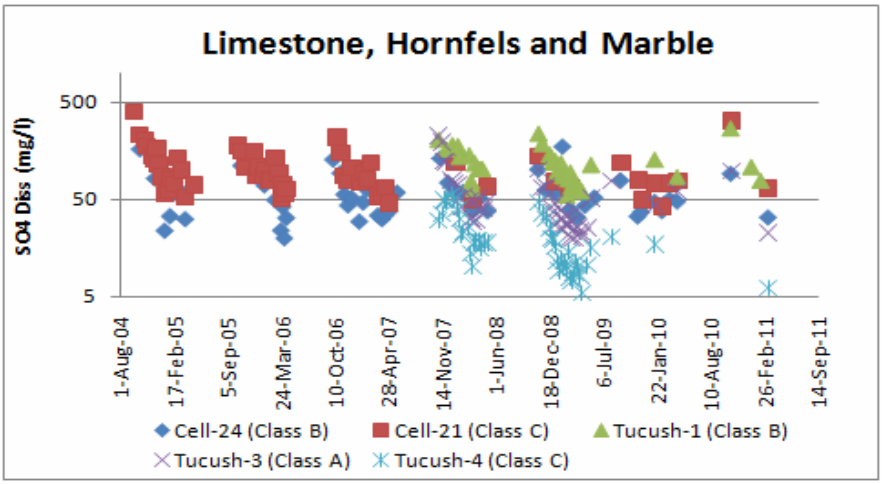

Figure 1.b: Sulfate concentration versus time

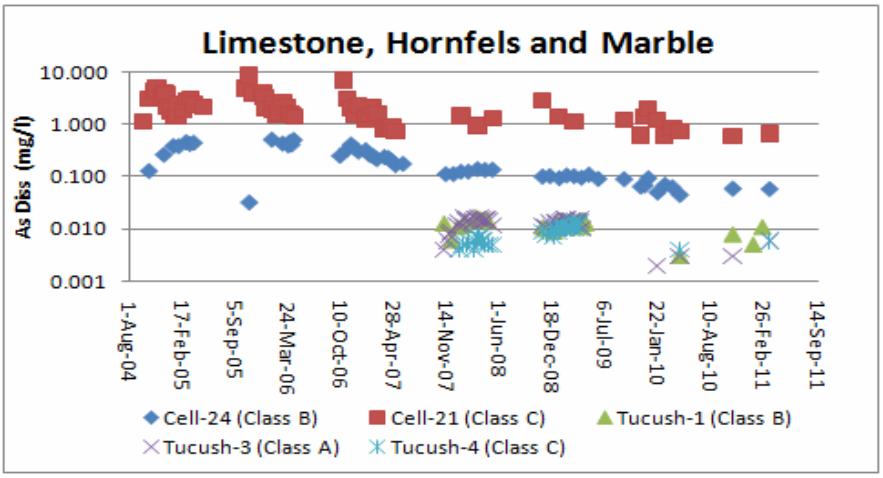

Figure 1.c: Arsenic concentration versus time

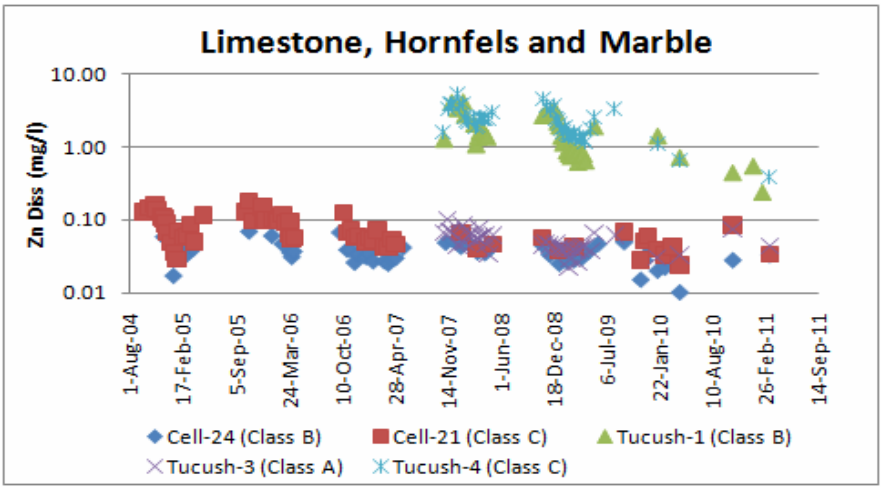

Figure 1.d: Zinc concentration versus time

Preliminary analysis of the field cell data indicates that arsenic and zinc sulfide oxidation is occurring in the samples (Figures 1.c and 1.d respectively). High leachate concentrations of these metals in some of the field cells selected for this study, 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 in 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.

Chemical Composition and Mineralogy of Waste Rock Samples

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

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

MLA analysis of the waste rock samples was used to determine modal mineralogy, providing the identification and quantification of minerals present, and to determine mineral associations, providing an indication of potential activation and passivation reactions. Sulfides were identified as the primary source of sulfur in the waste rock samples; 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 (these quantities are expressed in total wt% of the sample mass). 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 of the samples analyzed contained major quantities of calcite and only trace quantities of siderite and dolomite, indicating calcite as the primary source of acid neutralization. Sulfates, including gypsum and barite, were also identified in all of the waste rock samples, but were present in trace quantities only.

Table 4: Arsenic minerals (%) locked in binary or higherfor 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

Originally designated a Class C waste rock material, 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. Due to greater surface area relative to particle size, the fines would be more reactive than the coarse; one would expect to see relatively high levels of arsenic in the leachate that eventually taper off, exhibiting a gradual decrease in arsenic concentration. This behaviour would be accounted for by the rapid oxidation of liberated arsenic sulfides in the fines.The annual trends of increasing metal release at the onset of the rainy season, decreasing to a minimum at the end of the rainy season could be explained by the dissolution and flushing of soluble oxidation products at the start of the rainy season: adsorption or deposition of oxidation products onto sulfide minerals (or other zinc minerals) will passivate these surfaces rendering them unavailable for reaction; seasonal dissolution and flushing will once again render these mineral surfaces available for reaction. The behaviour of Cell 21 waste rock material, depicted in Figure 1.c, could be explained by such a reaction sequence.

Significant quantities of arsenic minerals 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 localized acidic conditions. The dissolution of carbonate to buffer the acidity produced by oxidation of the liberated arsenic sulfides in this fraction could lead to the liberation of additional arsenic sulfide mineralization. Another 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.

Cell 24

Originally designated a Class B marble, indicating slight reactivity, 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 minerals, primarily 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 could expose some, or perhaps all, of this locked sulfide, rendering it available for reaction. In the case of the coarse fraction, particle size effects would significantly limit the rate of carbonate dissolution; 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	Tucush-1						SUM
µm	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. 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 localized acidic conditions could

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 in the fines; in the absence of surface passivation due to adsorption or precipitation, previously locked zinc sulfides could become increasingly liberated as the carbonate in this size fraction is consumed. In terms of field cell behavior, this would be reflected by high initial zinc concentrations, due to oxidation of the liberated zinc sulfides in the fines, followed by decreasing zinc concentrations over time as more of the liberated zinc sulfides are consumed; exposure and oxidation of previously locked zinc sulfides in the fines would also contribute to the observed zinc concentrations. The concentration trend plotted in Figure 1.d could be explained by such a reaction sequence.

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

Sample ID	Tucush-3						SUM
µm	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
µm	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

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.

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 release of zinc metal cations to solution.
- only 6% of the zinc minerals 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 localized acidic conditions would not release significant amounts of additional zinc cations to solution.

With 22% of the zinc minerals liberated and in the fines (-600 µm), one would expect this material to exhibit relatively high initial zinc concentrations, which it does not. The mineralogical data does not adequately explain this anomalous behaviour, which may be strongly influenced by galvanic interactions between the various sulfides present in the fines or the presence of relatively inert zinc minerals.Additional work would need to be done on these fractions in order to obtain more detailed modal mineralogy and mineral associations for zinc sulfides only.

Tucush-4

Based on its solid phase zinc content of 35mg/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 minerals are in the +297 µm size fraction (Table 6). 36% of the zinc minerals 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 minerals 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 in 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.

Sequential Leaching

Data from the sequential leaching test work was used to calculate the percentage of leachable metal associated with each of the mineral phases as well as calculate the total metal extraction. This discussion will focus only on those results obtained for arsenic and zinc.

Cell 21 and Cell 24

The total arsenic extraction from Cell 21 and Cell 24 was 1.6% and 7.2% respectively. 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 minerals 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 (enargite and watanabeite). 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 (Figure 2). 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 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. Under alkaline conditions the anionic exchange capacity of oxyhydroxides is reduced and the solubility of anionic arsenic is increased any arsenic sorbed or adsorbed to the oxyhydroxide mineral surface can be released in the form of the $HAsO_4^{2-}$ oxyanion (Price 2009).

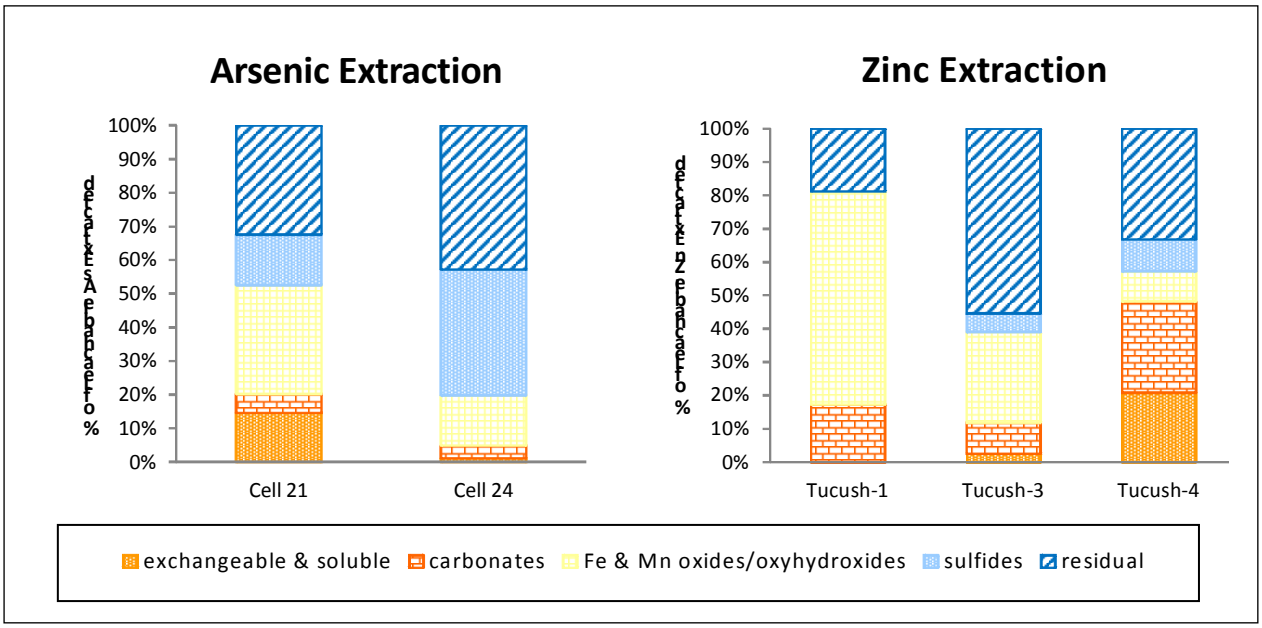

Figure 2:Arsenic extraction from Cell 21 and Cell 24 andzinc extraction from Tucush-1, Tucush-3 and Tucush-4

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 zinc (Figure 2). 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 minerals, 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. These results are of interest in that they highlight the importance of non-sulfide sources in sample weathering behaviour; both carbonates and oxyhydroxides will dissolve under localized circum-neutral to acidic conditions.

The sequential extraction results obtained for Tucush-3 are validated by the field cell observations but not by the MLA results; only 0.5% of the total solid phase zinc was extractable. Approximately 56% of this zinc was associated with silicates, rendering it effectively unreactive. Another 6% of the zinc was associated with sulfides. The most significant sources of zinc are the carbonate and oxide fractions at roughly 10% and 28% respectively. The reactivity of the zinc in these fractions is dependant not only upon Eh and pH, but also upon particle size. Further test work is recommended to explain the discrepancies between the results.

All five fractions in the sequential extraction of the Tucush-4 sample were demonstrated to be sources of leachable zinc. A total of 29.7% of the total zinc was leached from the sample. The presence of leachable zinc in the exchangeable and carbonate fractions, at 21% and 28% respectively, 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.

Conclusions

The objective of this study was to characterize the selected samples, using mineralogical techniques and sequential extraction, in order to explain the anomalous leaching behavior observed in the field cells. The main conclusions are summarized below:

- data from some of the hornfels, limestone and marble field cells within the Antamina field cell program were instrumental in validating conclusions drawn from mineralogical, MLA and sequential leaching data. They also highlighted the limitations of the MLA data for samples in which galvanic interactions or non-sulfide metal sources, such as carbonates and oxyhydroxides, play a substantial role.
- in addition to metal content, the following factors were found to be important in explaining field cell behaviour: *Metal distribution*; metal content as a function of particle size identifies where the bulk of the metal is located in the samples tested and if a metal is likely to be partially or fully liberated.*Modal mineralogy*; identifies mineral sources and their abundance within a sized fraction of a sample. It helps to identify the most reactive minerals and whether they are present in quantities of concern.*Mineral associations*; identifies the presence of associated sulfides and carbonates, particularly in the fines, and helps identify potential activation and passivation mechanisms (i.e. galvanic interactions, carbonate dissolution) that can influence metal leaching behaviour.
- sequential leach data underscored the importance of modal mineralogy and the significance of non-sulfide metal sources such as carbonates and oxyhydroxides. For waste rock samples in which arsenic or zinc is concentrated in the fine fractions (i.e. fully or partially liberated) sequential leaching can be used to determine the following information about the leachable portion of the metal:
  - the percentage associated with exchangeable and soluble fractions; much of which could be flushed from the field cell at the onset of the rainy season.
  - the percentage associated with the carbonate fraction. In the presence of significant quantities of sulfide, localized carbonate dissolution in response to sulfide oxidation would release these carbonate-bound metals.
  - the percentage associated with the oxyhydroxide fraction. Depending on pH and redox conditions, this mineral phase can act as either a source or a sink for dissolved metals.
  - the percentage associated with the sulfide fraction. Partially or fully liberated sulfide minerals will release metals under oxidizing conditions. The presence and quantity of carbonate and oxyhydroxide mineral phases will determine the extent to which the acidity and released metals are attenuated.

While the use of the MLA is not realistic in an operational environment, existing information on waste rock particle size distribution and ICP analysis of the sized fractions could be used in conjunction with leaching to improve the classification system as follows:

- in addition to whole rock sample, the -75 µm (or -53 µm) size fraction would be analyzed by ICP.
- for all those samples in which the fines represent a significant portion of the total waste rock mass,a comparison of ICP results and the wt% of the fines could be used for classification:
  - whole rock is classified as A; if the fines are classified as C the sample should be reclassified as C. If the fines are classified as B the sample should be sent for further testing.
  - whole rock is classified as B; if the fines are classified as C the sample should be reclassified as C. If the fines are classified as A, the sample should be reclassified as A.
  - whole rock is classified as C; if the fines are classified as A the sample should be reclassified as A. If the fines are classified as B the sample should be sent for further testing.
- samples sent for further testing would be leached with either a modified sequential leach, in which the first four extraction steps are combined (to demonstrate metal leachability from various mineral sources under neutral to acidic conditions), or a one-step cyanide leach (to demonstrate metal leaching from the sulfide fraction only).

Incorporating the suggested refinementsto better manage the portion of the limestone, hornfels and marble waste rock with the anomalous leaching behaviour focussed onin this study would need to be evaluated in terms of practical minability, taking into account both environmental and economic costs as well as operational time constraints.

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