# Environmental Attributes and Resource Potential of Mill Tailings from Diverse Mineral Deposit Types

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**Abstract** A suite of over 80 samples of mill tailings from more than 20 different mineral deposit types was geochemically analyzed to evaluate: 1. potential environmental risks to both humans and aquatic ecosystems associated with accidental release of tailings or their leachates; and 2. their resource potential for byproduct critical elements. Dissolved concentrations of metals such as Cd, Co, Cu, Ni, Pb, and Zn were highest in leachates with low pH, whereas concentrations of oxyanions such as As were more complex. Tailings from numerous deposit types show significant enrichment in byproduct critical elements such as In, Ga, and Te relative to average crustal abundances.

Key words tailings, leachate chemistry, byproduct, critical minerals, environmental risk

### Introduction

Sustainable mine development requires the identification of environmental risks and planning for the maximization of resource recovery at the earliest stages of mine development – even at the exploration stage. Studies have shown that the geology of various mineral deposit types influences the environmental attributes of those deposits (Plumlee 1999; Seal & Hammarstrom 2003). Mineral-deposit classification provides important information about a deposit's mineralogy, acid-generating potential, acid-neutralizing potential, ore commodities, and trace element associations – all of which define its environmental risks and resource potential. Waste rock compositions may vary from deposit to deposit because of differences in the local geology where a deposit has formed. However, the ore and the mill tailings resulting from its processing should have clear links to the ore deposit model. The fine grain size typical of mill tailings provides more reactive surfaces for weathering and makes downstream transport easier in the event of an unanticipated tailings release. From the resource perspective, the recovery of byproduct commodities is commonly highly inefficient. These byproduct elements can partition into a variety of waste stream components, with mill tailings likely being one of the volumetrically most important.

A suite of over 80 mill tailings samples from more than 20 mineral deposit types was assembled to evaluate environmental risks related to mill tailings and to evaluate their byproduct resource potential on the basis of mineral deposit type (tab. 1). Samples were obtained from active, inactive, and abandoned mines, and from material used for metallurgical testing at proposed mines. These samples and leachates derived from them were characterized by standard geochemical methods. Environmental risks associated with the mill tailings can be evaluated by comparing the bulk geochemistry of the solids to either sediment guide-lines for the protection of aquatic organisms or soil guidelines for the protection of human health, and the geochemistry of the leachates to surface water guidelines for the protection of aquatic organisms or the protection of human health.

# Methods

Mill tailings samples were characterized using standard bulk geochemical techniques such as wavelength dispersive X-ray fluorescence (XRF) spectroscopy on fused disks, inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS) preceded by a multiple acid digestion, and acid-base accounting. Leachates from mill tailings samples were generated using the USEPA Method 1312 (Synthetic Precipitation Leaching Procedure). USEPA Method 1312 reacts a 1:20 solid to solution mixture for 18 hours with end over end agitation. The solution is a dilute mixture of sulfuric and nitric acids adjusted to pH 5.0. The resulting leachates are characterized using standard procedures for water samples including measurement of unstable parameters (pH, specific conductance, dissolved oxygen, ORP, alkalinity), and filtration (0.45  $\mu$ m) for chemical analysis using ICP-AES, ICP-MS, and ion chromatography.

Potential environmental risks related to mill tailings and leachates can be evaluated by comparing their geochemical compositions to relevant guidelines for aquatic ecosystem health and human health. For aquatic ecosystem health, surface-water guidelines are found in USEPA (2006) and sediment quality guidelines are found in MacDonald et al. (2000). For human health, drinking water guidelines are found in USEPA (2009) and soil quality guidelines are found in USEPA (2016). Concentrations of trace elements can be compared to the average crustal abundance of those elements to identify samples that show enrichment (Rudnick & Gao 2003).

#### **Results and Discussion**

# **Environmental Risks**

The samples span a range of net neutralization potentials (NNP) from -700 to 500 kg  $CaCO_3/t$ , paste pH values from 3 to 8.5, and leachate pH values from 2.4 to 10.5. The specific conductance of leachates spanned a wide range from 0.025 to 4.1 mS/cm. In general, the higher specific conductance values were found at lower pH and the lower specific conductance values were found at higher pH.

A comparison of dissolved Cu and As in leachates as a function of pH (fig. 1) and in solids (fig. 2) illustrates many of the salient features of this data set. Copper solubilizes as a cationic species and is highly toxic to aquatic organisms; in contrast, it is an essential micronutrient for humans. Arsenic typically solubilizes as an oxyanion. It is a carcinogen toxic to humans and to a lesser extent to aquatic organisms.

Dissolved Cu concentrations in leachates generally correlate inversely with pH; the highest concentrations are found at low pH (fig. 1A). The deposit types exhibiting low leachate pH are those types in which pyrite or pyrrhotite are important constituents of the mill tailings and the acid-neutralizing potential is minimal. These deposit types include volcanic-associated massive sulfide deposits and mesothermal low-sulfidation base metal-rich veins. Leachate from magmatic mafic Ni-Cu-platinum group metal (PGM) deposits vary from low to high pH because of the range of acid-generating potential due to this grouping including

Deposit Type	Graph category	Number of deposits	Number of samples
Orogenic Au	Au	4	7
Low-sulfidation epithermal Au	Au	1	1
Intrusion-related Au	Au	1	1
Porphyry Cu	Porphyry Cu	1	3
Volcanic-associated massive sulfide	VMS	7	24
Sedimentary-exhalative Zn-Pb-Ag	Sedex	1	1
Mississippi Valley-type Pb-Zn	MVT	1	7
Mesothermal Cu-Zn-Pb-Ag	Mesothermal	1	12
Carbonate replacement Zn-Pb-Ag	Mesothermal	1	4
Simple Sb vein	Sb	2	2
Magmatic Ni-Cu-PGM massive sulfide	Mafic	4	4
Magmatic Cu-Ni-PGM disseminated sulfide	Mafic	1	1
Magmatic reef PGM	Mafic	1	1
Banded iron formation	BIF	3	3
Iron oxide Cu-Au	REE	1	1
Alkaline intrusion REE	REE	1	4
Carbonatite REE	REE	1	1
Sandstone U	U	1	1
Pegmatitic U	U	1	1
Conglomeritic U	U	1	1
Unconformity U	U	2	2
Metasomatitic U	U	1	2

Table 1 Mineral deposit classifications and samples included in study

massive sulfide deposits, disseminated sulfide deposits, and sulfide-poor PGM "reef" deposits. Deposit types with leachates that cluster at higher near-neutral to alkaline pH values, such as most orogenic Au deposits and REE deposits, banded Fe formations, and a variety of U deposit types, generally have tailings with low acid-generating potential and high acid-neutralizing potential. The leachates accordingly have low dissolved Cu concentrations. The low concentrations of Cu reflect a combination of the low solubility of Cu at high pH and low endowment of Cu in these mill tailings (fig. 2A). In general, the leaching of Cu from tailings from volcanic-associated massive sulfide deposits, mesothermal base metal vein deposits, and magmatic Ni-Cu massive sulfide deposits poses the greatest potential risks for aquatic organisms, but only under limited circumstances are likely to be a concern for human health (fig. 1A). In contrast, for deposit types with mill tailings not likely to generate low-pH leachates, concerns for aquatic ecosystem health due to Cu would appear to be minimal and concerns for human health should be essentially non-existent (fig. 1A). The other base metals (Cd, Co, Ni, Pb, Zn) show similar solubility trends in leachates. However, conclusions about their potential toxicity to humans and aquatic organisms will vary on an element and concentration basis.

Dissolved As concentrations in leachates display a "U"-shaped solubility patterns as a function of pH (fig. 1B). Oxyanions, such as As, generally have higher solubility at high pH and absorb onto hydrated ferric oxides at lower pH. The increased solubility at low pH presumably reflects the higher solubility of Fe under these conditions and thus the lack of a substrate for sorption. Leachates from tailings from simple Sb vein deposits pose significant potential risks to both aquatic organisms and humans regardless of leachate pH. Arsenic is a common minor element in these deposits that is not separated from the crushed ore during processing. Some leachates from mill tailings from mesothermal veins, orogenic Au deposits, volcanic-associated massive sulfide deposits, U deposits and banded Fe formations may pose potential human health risks. Other elements that tend to dissolve as oxyanion species (Cr, Sb, Se, Mo, U, V) show similar solubility trends, but their potential toxicity to humans and aquatic organisms will vary on an element by element basis.



Figure 1 Variations of dissolved Cu (A) or As (B) with pH for various deposit groups. Dashed lines represent human drinking water guidelines (red) and acute aquatic ecosystems guidelines (blue). The acute aquatic guideline for Cu assumes a water hardness of 100 mg/L CaCO3. See table 1 for an explanation of the legend.

Potential pathways of impacts from Cu and As to aquatic organisms from mill tailings can be identified from considering leachate and bulk solid geochemical compositions together (fig. 2). Some deposit types, such a volcanic-associated massive sulfide deposits, pose potential risks from both the leaching of trace elements from tailings and the accidental release of tailings to surface water settings. In contrast, tailings from mesothermal vein deposits primarily appear to be a greater concern from the leaching of trace elements from tailings. Most Au deposit types, REE deposits types, banded Fe formations, and U deposits types have limited potential to impact aquatic organisms from leachate or tailings releases with respect to Cu. In contrast, leachates from tailings from most deposit types have limited potential to affect aquatic organisms from As with the exception of some orogenic Au deposits and mesothermal veins, but accidental release of tailings from these two deposits types pose risks of universal concern related to As. The knowledge gained from this analysis should be beneficial to environmental risk assessments of proposed mines, active mines, and abandoned or inactive mines.



Figure 2 Variations of Cu (A) or As (B) in bulk mill tailings and leachates from mill tailings for various deposit groups. Dashed lines represent guidelines for aquatic ecosystem health. Horizontal lines are for acute toxicity in surface water; vertical lines are probable effect concentrations for sediment. See table 1 for an explanation of the legend.

# **Resource Potential**

The geochemical data set assembled is useful for identifying mill tailings from deposit types for which byproduct commodities, such as technologically critical elements, are anomalously enriched. The variations in the bulk concentrations of Ga, In, and Te compared with the concentrations of elements that are the major commodities extracted, such as Cu, Sn, and Zn, illustrate the value of these data. The concept of an "ore grade" for byproduct commodities is meaningless because their recovery alone does not determine the viability of a mining project. Instead, their anomalous concentrations are best considered relative to the average crustal abundances of these elements (Rudnick & Gao 2003). Maximum concentrations of Ga (58.9 mg/kg), In (20.5 mg/kg), and Te (5.6 mg/kg) were high relative to average crustal abundances for these elements (fig. 3); these maximum concentrations exceed average crustal values for these elements by factors of 3 for Ga, 130 for In, and 5,700 for Te (fig. 3). In fact, maximum concentrations of Cu (11,400 mg/kg), Sn (54.2 mg/kg), Zn (8,740 mg/ kg) are also high relative to average crustal abundances. The significant enrichments of Cu, Sn, and Zn presumably reflect inefficient recovery or lack of recovery of these commodities at individual mines. The higher concentrations of Cu are from deposit types for which Cu would have been a primary commodity (porphyry Cu deposits and volcanic-associated massive sulfide deposits), indicating inefficient recovery (fig. 3A). Likewise, the high Zn concentrations were found in tailings from deposits commonly mined for Zn, such as volcanic-associated massive sulfide deposits, sedimentary-exhalative deposits, mesothermal vein deposits, and Mississippi Valley-type deposits (fig. 3B).

Significant byproduct critical elements may be available for recovery at existing mines or by processing mill tailings at inactive or abandoned mines on a deposit type basis. For example, In shows the greatest enrichment in tailings from volcanic-associated massive sulfide deposits and mesothermal vein deposits (fig. 3A,C). Its concentration shows moderate correlations with Cu and Sn concentrations, which implies that it may substitute into Cu or Sn minerals. Gallium is only locally enriched in tailings from some U deposits, porphyry Cu deposits, and volcanic-associated massive sulfide deposits (fig. 3B), and does not appear to correlate with other elements. Tellurium reaches its highest concentrations in tailings from porphyry Cu deposits and orogenic Au deposits, and lacks significant correlations with other elements, such as Cu (fig. 3D). Because of the low crustal abundance of Te (0.001 mg/kg), tailings from most deposits are nominally enriched in Te. Banded Fe formations and most U deposit types tend to be depleted in these byproduct critical elements relative to average crustal abundance es. The identification of specific critical elements with specific deposit types may enhance resource recovery at active mines or during remediation of abandoned mines.



Figure 3 Variations of byproduct critical elements with other trace elements in mill tailings. A. In vs. Cu; B. Ga vs. Zn; C. In vs. Sn; and D. Te vs. Cu. Dashed lines represent the average crustal abundance of these elements. See table 1 for an explanation of the legend.

#### Conclusions

Insights gained from the geochemistry of mill tailings and their leachates on a deposit type by deposit type basis can be used to anticipate potential environmental risks related to the development of these deposit types, even at the earliest stages of potential mine development – the exploration stage. The knowledge gained from this analysis should be beneficial to environmental assessments of proposed mines, active mines, and abandoned or inactive mines. Tailings from numerous deposit types show significant enrichment in byproduct critical elements such as In, Ga, and Te relative to average crustal abundances, suggesting that increased demand for these critical elements could potentially be met by recovering them at existing mines or by remining tailings at abandoned mines.

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