Effect of a pH gradient on lead and zinc speciation in semiarid mine tailings

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Introduction

As a result of the physical grinding of the mining process, mine tailings have a high surface area exposed to atmospheric conditions (water, O_2) and undergo significantly accelerated weathering reactions. Many of the metal rich parent materials produce hydronium ions as part of their weathering transformations, thus lowering pH and aiding solubilization of many metals. Change in the pH of the system during weathering reactions impacts the speciation and thus the bioavailability of the principle contaminant metals.

Mine tailings represent a significant health risk to humans. Because they are characterized by high concentrations of toxic metals, low pH, and small particle size, they are readily transported by wind and water erosion. The toxicity and bioavailability of metals are governed by speciation more than by total quantity, which makes understanding speciation essential to assessing the health risk as well as the effectiveness of a remediation strategy.

Research Objectives

As part of a larger pytoremediation project at the Klondyke State Superfund Site, we are studying the effect of mineral weathering on the speciation of lead (up to 13 g/kg^{-1}) and zinc (up to 7 g/kg^{-1}), the primary contaminants. This site is unique because it has a significant pH range across the tailing. We hypothesize that the pH gradient corresponds to a "weathering" gradient that could be used to study different stages of mineral transformations. In this work, four samples from across this gradient were studied by a combination of wet chemistry, sequential chemical extractions, and synchrotron-based spectroscopy to assess changes in metal speciation. Data were analyzed in collaboration with the Kretzschmar group at ETH Zurich.

The Klondyke Mine Tailings

Physical characteristics of the tailings

Tailing	pH	EC (us/cm)	Zn (mg/kg)	Pb (mg/kg)
K4*	2.7	5,300	420±3	4,630±9
T1#	4.5	1,820	1,560±6	5,050±10
T2#	6.4	1,596	6,260±14	12,620±20
K6*	5.7	3,500	4,020±10	4,640±10

Mineralogy: Quartz, Feldspars (orthoclase/ plagioclase), jarosite, plumbojarosite, zinc-talc, iron oxides (hematite/ goetite), clays, and gypsum.

Data collected by: #A. Vazquez and *M. Mendez, photo by A. Vazquez

Methods

Sequential extraction

The following sequential extraction method, adapted from Dold (2003), was used to measure metal lability in the tailings: **(1)** 18MW water, 25°C (gypsum, salts); **(2)** 1.0 M NH_4-acetate, pH=4.5, 25°C (exchangeable, calcite); **(3)** 0.2 M NH_4-oxalate, pH=3.0, 25°C (short range order iron oxides, secondary jarosites); **(4)** 0.2 NH_4-oxalate, pH=3.0, 80°C (long range order iron oxides, primary jarosites); **(5)** 30% H_2O_2, 60°C (organics); **(6)** $KClO_3$, 12 M HCl, 4M HNO_3, 90°C (primary sulfides).

Bulk XRF, XRD, and epoxy section preparation

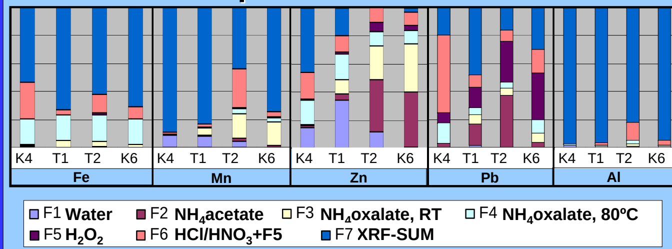
XRF was performed in the Kretzschmar Lab at ETH using a Spectro X-lab 2000. XRD data was collected at SSRL at BL 11-3 and Fit 2D was used for data reduction. To make the thick section, unground tailings were impregnated under vacuum and cured under nitrogen at 60ºC for 24 hrs. The 0.3mm section was cut for analysis.

XAFS data collection and analysis

Lead LIII-edge EXAFS data were collected at SSRL BL 11-2 at 4K. Zinc K-edge EXAFS was collected at GSE-CARS 13-BM at APS at room temperature. The microfocused data was collected at SSRL beam line 2-3.

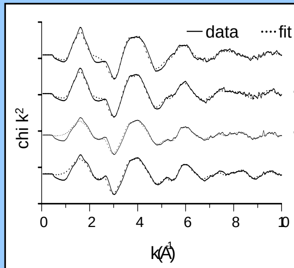
Data analysis was performed using Athena suite. E_0 was calibrated to the inflection point of the adsorption edge of lead foil. E_0 for the lead foil was set to 13035 eV. The lead linear combination fits were done in k space (k=1) with a fit range of k=2-9.5 to avoid the bismuth edge (13419eV).Zinc linear combination fits were done with k=2 with a fit range of k=2-10.

Sequential extraction



The sequential extraction demonstrates the relative recalcitrance of each element.

Zinc EXAFS

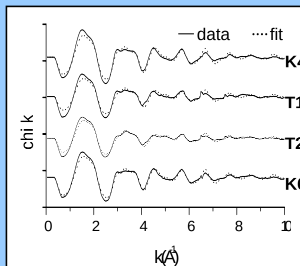


	pH	(1)	(2)	(3)	R-factor
K4	2.7	88%	12%	18%	0.05
T1	3.9	65%	32%	18%	0.04
T2	4.2	8%	41%	46%	0.05
K6	5.7	0%	53%	48%	0.04

(1) goslarite $ZnSO_4 \cdot 7H_2O$
(2) Zn clay $(Zn_{0.8}Mg_{0.2})_3Si_4O_{10}(OH)_2$
(3) Zinc phytate

The zinc speciation demonstrates a strong pH dependence. At lower pH, the zinc appears to exist in an octahedral bonding environment similar to that in $ZnSO_4 \cdot 7H_2O$, although this is not likely the precise phase because its high solubility is inconsistent with the extraction data. As the pH increases, the peaks characteristic of a zinc magnesium clay develop. Zinc phytate was used in the fits to represent all tetrahedral zinc such as sorbed species and does not necessarily imply bonding to phosphate. The data is shown in the solid line and the fit is the dotted line.

Lead EXAFS

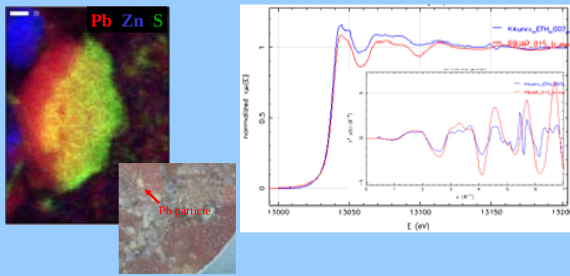


	pH	(1)	(2)	(3)	R-factor
K4	2.7	59%	14%	12%	0.07
T1	3.9	36%	32%	0	0.10
T2	4.2	45%	22%	0	0.07
K6	5.7	65%	15%	0	0.07

(1) Plumbojarosite $Pb(Fe_3(SO_4)_2(OH)_6)_2$
(2) Anglesite $PbSO_4$
(3) Pb sorbed hematite 11,800 mg kg^{-1}

The lead is weathering incongruently between sulfate phases, mainly plumbojarosite and lead sulfate. At lower pH, the lead data are consistent with sorption to iron oxides. Lead speciation does not demonstrate the same pH dependence as zinc. The data is shown in the solid line and the fit is the dotted line.

Micro-focused EXAFS of K4



As a result of the apparent self absorption in bulk spectra it is believed that the lead is highly concentrated in discrete particles rather than spread diffusely throughout the matrix. This is an example of an aggregate that has a significant amount of lead. The XRF demonstrates that lead and sulfur are clearly co-located, supporting the bulk data that lead is primarily in sulfate phases. Extended XANES of the aggregate exhibits the characteristic beat pattern associated plumbojarosite.

Conclusions

- Zinc speciation demonstrates a strong dependence on pH. The speciation is dominated at low pH by octahedral zinc in $ZnSO_4$ and at higher pH by a zinc clay.
- Lead speciation doesn't show the same clear dependence on pH, but is present in sulfate phases such as anglesite and plumbojarosite.
- The lead is highly concentrated in small aggregates. The speciation of the lead in the aggregate is a representative of the bulk
- There is not sufficient evidence to support the idea that the pH gradient represents a natural weathering series in the tailings.

Questions Guiding Future Research

What changes in lead and zinc speciation can be expected during phytostabilization?

- What effect does the irrigation water have on the tailings?
- In terms of root, root exudates and microbial interactions, what is the effect of the rhizosphere on the tailings?

Acknowledgments

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