



Geochemical Controls on Mobilization of Metals from Tailings and Implications for Cover Amendments

Linda Figueroa¹, Sarah Doyle²

¹*Civil & Environmental Engineering, Colorado School of Mines, Golden, Colorado, USA, lfiguero@mines.edu, ORCID 0000-0003-3588-6705*

²*Itasca Denver Inc., Denver, Colorado, USA, sdoyle@itascadenver.com, ORCID 0000-0001-8093-9461*

Abstract

Closure or reclamation of tailings impoundment options include constructing a vegetative cover with amendments to improve conditions for growth. However, cover amendments have potential to mobilize metals in waste by introducing new chemicals and altering pH and redox conditions. Copper, lead and zinc mobilization potentials from fine grained materials were evaluated by sequential extraction and amendment by topsoil, spent brewery grain, biochar, compost, commercial soil media, and phosphate. Amendment induced metal mobilization could occur from reducing conditions, low pH, formation of stable aqueous metal-organic complexes, and ligand exchange. Cover amendment selection must consider waste metal phases to limit mobilization potential.

Keywords: Reclamation, lead, copper, compost, biochar

Introduction

Vegetation can be part of a number of different types of tailing covers. The cover could be for reduction of dust, erosion, infiltration and limiting direct exposure to atmospheric conditions. Vegetation could also be part of store-and-release covers. To promote vegetation on covers, amendments are added to create favorable soil characteristics such as water-holding capacity, organic matter content, and nutrient availability.

Amendments may also alter geochemical conditions within the tailings storage facility and lead to unintended consequences. Cover amendments may enhance metals mobilization due to changes in the reduction/oxidation (redox) and/or pH conditions leading to desorption and/or mineral dissolution. Xie and van Zyl (2023) reported that soluble organic compounds released by decomposition of organic matter and plant roots resulted in decreased pH and increased metal concentrations from amended tailings. In studies of soil contaminated with smelting slag, (Navarro 2012) found that organic rich solid amendments mobilized selenium and arsenic. Further, a decrease in redox conditions, led to reductive dissolution of metal oxides on which the selenium and

arsenic were sorbed. Amendments also introduce new chemical compounds that can alter the mobility of metals. The presence of dissolved organics has potential to enhance mobilization of metals by forming stable aqueous metal-organic complexes. In studies of mine tailings and metal-contaminated soil, increased leaching of metals including lead, zinc, and copper, corresponded to increases in organic carbon leaching, when organic amendments were added (Clemente et al. 2006). Other amendments, such as phosphate fertilizers can also have unintended results. In a study of mine tailings amended with phosphate, (Munksgaard and Lottermoser 2013) found that both arsenic and antimony were mobilized due to the replacement of the original ligand (complexing compound) with phosphate.

The extent to which these various mechanisms can mobilize metals depends on the metal forms present in the tailings. In the initial sulfidic ore, the mineralogy is often well characterized and relatively simple. TSF closure may aim to immobilize metals by minimizing oxidation of metal sulfides. However, reclamation of tailings presents a challenge because mineralogy is often more complex from mineral alternations during

metallurgical processing and aging. Over time, exposure of tailing surfaces to atmospheric oxygen during processing, emplacement and retention causes oxidation of primary sulfide minerals (weathering) releasing metals that may form numerous secondary minerals. For example, in oxidizing conditions, lead sulfide weathers to form secondary phases which may include lead sulfate, lead carbonate and several lead phosphate minerals {Frau et al. 2009; Ramos and Siebe 2007; Ruby et al. 1994}. In addition, metals from oxidation of metal sulfides may be sorbed onto metal oxides or coprecipitated with other phases. Achieving geochemical stability during reclamation may be difficult because the geochemical controls for the new metal phases may differ from one another and from the primary metal sulfides remaining in the pile. Furthermore, common characterization tools such as X-ray diffraction (XRD) may be ineffective at identifying metal phases due to low content (less than a few percent) and poorly crystalline properties that are typical for secondary phases in tailings and mine waste (Jamieson et al. 2015).

The objective of this study was to evaluate the effects of reclamation amendments on the mobilization of metals from weathered mine waste materials. Metal mobilization was expected to vary with mineralogy and metals in the waste material and the chemistry of amendment leachate.

Methods

Source material for this study was obtained from a historical site located in Colorado, USA. The material originated from a complex sulfide deposit that was mined for lead, copper, silver, and gold more than 100 years ago. Common minerals in the ore included galena (PbS), sphalerite (ZnS), chalcopyrite (CuFeS₂), and pyrite (FeS₂) (Ransome 1901). The material fraction less than 2 mm used for analyses in this study.

Metals content of the source material was analyzed by ICP-AES, following a microwave-assisted nitric acid digestion (USEPA 2007). The material was also analyzed by sequential extractions to evaluate metals present in the exchangeable fraction, the fraction bound to carbonates, the fraction bound to iron

and manganese oxides, and the residual. Extractions were conducted using a modified method of the procedure developed by Tessier (1979). The supernatant was filtered through a 0.45-micron disposable filter, diluted, acidified with nitric acid, and analyzed by ICP-AES.

The potential for cover amendments (brewing grain, biochar, compost, soil media, phosphate) to mobilize metals in the source material was evaluated through a leach test in which the fine-grained waste material was leached with solutions prepared from the amendments. The extract solutions from brewing grain, biochar, compost and soil media were prepared by adding 2 g of dried material to 300 mL of deionized water and mixing at room temperature for 48-hours. The phosphate solution was prepared with calcium phosphate monobasic monohydrate at a concentration of 4 mmol P/L. The leach tests were done to simulate conditions in which cover material is placed over the tailings and water flows through the cover and into the tailings. Batch leach tests were conducted by mixing 1 g of source material with 20 mL of the solutions prepared from the cover amendments plus a deionized water control.

Source material and amendment solutions were mixed in 50 mL tubes for 1 hour on an end-over-end mixer, followed by settling for 10 minutes. After settling, the pH was measured and an aliquot of solution was removed, filtered through a 0.45-micron disposable filter, acidified, and analyzed for metals by ICP-AES.

Results and Discussion

Material Elemental Composition

The fine-grained altered ore source material has high content of lead (3.5%), copper (0.75%), and zinc (0.80%), suggesting a risk to downgradient bodies of water should these metals mobilize because of changing geochemical conditions. Table 1 presents results of elemental analysis by ICP-AES after acid-digestion. Mobilization of even a small fraction of these metals could result in aqueous concentrations that are greater than aquatic life standards. Assuming a 20:1 water to rock ratio, mobilization of 1% of

Table 1 Selected elements in the source material, average and (range) as % by mass

Al	Ca	Cu	Fe	Mn	P	Pb	S	Zn
1.3	2.5	0.75	4.4	1.3	0.12	3.5	1.0	0.80
(0.95-1.8)	(1.6-3.6)	(0.36-1.2)	(3.3-5.6)	(1.1-1.8)	(0.08-0.14)	(2.2-5.0)	(0.35-1.7)	(0.34-1.1)

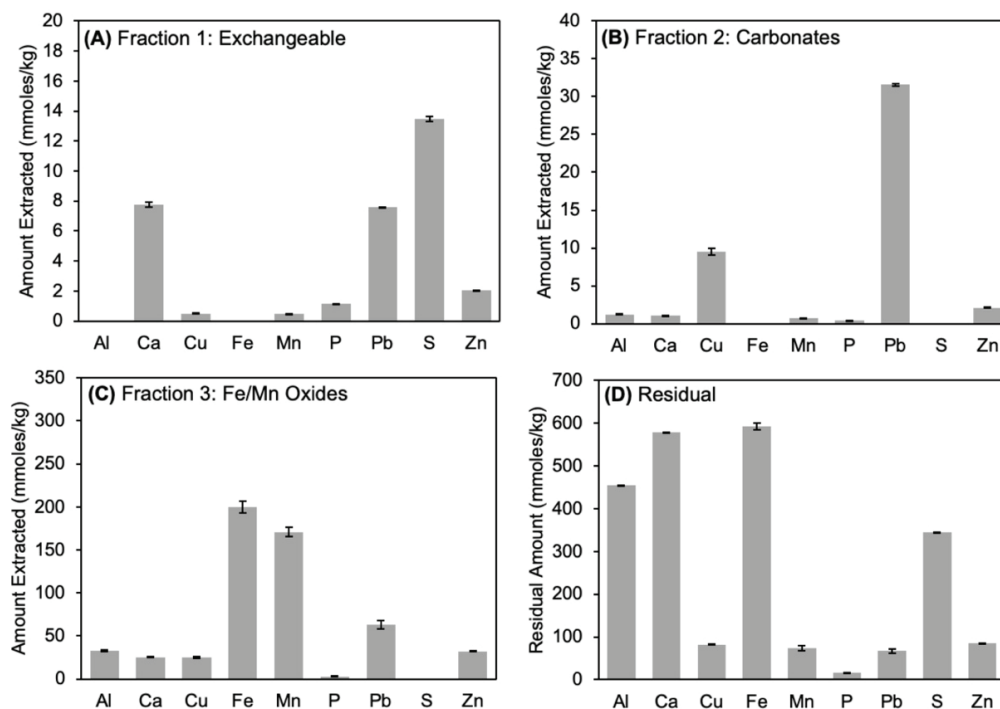


Figure 1 Sequential extraction results in mmoles per kg of rock: (A) Fraction 1 – exchangeable fraction; (B) Fraction 2 – bound to carbonates; (C) Fraction 3 – bound to iron and manganese oxides; and (D) residual fraction. Bars are average values for two replicate extractions. Error bars show the range

the lead would result in a concentration of 1.8 mg/L, compared to a chronic aquatic life standard of 0.01 mg/L (Colorado Code of Regulations 2021).

Metal mobilization by Sequential Extraction

Sequential extractions show the degree of metals mobilization under various geochemical conditions, from which the metal forms of the source material can be inferred. The extractions are useful in characterizing metals that are of environmental concern even at low contents, such as less than a few percent. Other analytical methods such as XRD may be unable to identify these phases,

due to low content and poorly crystalline phases (Jamieson et al. 2015). Fig. 1 presents the millimoles mobilized per kg of rock. Results of the sequential extractions indicate that an average of 60% of the lead by weight and approximately 30% of the zinc and copper were mobilized during the extractions. The non-extracted (residual) is attributed to unaltered sulfide minerals in the source material.

Fraction 1 is commonly referred to as the exchangeable fraction. Metals may be released by dissolution and/or desorption of weakly sorbed phases. In Fraction 1, 4.5% of the lead was extracted, 1.7% of the zinc, and 0.4% of the copper. As shown in Fig. 1, a similar magnitude of sulfur was also extracted

suggesting dissolution of metal sulfates. Lead in Fraction 1 may be present in the source material as anglesite (PbSO_4).

Fraction 2 is intended to dissolve carbonates and release associated metals. The primary elements extracted in Fraction 2 are lead (19%) and copper (8%), suggesting the presence of cerussite (PbCO_3) and copper carbonate secondary minerals, such as malachite. The presence of lead carbonate is of concern due to its potential to mobilize in low pH conditions.

Fraction 3 is intended to reductively dissolve iron and manganese oxides and release metals bound to them. Of the three extractions performed, Fraction 3 extracted the largest percentage of metals from the source material (37% of lead, 22% of copper, and 26% of zinc). Metals associated with Fraction 3 may be mobilized from the waste rock pile if reducing conditions occur from cover placement. Ribeta et al. (1995) noted similar findings in a study of sulfidic tailings that had weathered for several decades. Covering the tailings with an organic-rich cover was therefore identified as an environmental risk due to the potential for metals release from reductive dissolution of ferric (oxy)hydroxides.

Metal Mobility with Amendments

Results of the amendment evaluation (Fig. 2) demonstrate the potential deleterious effects of selecting cover amendments that are unsuitable given the mineralogy of the source material. In the leach tests using spent brewery grain the highest amounts of lead, copper, and zinc were released. Spent brewery grain is a readily available organic carbon source that is a waste product of brewing beer. Spent brewing grain was tested as an amendment in field cells of freshly deposited, pyrite-rich tailings at the Greens Creek Mine in Alaska. The use of spent brewery grain as an amendment led to sulfate reduction and metals immobilization in a three-year field study (Lindsay et al. 2011). For the source material evaluated in this study, the reducible content averages 1,700 mg/kg copper, 13,000 mg/kg lead, and 2,100 mg/kg zinc. Mobilization of these metals presents a high risk for water quality issues in drainage

from a tailings impoundment and receiving water bodies.

Mobilization of metals is attributed to low pH of the spent brewery grain (pH of 4) and the resulting mineral dissolution and desorption of metals. Cerussite in the source material is estimated to account for an average of 19% of lead by weight. The presence of lead phosphate in is suspected based on both elemental content of phosphorus in the waste rock (0.12% by weight) and the presence of phosphorus at 0.42 mg/L in leachate from tests in which waste rock is mixed with deionized water. Solubility of both cerussite and lead phosphates decreases with pH and dissolution would be expected at pH 4 for the leached solution (Sauve 1998). A decrease from pH 7 to pH 4 would desorb zinc, copper, and the majority of the lead (Dzombak and Morel 1990).

Increased metal concentrations in tests with spent brewery grain may also be due in part to the presence of organic matter. Decomposition of organic matter releases organic acids, which are known to form stable aqueous metal-organic complexes (Misra and Pande 1974). In studies with oxidized Pb-Zn tailings, (Wang and Mulligan 2013) found that low molecular weight organic acids increased mobilization of Cu, Pb and Zn at pHs above 7 due to formation of soluble aqueous organic complexes.

In leach tests using biochar solution, decreases in leaching of zinc, copper, and lead were observed compared to concentrations leached with deionized water (Fig. 2). Leaching of lead decreased the most (93%), with a leached concentration of 7.0 mg/L for deionized water and 0.46 mg/L for biochar solution. Decreases in leaching with biochar solution are attributed to both to sorption onto suspended solids in the extracted biochar solution and the high pH of the initial solution (pH 9.1). Ippolito (2017) found that biochar addition to mine land soil decreased bioavailability of lead by forming lead oxyhydroxides.

The largest reduction in lead leaching occurred in leach tests using 4 mM phosphate solution, in which leaching decreased by 96%, from 7.0 mg/L for deionized water to 0.29 mg/L for the phosphate solution.

Phosphate is known to form stable lead phosphate minerals, such as pyromorphite and hydroxypyromorphite (Ruby et al. 1994). Although the phosphate solution reduced lead leaching by 96%, results suggest there may be drawbacks to its use at field scale. In leach tests with phosphate solution, copper and zinc concentrations increased by 59% and 37%, respectively, relative to deionized water. The increase in leaching may be due to a slight decrease in leachate pH (5.7 for deionized water, compared to 5.4 for phosphate solution), which highlights the sensitivity of the fine-grained mined waste material to small decreases in pH. In addition to zinc and copper, arsenic concentrations may also increase from phosphate amendment. Arsenic leached up to 0.12 mg/L in leach tests with phosphate solution, despite low arsenic content in the source material (56 mg/kg) and below detection concentrations in other leach tests (less than 0.08 mg/L). Addition of phosphate is known to release arsenic, due to ligand exchange with arsenic oxyanions (Munksgaard and Lottermoser 2013).

Conclusions

Laboratory tests showed that metal sulfide minerals initially present in the ore (galena, sphalerite, chalcopyrite) had been altered to form numerous phases, including metal sulfates, phosphates, carbonates, and phases associated with manganese/iron oxides. Sequential extraction test demonstrated that the largest extractable fraction of lead, copper

and zinc were associated with iron and manganese oxides, followed by carbonate-bound phases. Results of characterization suggest that the largest risk is the mobilization of metals from development of geochemical reducing conditions. These conditions could occur with amendments having high organic carbon content, but also due to physical barriers to oxygen entry into the pile, as may occur with fine-grained covers.

Results of this study demonstrate the importance of identifying metal phases present in a fine-grained altered ore materials prior to selecting cover amendments. Organic amendments with high labile/soluble carbon, such as spent brewery grain, present the greatest risk for reclamation of fine-grained altered ore materials due to many possible mechanisms of mobilization. These amendments may cause geochemically reducing conditions which release metals associated with iron and manganese oxides. They may also result in decreased pH from organic acids, leading to dissolution of carbonate phases and desorption of metals. Lastly, introduction of dissolved organic matter may increase aqueous metal content by formation of stable metal-organic complexes. Additional research is needed to develop characterization methods for organic amendments so that formation of metal-organic complexes can be minimized in settings deemed high risk based on metal phases present.

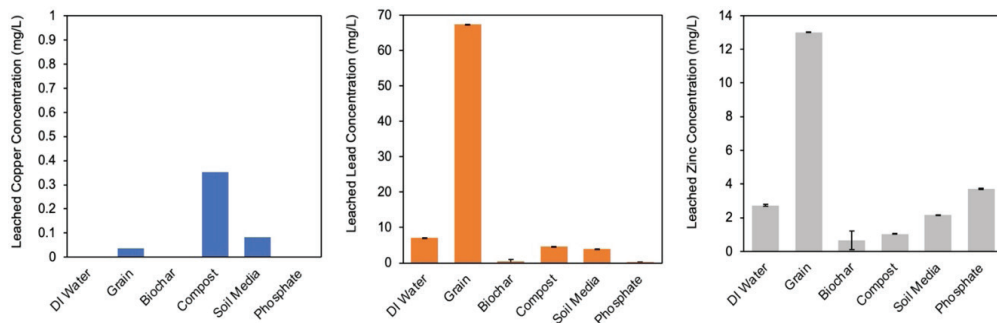


Figure 2 Leached metal concentrations and pH after leach tests with amendment solutions. Results are average of duplicate tests and error bars show range of values

References

- Clemente R, Escolar Á, Bernal MP (2006) Heavy metals fractionation and organic matter mineralisation in contaminated calcareous soil amended with organic materials. *Bioresour Technol* 97:1894–1901. <https://doi.org/10.1016/j.biortech.2005.08.018>
- Colorado Code of Regulations (2021) Regulation No. 24. Classifications and Numeric Standards for San Juan River and Dolores River Basins, 5 CCR 1002-34, Department of Public Health and Environment, Water Quality Control Commission
- Dzombak, DA, Morel FF (1990) Surface complexation modeling – Hydrous ferric oxide: John Wiley and Sons, New York.
- Frau F, Ardaù C, Fanfani L (2009) Environmental geochemistry and mineralogy of lead at the old mine area of Baccu Locci (south-east Sardinia, Italy). *J Geochemical Explor* 100:105–115. <https://doi.org/10.1016/j.gexplo.2008.01.005>
- Ippolito JA, Berry CM, Strawn DG, et al (2017) Biochars Reduce Mine Land Soil Bioavailable Metals. *J Environ Qual* 46:411–419. <https://doi.org/10.2134/jeq2016.10.0388>
- Jamieson HE, Walker SR, Parsons MB (2015) Mineralogical characterization of mine waste. *Appl Geochemistry* 57:85–105. <https://doi.org/10.1016/j.apgeochem.2014.12.014>
- Lindsay MBJ, Wakeman KD, Rowe OF, et al (2011) Microbiology and geochemistry of mine tailings amended with organic carbon for passive treatment of pore water. *Geomicrobiol J* 28:229–241. <https://doi.org/10.1080/01490451.2010.493570>
- Misra SG, Pande, P (1974) Short Communication: Effect of organic matter on availability of nickel. *Plant and Soil*, 40, 679–684.
- Munksgaard NC, Lottermoser BG (2013) Phosphate amendment of metalliferous tailings, Cannington Ag-Pb-Zn mine, Australia: Implications for the capping of tailings storage facilities. *Environ Earth Sci* 68:33–44. <https://doi.org/10.1007/s12665-012-1711-2>
- Navarro A (2012) Effect of sludge amendment on remediation of metal contaminated soils. *Minerals* 2:473–492. <https://doi.org/10.3390/min2040473>
- Ramos Arroyo YR, Siebe C (2007) Weathering of sulphide minerals and trace element speciation in tailings of various ages in the Guanajuato mining district, Mexico. *Catena* 71:497–506. <https://doi.org/10.1016/j.catena.2007.03.014>
- Ransome FL (1901) A Report on the Economic Geology of the Silverton Quadrangle, Colorado, United States Geological Survey, No. 182
- Ribeta I, Ptacek CJ, Blowes DW, Jambor JL (1995) The potential for metal release by reductive dissolution of weathered mine tailings. *J Contam Hydrol* 17:239–273. [https://doi.org/10.1016/0169-7722\(94\)00010-F](https://doi.org/10.1016/0169-7722(94)00010-F)
- Ruby M V., Davis A, Nicholson A (1994) In Situ Formation of Lead Phosphates in Soils as a Method to Immobilize Lead. *Environ Sci Technol* 28:646–654. <https://doi.org/10.1021/es00053a018>
- Tessier A, Campbell PGC, Bisson M (1979) Sequential Extraction Procedure for the Speciation of Particulate Trace Metals. *Anal Chem* 51:844–851. <https://doi.org/10.1021/ac50043a017>
- Wang S, Mulligan CN (2013) Effects of three low-molecular-weight organic acids (LMWOAs) and pH on the mobilization of arsenic and heavy metals (Cu, Pb, and Zn) from mine tailings. *Environ Geochem Health* 35:111–118. <https://doi.org/10.1007/s10653-012-9461-3>
- USEPA (2007) Method 3051A (SW-846): Microwave Assisted Acid Digestion of Sediments, Sludges, and Oils, Revision 1, Washington, DC
- Xie L, van Zyl D (2023). The geochemical processes affecting the mobility of Cu, Pb, Zn during phytostabilization on sulfidic mine tailings revealed by a greenhouse study. *Journal of Cleaner Production*, 418, 138119