

## Leachability of Cu, Zn, As, Ba and Pb from Refuse in the Zelazny Most Tailings Dam

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**Abstract** In order to establish plants on any kind of mine waste it is essential to determine its chemical properties, i.e. the potential to release elements. In this study we combine chemical extraction of six different solid metal species (water soluble, ion-exchangeable, carbonate, reducible, oxidizable acid leachable) on tailings from Zelazny Most, Poland. The results show that the plants encounter an environment with circumneutral pH and high availability of Ca, Na, and Cu. During reducing conditions there is also an increasing availability of As, Fe, Pb, and Zn.

**Keywords** copper tailings, zelazny most, metal leachability

### Introduction

On many sites with mine waste or metal polluted soil, environmental conditions can be improved by establishing vegetation on disturbed surfaces. This generally attributes to reduction of runoff due to lowered infiltration as evapotranspiration increases. As an ecosystem becomes established this will under most circumstances also favor the physical retention of metals. Establishing plants on toxic substrates usually requires some kind of conditioning to improve growth. Traditionally this is made by adding fertilizers and possibly also some agent that will lower metal bioavailability. Recently it has been shown that biological principles can be used (Turnau et al. 2008). They include for instance the use of mycorrhiza that has been selected to tolerate the toxic elements at the site. In addition, by selecting the appropriate combination of plant and mycorrhiza it is also possible to extract one or several metals from the substrate into the plant, which allow for both soil cleaning from hazardous metals and phyto-mining of valuable elements.

Mine wastes are substrates that are difficult to colonize with plants since they typically have a low water holding capacity in combination with a wide range of toxic metals. Depending on their original mineral composition and extraction procedures the waste quite often has extreme pH. This makes it even more difficult to establish vegetation although it would lower environmental risks and also have the potential for enriching elements. The latter is particularly important on waste sites where the concentration of valuable elements is below the cost limit for conventional technical re-extraction. One such material is historic mine waste where element concentrations quite frequently exceeds the present ores.

In an ongoing study of plant establishment and survival on complex mine wastes it has been demonstrated that selection of mycorrhiza and addition of bark compost was a successful combination (Sjöberg et al. 2014). It sustained the germination and growth of *Agrostis capillaris* var. *metallica* on the nutrient poor and highly toxic historic sulphidic mine waste from Ljusnarsberg, Sweden (Karlsson et al. 2012). In these experiments the acidic pore water had high concentrations of notably copper, zinc, and lead. The concentrations were high enough to prevent the growth of all tested plant species, including the *A. capillaris* in the absence of the correct strain of mycorrhiza.

Here we report on the extension of the study with focus on the same elements but at circumneutral pH with the flotation waste from Zelazny Most in Poland. This material also allows to include arsenic and barium in the study. The tailings comes mainly from the

processing of ore from the Rudna mines and has a different origin and mineral composition than the historic sulphidic waste previously studied, although some features are similar. In both wastes the polluting elements are originally found as sulphides in the Polish tailings that originates from Kupferschiefer (Kucha 1990, Sawlowicz 1990, Oszczepalski 1999), while skarns dominate on the Swedish site. Further, the leachates from both the Zelazny Most impoundment (Lasocki et al. 2003) as well as the Ljusnarsberg waste site are rich in trace metals and have a circumneutral pH, but there are differences as well. The Zelazny Most impoundment is one of the largest in the world and its potential environmental impact has been discussed by several studies (Duda 2004, Baran et al. 2013) while the Ljusnarsbergs site only has a local impact.

An initial study on solid speciation and bioavailable toxic elements in tailings from the Zelazny Most was made before any plant experiments began. Principal mineral forming metals were also included. The characterization followed the geochemical characterization scheme presented by Tessier et al. (1979) but was performed in batch instead of the sequential procedure in the original scheme.

### **Materials and methods**

All chemicals that were used were of reagent grade or better. The 18.2 M·Ω water was produced by a central purification unit and the nitric acid by sub boil distillation of reagent grade acid.

Tailings from Zelazny Most were sampled and transported to the laboratory in closed barrels. Upon arrival the material was sieved (0.56 mm) and then subjected to the treatment below. A portion of the sifted sample was dried at 105 °C and then leached with concentrated nitric acid in a microwave oven. This treatment is referred to as acid leachable in the following text. The different treatments are arbitrary named after the operationally released metal forms rather than thermodynamically defined species. All extractions were made in triplicate at a solid solution ratio of 10:1. The extracts were filtered (0.20 μm) and acidified to 1% HNO<sub>3</sub> immediately after the extraction. Appropriate dilutions for ICP-MS analysis were made with 1% HNO<sub>3</sub>.

*Water soluble* – Extraction with 18.2 M·Ω water for 24 hours at room temperature on a rotary tumbler.

*Ion-exchangeable* – 1.0 M NH<sub>4</sub>Ac at pH 7.0 at room temperature for 5 hours with intermittent shaking.

*Carbonates* – 1.0 M NH<sub>4</sub>Ac at pH 5.0 (adjusted with HNO<sub>3</sub>) at 90 °C for 5 hours with intermittent shaking.

*Hydrous oxides* – 0.04 M NH<sub>2</sub>OH-HCl in 25% HAc at 90 °C for 5 hours with intermittent shaking.

*Organics and amorphous sulphides* – 0.02 M HNO<sub>3</sub> + 30% H<sub>2</sub>O<sub>2</sub> (3:5 v/v) at pH 2 (adjusted with HNO<sub>3</sub>) at 85 °C for 3 hours followed by addition of 3.2 NH<sub>4</sub>Ac in HNO<sub>3</sub> (20%) + double volume 18.2 M·Ω water.

Metal analysis was made with an Agilent 7500cx ICP-MS that was equipped with a MicroMist nebulizer and a Scott type double pass spray chamber. The spray chamber temperature was kept at 2 °C to minimize formation of oxides. An internal standard of <sup>103</sup>Rh was added manually to all solutions to give a concentration of 10 μg/L. The following isotopes were used: <sup>111</sup>Cd, <sup>63</sup>Cu, <sup>206+207+208</sup>Pb and <sup>66</sup>Zn. The octopole reaction cell was

operated in collision mode for the quantification of  $^{75}\text{As}$ . For that element the cell conditions were set to a flow of He at 5 ml/min with octopole RF and Bias parameters at 180 V and -20 V, respectively.

## Results and discussion

The leachability of the principal mineral forming elements is presented in Figure 1. It is evident that aluminium is mainly released by the acid leaching with an average of 7200 mg/kg. Less than 1% was released in the reductive treatment which would indicate a coprecipitation with mainly iron secondary mineral phases. Less than 0.01% was plant available, using the carbonate fraction as proxy. An average of 46% of the acid leachable iron at 2400 mg/kg was released in the reductive treatment, while water extractable and ion-exchangeable were negligible, which is a clear indication that hydrous oxides were present. This is not too surprising considering that the tailings had been exposed to air and that the pH was 8.2 in the water extracts. Manganese had a more complex extraction pattern. An average of 700 mg/kg was found in the acid leaching, 6% was released in the carbonate fraction, although 92% was extracted in the reductive treatment. Just as for iron there are reasons to expect the presence of ion-exchangeable, carbonate and hydrous oxide manganese species. The water leachable fraction was below 0.1%. Acid leachable calcium was on average 6600 mg/kg, which is expected considering the composition of the ore and the extraction process. As much as 63% of the inventory was released in the water extraction and an additional 20% in the ion-exchangeable. There was a quantitative release in the carbonate extraction step. High acid leachable amounts of Na (300 mg/kg), K (3200 mg/kg) and Mg (14200 mg/kg) were also found but with different availabilities to plants (carbonate fraction) with 100% Na, 1.5% K, and 1% Mg.

The acid leachable concentrations reported here support the data presented by Duda (2004) and Baran et al. (2013), where the latter study found 2600 mg/kg Fe and 540 mg/kg Mn. Baran et al. (2013) also reported that 86% and 25% of Mn and Fe, respectively, were mobilized when the tailings were extracted with 1.0 M HCl. There is a close correspondence with our results for Mn, but Fe differs. Ferric hydrous oxides are partly soluble in 1.0 M HCl but since our reductive treatment released almost double the amount, the results further support the presence of ferric hydrous oxides. Hence, the characterization of the tailings shows that plant species would have to tolerate high concentrations of Na and Ca, in addition to the very high Cl concentrations reported by Baran et al. (2013). The potential of mobilization of Fe and Mn under reducing conditions must also be considered.

The trace elements in the present study (Table 1) were dominated by copper that reached 1772 mg/kg in the acid leaching. The quantitative order for the others in this treatment were: Ba (972 mg/kg) > Pb (358 mg/kg) > As (287 mg/kg) > Zn (53.6 mg/kg). All trace metals have rather low extractability in water but their plant availability (carbonate fraction) is very high for Cu (67%), but is also quite high for Pb (23%) and Zn (37%). For Ba and As the fraction was 0.3% and 0.6%, respectively. It is noteworthy that the reductive treatment mobilized As (10%), Zn (88%), and the whole inventory of Pb while the increase for Cu was negligible in comparison with ion-exchangeable and carbonate fractions.

In our samples the trace metal contents that were released in the acid treatment are lower than the values reported by Baran et al. (2013). This might be related to different methods for sample preparation since Baran et al. (2013) used a more aggressive acid mixture for digestion. However, the total concentrations of trace metals in combination with their extractability found in this study show that the plant species must be highly tolerant to copper. In addition, if the system becomes anaerobic the leachability of all elements except Ba

increases. Hence, in order to establish a sustainable plant cover it is essential to control the redox potential of the system and the impact from heterotrophic activity and water logging.

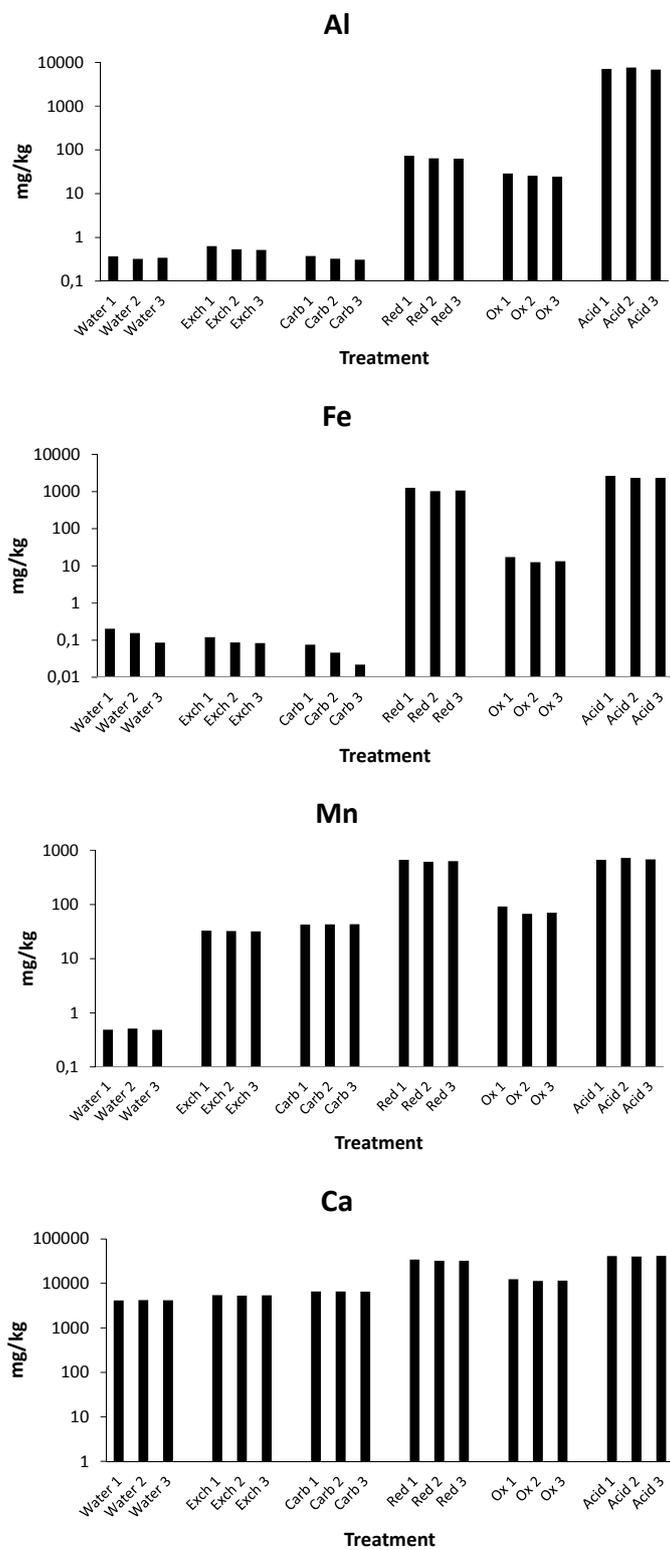


Fig. 1 Concentration (mg/kg) of some dominating mineral forming elements in each sample.

**Table 1** Extracted amounts and the relative standard deviation (RSD).

	As (mg/kg)	RSD (%)	Ba (mg/kg)	RSD (%)	Cu (mg/kg)	RSD (%)	Pb (mg/kg)	RSD (%)	Zn (mg/kg)	RSD (%)
Water	0.32	38	0.07	25	0.09	12	0.04	3.5	0.12	11
Ion exch.	0.28	7.4	6.8	0.4	1167	0.8	82.9	2.5	19.9	0.9
Carbonates	1.81	5.8	7.2	1.3	1195	0.6	82.8	2.8	19.8	0.9
Reducible	29.1	11.8	2.9	6.0	1214	15	358	22	47.2	15
Oxidizable	3.0	9.6	35.5	9.5	1720	9.9	172	12	32.4	8.9
Acid leach.	287	9.0	972	2.9	1772	1.2	358	4.0	53.6	3.8

## Conclusions

This study has demonstrated that both the acid leachable fractions of principal and trace metals are important for the establishment of plants on the tailings. The plant species must tolerate very high accessibility of primary metals, notably Na and Ca, as well as Cu. Reducing conditions must be avoided because of increased leachability of Fe and Mn but also As, Pb, and Zn.

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## References

- Baran A, Sliwka M, Lis M (2013) Selected properties of flotation tailings wastes deposited in the Gilow and Zelazny Most wastes reservoirs regarding their potential environmental management. *Arch. Min. Sci.* 58(3): 969-978
- Duda R. (2004) Regional prediction of the transport of contaminants from the flotation tailings dam: a case study. In: Twardowska, Allen, Kettrup and Lacy (Eds) *Solid Waste: Assessment, Monitoring and Remediation*. Elsevier, p693-715
- Karlsson S, Sjöberg V, Grandin A, Allard B (2012) Revegetation of historic mine waste with *Agrostis capillaris* – Impact on leachate composition in pot experiments. In: McCullough CD, Lund MA, Wyse L (Eds), *International Mine Water Symposium*, Bunbury, Australia, p 489-497
- Kucha C (1990) Geochemistry of the Kupferschiefer, Poland. *Geologische Rundschau* 79(2):387-399
- Lasocki S, Antoniuk J, Moscicki J (2003) Environmental protection problems in the vicinity of the Zelazny Most flotation wastes depository in Poland. *J. Environ. Sci. Health, Part A*, A38(8):1435-1443
- Oszczepalski S (1999) Origin of the Kupferschiefer polymetallic mineralization in Poland. *Mineralium Deposita* 34: 599-613
- Sawlowicz Z (1990) Primary copper sulphides from the Kupferschiefer, Poland. *Mineral. Deposita* 25:262-271
- Sjöberg V, Karlsson S, Grandin A, Allard B (2014) Conditioning sulfidic mine waste for growth of *Agrostis capillaris* – impact on solution chemistry. *Environmental Science and Pollution Research* (In press)
- Tessier A, Campbell PGC, Bisson M (1979) Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry* 51:844-851
- Turnau K, Anielska T, Ryszka P, Gawroński S, Ostachowicz B, Jurkiewicz A (2008) Establishment of arbuscular mycorrhizal plants originating from xerothermic grassland on heavy metal rich industrial wastes – new solutions for waste revegetation. *Plant Soil* 305(1-2):267-280