Weathering of metallurgical slags exposed to rhizosphere conditions

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Abstract. Metallurgical slags disposed in the vicinity of historical industrial centers are the reason of environmental concern due to the potential release of the elements including toxic ones. This study addresses the impact of organic acids rich root exudates on the weathering of copper metallurgical slags. The simulation was made to reflect conditions encountered in the field and to assess the potential environmental risk associated with disposal of these wastes.

Keywords: rhizosphere, root exudates, metallurgical slags

1. Introduction

Metal mining and processing entail generation of solid wastes including slags, ashes, waste rocks (Piatak *et al*. 2015). Metallurgical slags are essential in terms of production volume and high residual content of metal(loid)s (Potysz *et al*. 2015). The slags are currently classified as potentially hazardous wastes and sustainable waste management requires appropriate handling of these industrial residues. That is contrary to the past when environmental-safe waste management concept has not yet been appropriately defined and industrial wastes have often been disposed of without right precautions. As the result, the existence of formerly created dumping sites is a case of numerous historical industrial centers around the world (Ettler *et al*. 2000; Lottermosser 2002; Piatak and Seal 2010; Kierczak *et al*. 2013; Potysz *et al*. 2016a).

The lack of physical barriers isolating the wastes from the surrounding environment caused that weathering processes have not been prevented. The work of various weathering factors including pH variations, content and type of organic matter, activity of microorganisms and plant exudation may have deteriorative effect on slag phase constituents (synthetic equivalents of minerals) (Potysz *et al*. 2016b). The latter may release toxic elements into surroundings. The leachate effluent charged in metallic elements can migrate downward and sideward soil profile and consequently may reach other environmental components including sediments, ground and surface waters. Therefore, environmental risk assessment and development of remediation strategies on historical disposal sites receive the relevant attention of scientific communities (Tyszka *et al*. 2014; Ettler *et al*. 2015; Potysz *et al*. 2017).

The main objective of this study was to evaluate the geochemical stability of two types of copper metallurgical slags landfilled in Poland. The laboratory tests were designed to simulate rhizosphere-like conditions and the slags were exposed to organic rich artificial root exudates and organic free solutions.

2. Material and methods

2.1. Materials

The metallurgical slags selected for this study originate from historical copper processing that has long ago been held in Lower Silesia District in Poland. The materials display different structural (crystalline and amorphous) and chemical properties (Table 1).

2.2. Experimental approach

The 30 days long leaching experiments were carried out by putting 2.5 grams of 1-2 mm slag particles into drilled (0.5 mm pore size) polypropylene tube following its immersion in the respective 100 mL solution such that liquid to solid ratio (40) was kept constant throughout the experiment. The four leaching solutions were used: i) artificial root exudates fixed at pH t_0=3.5 (ARE 3.5), ii) acidified demineralized water adjusted to pH t_0=3.5 (DW 3.5), iii) artificial root exudates fixed at pH t_0=6.7 (ARE 6.7) and iv) demineralized water (DW) without pH adjustment. The artificial root exudates solution was composed of sugars (glucose, fructose and sucrose) and organic acids (citric, lactic and succinic acid).

The reactors worked in a semi-open flow through mode. Every 5 days weathering solution was replaced by the fresh corresponding medium. The slags and used glasswares were sterilized at 121°C for 15 minutes, whereas solutions were sterilized by filtration using polyethersulfone (PES) 0.45 μm filters. The reason for maintenance of sterile conditions was to eliminate the effect of microbial activity on slag alteration and to avoid organic acids degradation. The bottles were wrapped up with aluminum foil in order to maintain dark condition.

2.3. Analytical measurements

The elemental composition of the solutions resulting from each sampling point was determined by inductively coupled plasma atomic mass spectrometry (ICP-MS Nexion 300D Perkin Elmer). Characterization of experimentally weathered slags was performed using (JEOL JSM-IT100) coupled with an Energy Dispersive Spectrometer (EDS) at high vacuum 15-20 kV working mode.

3. Results

The laboratory simulation of the slags weathering in the rhizosphere revealed that these wastes are susceptible to dissolution in the presence of organic rich and organic free solutions. Artificial root exudates (pH t_0=3.5) were found to enhance element release relative to DW (pH 3.5) . For example, the Cu release was even 429 times higher in ARE 3.5 solution as compared to DW 3.5. The slag dissolution was generally lower under exposure to near-neutral (pH t_0=6.7) conditions as compared to acidic (pH t_0=3.5) conditions. Exceptionally, Cu that was released in a higher quantities when slags were exposed to ARE 6.7 compared to acidic DW 3.5. Furthermore, the slags exposure to near-neutral organic rich conditions (ARE 6.7) amplified Cu release by the factor up to 87 relative to corresponding organic free DW. Scanning electron microscopic observations demonstrated greater weathering features on mineral phase components of the slags resulting from acidic weathering. That is in accordance with solution chemistry having higher concentrations of elements in acidic solutions as compared to the near-neutral ones. The quantitative comparison made based on relative values of leached elements, has demonstrated that metal-bearing phases are more prone to dissolution as compared to silicates (*e.g.* glass). Additionally, a comparison made on the slags themselves has shown that amorphous slag is more prone to dissolution as compared to crystalline slag.

4. Conclusions and perspectives

As the result of this study, we conclude that copper metallurgical slags are susceptible to dissolution under exposure to rhizosphere-like conditions. Acidic conditions strongly affected the stability of mineral phases which resulted in a high release of elements, including toxic ones. Near-neutral conditions affected the slags stability to the much lower extent. The pH is an important factor governing slag dissolution, however the presence of organic rich root exudates clearly escalates the weathering process.

The main perspective stemming from this work is the use of naturally-derived root exudates as weathering agents as well as including the plants in a laboratory weathering system. The aim is to estimate a counterbalance between the metals released from the slags and these uptaken by the plants.

Table 1. Chemical composition of the metallurgical slags.

Metallurgical slag	
Type 1: Crystalline slag (CS)	Type 2: Amorphous slag (AS)
Si: 22.6 wt.%	Si: 21.7 wt.%
Fe: 9.41 wt.%	Fe: 3.3 wt.%
Cu: 7330 mg/kg	Cu: > 4060 mg/kg
Zn: 587 mg/kg	Zn: 164 mg/kg
Pb: 53.3 mg/kg	Pb: 59.4 mg/kg

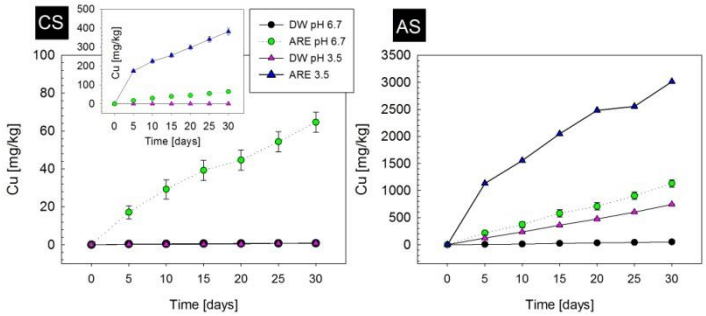

Figure 1. The cumulative release of elements from the slags exposed to different weathering conditions.

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