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Metal mobilization from metallurgical wastes by soil organic acids

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HIGHLIGHTS

- Organic acids enhance metallurgical wastes dissolution.
- Artificial root exudates have a higher impact on metal release than humic/fulvic acids.
- Slags susceptibility to weathering depends on their chemistry and mineralogy.

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ABSTRACT

Three types of Cu-slags differing in chemical and mineralogical composition (historical, shaft furnace, and granulated slags) and a matte from a lead recovery process were studied with respect to their susceptibility to release Cu, Zn and Pb upon exposure to organic acids commonly encountered in soil environments. Leaching experiments (24–960 h) were conducted with: i) humic acid (20 mg/L) at pH $t_0 = 4.4$, ii) fulvic acid (20 mg/L) at pH $t_0 = 4.4$, iii) an artificial root exudates (ARE) (17.4 g/L) solution at pH $t_0 = 4.4$, iv) ARE solution at pH $t_0 = 2.9$ and v) ultrapure water (pH $t_0 = 5.6$). The results demonstrated that the ARE contribute the most to the mobilization of metals from all the wastes analyzed, regardless of the initial pH of the solution. For example, up to 14%, 30%, 24% and 5% of Cu is released within 960 h from historical, shaft furnace, granulated slags and lead matte, respectively, when exposed to the artificial root exudates solution (pH 2.9). Humic and fulvic acids were found to have a higher impact on granulated and shaft furnace slags as compared to the ultrapure water control and increased the release of metals by a factor up to 37.5 (Pb) and 20.5 (Cu) for granulated and shaft furnace slags, respectively. Humic and fulvic acids amplified the mobilization of metals by a maximal factor of 13.6 (Pb) and 12.1 (Pb) for historical slag and lead matte, respectively. The studied organic compounds contributed to different release rates of metallic contaminants from individual metallurgical wastes under the conditions tested.

1. Introduction

Copper is an essential metal for human civilization since ancient times and remains indispensable for modern day culture. Therefore, its pyrometallurgical processing is currently well developed worldwide (Radetzki, 2009). The smelting industry generates wastes that are unavoidable even at a very high level of process efficiency. Slags are important by-products in terms of production volume and the residual metal content that results from smelting process losses (Ettler et al., 2009; Fernández-Caliani et al., 2012; Potysz et al., 2015). Currently Cu-slags are used for civil and hydraulic engineering applications (Shi et al., 2008; Schmukat et al., 2012). However, appropriate metallurgical waste management and environmental risk assessment require the evaluation of the potential release of metallic contaminants from the wastes (Schmukat et al., 2013).

Due to lack of environmental awareness in the past, slags were

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considered to be non-hazardous materials and their “life cycle” was limited to two stages: production and disposal. A long-term exposure of these wastes to weathering leads to mobilization of metals and undesirable effects on soil, sediment and water such as contamination which is experienced nowadays (*e.g.* Manz and Castro, 1997; Sobanska et al., 2000; Parsons et al., 2001; Lottermoser, 2002; Ettler et al., 2004; Piatak et al., 2004; Kierczak et al., 2013). In spite of playing essential biological functions, metals can accumulate in living organisms (*e.g.* plants) or even have a toxicological effect if concentrations exceed toxicity thresholds (Nederlof et al., 1993; Stobrawa and Lorenc-Plucińska, 2008). Furthermore, the transfer of metals to soil or surface water and their subsequent passage into the higher levels of the food chain is of a great concern too. For this reason, an evaluation of slags weathering and metal release under different environmental conditions/scenarios is important for existing dumping sites at which remediation operations might be of strong need in order to comply with regulatory requirements of environmental quality.

Soluble organic acids in soils represent a large spectrum of polymers consisting of specific low- and high-molecular weight compounds varying in chemical composition, aromaticity and functional groups (Chin et al., 1994; Fu et al., 2006; Sposito, 2008; Güngör and Bekbölet, 2010). Soluble organic acids directly and/or indirectly affect the weathering rate of minerals. By adsorption onto mineral surfaces, formation of aqueous complexes with dissolving cations or changing the solution pH, organic acids influence the thermodynamic equilibrium and/or weaken the chemical bounds of the dissolving mineral structure (Welch and Ullman, 1993; Drever and Stillings, 1997; Oelkers and Schott, 1998; Jahnson et al., 2005; Li et al., 2006; Ganor et al., 2009; Lawrence et al., 2014). Furthermore, proton release from the functional groups (*e.g.* −COOH) of organic molecules creates negative charges and thus binding sites exhibiting a high complexation affinity towards cations. Moreover, metal complexation with dissolved organic compounds controls metal speciation, toxicity and bioavailability as well as facilitates its migration or transport (Rashid, 1971; Hinsinger, 2001; Renella et al., 2004; Bravin et al., 2012; Mostofa et al., 2013).

The predominant inputs of soluble organic acids to the soil environment are decaying plants, microbial decomposition products as well as roots exudates (Jones, 1998; Wu et al., 2002), even if some organic compounds may be deposited onto the soil by winds or rainwater (Millet et al., 1997). The most common components of soluble organic acids are humic substances (humic and fulvic acids), although other biomolecules including lipids, amino acids, organic acids and carbohydrates are frequently present as well (Jones and Darrah, 1994). According to the recent concept concerning soil organic matter, humic substances are not large molecules, but aggregates of small molecules (Schmidt et al., 2011; Lehmann and Kleber, 2015). Furthermore, alkali-derived soil organic extracts are considered to be more reactive than truly existing humic and fulvic fractions present in the natural soils. Additionally, these extracts may not include the complete assembly of the molecules that belong to humic substances occurring in a soil (Schmidt et al., 2011; Lehmann and Kleber, 2015).

In the majority of soils, the highest concentrations of organic compounds are found in a near surface soil horizon and particularly in the rhizosphere (Drever and Vance, 1994; van Hees et al., 2000; Degryse et al., 2008). Non-humified organic acids in soils are typically present at micro-molar concentrations, however milli-molar ranges have been reported as well. The content might vary depending on the plant species and their age as well as the soil type and environmental conditions (*e.g.* moisture content) (Jones, 1998; Strobel, 2001). Humic substances usually contribute to 75–80% of the dissolved organic matter in soils and originate from the transformation (humification) of various organic compounds (Pettit, 2004). Thus, slag weathering enhanced by humic substances and root exudates is especially relevant because disposed slags are often in direct contact with soil. Moreover, the vegetation cover developing on a dump surface might not only serve as protective layer minimizing erosion (Roy et al., 2002), but may also supply organic compounds derived from root exudation (Bunzl et al., 2001; Houben et al., 2013). Fig. 1 presents a possible weathering scenario which may be encountered in soil and rhizosphere environments, underlining the potential metal mobilization by soil organics.

Soluble organic acids affect even highly insoluble mineral phases such as silicates (*e.g.* fayalite, diopside) (Jones and Darrah, 1994; Bennett, 1991; Cama and Ganor, 2006). The interactions of organic compounds with silicate minerals may enhance their weathering due to intensification of Si—O—Si bond cleavage (Bennett, 1991). The disturbance of metal bearing mineral phases might result in the release of important quantities of elements including toxic ones (Baker, 1973). In turn, plant uptake of metals in excess might lead to (i) H^+ exudation as charge balancing reaction, enhancing local acidification (Dakora and Phillips, 2002) or (ii) metal transfer

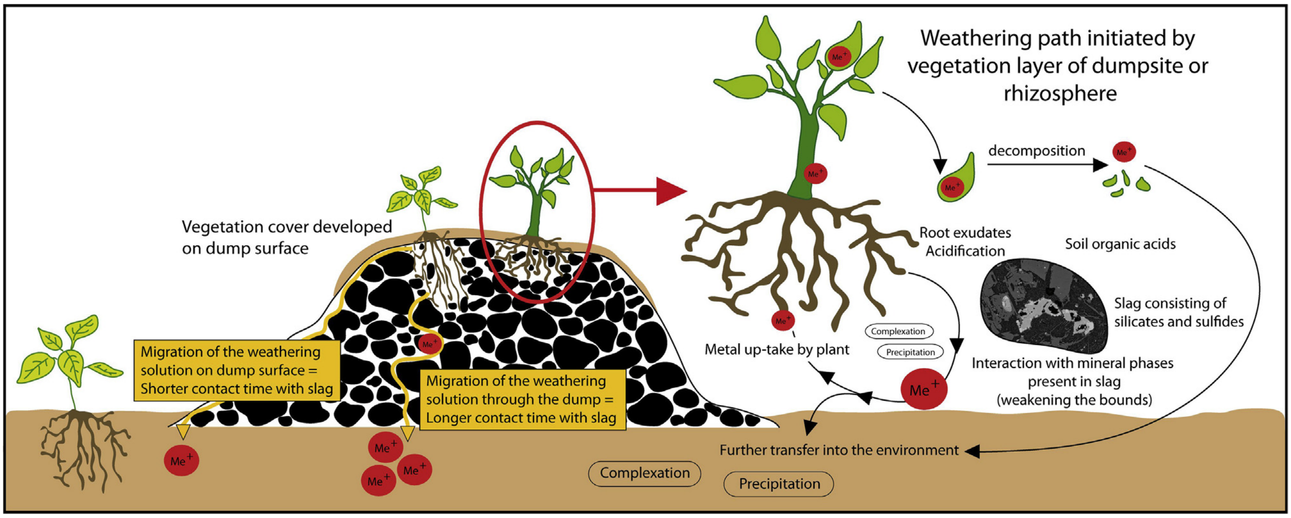

Fig. 1. Weathering processes that may occur at slag dumping sites.