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Bacterially-mediated weathering of crystalline and amorphous Cu-slags

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Two types of Cu-slags (CS: crystalline massive slag and GS: granulated amorphous slag) exhibiting a different chemical and mineral phase composition were compared with respect to their susceptibility to bacterial weathering using *Pseudomonas aeruginosa* (n° CIP 105094). Abiotic conditions *e.g.* sterile growth medium and ultrapure water were used for comparison. The experiments were extended up to 112 days with a systematic liquid phase renewal every 14 days. The results revealed significant release of elements in the bacterially mediated weathering experiments. Concentrations of elements (Si, Fe, Cu, Zn and Pb) in the biotic solutions were increased at least by 20% up to 99% compared to abiotic ones. From 3 to 77% of the leached elements were associated to the fraction >0.22 μm. Scanning electron microscope observations demonstrated greater weathering of mineral phases in biotic experiments than in abiotic ones which is in accordance with the solution chemistry exhibiting higher concentrations of elements leached in biotic set-ups. In the case of CS, glass and sulfides weathering was yet observed in abiotic experiment, whereas partial dissolution of fayalite (Fe_2SiO_4) was solely affected by the presence of bacteria. GS having a higher bulk content of metallic elements was found to be more stable than sulfide-bearing CS, while its (GS) glass matrix was found to weather easier under biotic conditions.

1. Introduction

Copper pyrometallurgical slags constitute important by-products with respect to their volume of production and high residual content of metallic elements depending on the ore origin and characteristic of the industrial process. Due to a lack of sustainable practices in the past, slags disposal has been a common manner, regardless of the weathering and its potential environmental consequences. As a result, there are many industrial areas where slags have been proven to be a source of metallic pollution of the surrounding soils, sediments, and surface waters (*e.g.* Gee et al., 1997; Manz and Castro, 1997; Sobanska et al., 2000; Parsons et al., 2001; Lottermoser, 2002; Ettler et al., 2003; Piatak et al., 2004; Kierczak et al., 2013; Ettler and Johan, 2014). At present, Cu-slags are often used as secondary raw materials, for example in coastal engineering in north Germany (Schmukat et al., 2012). However, some studies pointed out that such application of Cu-slags could lead to deleterious consequences for the environment (Schmukat et al., 2012). Consequently, slags weathering has gained essential importance for environmental reasons. However, most studies regarding slags weathering have focused on physico-chemical aspects of the process (*e.g.* Sobanska et al., 2000; Parsons et al., 2001; Ettler et al., 2004; Seignez et al., 2006; Kierczak et al., 2009; Tyszka et al., 2014), whereas impact of microbial activity is often neglected and very few publications concerning this issue could be found in the literature (Yin et al., 2014; van Hullebusch et al., 2015).

Bio-weathering is a natural process occurring on the mineral and rock surfaces as the result of various metabolic actions of microbial inhabitants (*e.g.* bacteria, fungi) of the environment (Ehrlich, 1998; Brandl and Faramarzi, 2006; Gadd, 2007). Microbial-mediated weathering is known to enhance mineral dissolution through redox reactions, excretion of inorganic and organic acids as well as complexing compounds (White et al., 1995; Brandl and Faramarzi, 2006; Uroz et al., 2009; Gadd, 2010). Due to local changes of

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solution chemistry (pH and Eh), the mineral surface may be disturbed by the release of cationic constituents from the mineral lattice, consequently facilitating its further tendency to breakdown. Such a process is often initiated by microbial attachment to the solid surface and may be driven by nutrient requirements of microbial consortia. For example, under oxic conditions, many bacteria (*e.g. Rahnella* sp., *Pseudomonas* sp., *Bacillus sp.*) produce iron-scavenging compounds, so-called siderophores, as the response to iron starvation conditions (Oulkadi et al., 2014; Ahmed and Holmström, 2014). Then, Fe-bearing mineral phases might be a potential iron source targeted by microorganisms (Konhauser et al., 2011). Furthermore, microbial attachment to the mineral surface tends to form a biofilm composed of bacterial cell assemblages surrounded by an extracellular polymeric matrix (Wingender et al., 1999). Biofilm increases the microbial density and/or the concentration of weathering agents and thus enhances weathering of the mineral surface. On the other hand, extracellular polymeric substances (EPS) associated with biofilm can entrap mobilized elements due to the presence of various binding sites such as: carboxyl, hydroxyl, amino functional groups (Guibaud et al., 2008; Comte et al., 2006; Fein, 2006; Pal and Paul, 2008; Tourney and Ngwenya, 2014; van Hullebusch et al., 2015). Additionally, the microorganisms may assist in immobilization of elements due to sequestering activity (*e.g.* biosorption, bioaccumulation, biomineralization) and may show great resistance towards metals govern by *e.g.* efflux transport, sequestration in the cytosol, and chelation of metals outside the cell (Haferburg and Kothe, 2007; Gadd, 2010).

The weathering conditions encountered in the slag landfill environment are site-specific and might vary considerably depending on local bio-hydro-climatic conditions. Those encompass a broad array of issues such as frequency of rainfall, humidity level, temperature, pH conditions, content and quality of organic matter as well as microbial diversity that collectively determine weathering situation (Potysz et al., 2015a). Since the microorganisms are known to contribute substantially or even escalate the strength of mineral weathering, a number of exhaustive studies have been devoted to the isolation, characterization and potential application of organisms hosted at dumping sites. Male et al. (1997) showed the ability of *Acidithiobacillus ferrooxidans, Acidithiobacillus thiooxidans, and Thiobacillus thioparus* to grow on Cu/Ni slag and noted that the slag might serve as source supporting growth of the isolates. Schippers et al. (2002) characterized the indigenous bacterium *Nocardiopsis metallicus* sp. from alkaline slag dump and highlighted the significance of bacteria in metal mobilization. Willscher and Bosecker (2003) isolated heterotrophic microorganisms such as a *Arthrobacter oxydans*, *Microbacterium* sp. and *Dietzia natronolimnaea*, *Promicromonospora* sp., *Pseudonocardia autotrophica, Nocardiopsis metallicus* and observed good performance of those isolates in terms of bioleaching activity. Likewise, Cheng et al. (2009) reported the presence of *Bacillus* spp., *Sporosarcina* spp., and *Pseudomonas* spp. associated with a Pb/Zn slag dump. Isolates were examined with respect to their ability to extract metals from slags and were found to carry out the process efficiently. Pandey et al. (2010, 2011) demonstrated the occurrence of As and Pb tolerant bacteria which belong to *Bacillus* sp. and Cd resistant bacteria *Ochrobactrum* sp. At present, the composition of the microflora of dumping sites is not exactly determined. However, the environment of mining and industrial sites provides a unique habitat for microbial life. This environment contains a variety of minerals and involves alteration processes which provide an important chemical gradient impacting the structure and functionality of microbial communities through the dumps. Thus, a variety of microorganisms affiliated to landfill areas and their potential in mobilization of metals in the field should be acknowledged.

Pseudomonas aeruginosa is recognized to be an ubiquitous heterotrophic bacteria in soil, water, air and plants (Stanley et al., 2007). Due to its abundance and well-established features, *P. aeruginosa* can be considered as environmental representative of bacteria appropriate for studying slag weathering. Numerous studies concerning the extent to which *Pseudomonas* sp. contributes to the weathering were implemented for a wide variety of solid materials such as metallurgical slags (Yin et al., 2014; van Hullebusch et al., 2015), glass (Aouad et al., 2006; Chen et al., 2014) and municipal solid waste incinerator bottom ash (Auoad et al., 2008). Authors demonstrated that bacteria accelerate the degradation of mineral phases and elements are released in both equilibrated and far from equilibrium conditions (Aouad et al., 2006; Yin et al., 2014; van Hullebusch et al., 2015).

Despite the fact that important progress has been made towards understanding the interactions of bacteria with solid materials, yet relatively little is known about the impact of bacteria on slags weathering, especially concerning the mobilization of metallic elements. In this regards, the aspect of slags bio-weathering has gained relevant interest in recent years.

The present study examined the role of *P. aeruginosa* on the weathering of two types of Cu-slags displaying different chemical and structural properties. The following research questions have been addressed: i) whether bacteria enhance bio-weathering of Cu-slags in a long term perspective, ii) whether bacteria can sorb mobilized metallic elements released from slags and iii) which mineral phases undergo weathering under exposure to biotic/abiotic conditions Experimental set-ups included biotic experiments with *P. aeruginosa* as well as abiotic experiments with sterile growth medium and ultrapure water.

2. Materials and methods

2.1. Copper slags

Two different types of Cu-slags, crystalline massive slag (CS) and granulated amorphous slag (GS), were selected for this study. Crystalline slag corresponds to historical slag, whereas granulated slag originates from modern-day copper production. Table 1 compares their chemical and mineralogical compositions and more detailed information concerning their characteristics is given elsewhere (Potysz et al., 2015b).

2.2. Experimental approach

All incubations were performed according to the same protocol.

Table 1
Chemical and mineralogical features of Cu-slags (Potysz et al., 2015b).

	Crystalline Cu-slag (CS)	Granulated Cu-slag (GS)
Bulk chemical composition		
Major compounds (wt.%)		
Si	17.6	15.2
Fe	35.5	11.5
Metallic elements (mg/kg)		
Cu	5657	11425
Zn	3962	7810
Pb	111	21135
Structure		
Crystalline		Amorphous
Mineral phases: *(++ major, + minor, (+) traces)*		
• Fayalite ($Fe^{2+}{}_2SiO_4$) ++		• Glass ++
• Glass ++		• Metallic Cu-droplets +
• Bornite (Cu_5FeS_4) +		
• Chalcopyrite ($CuFeS_2$) (+)		
• Pyrrhotite ($Fe_{(x-1)}S$) +		