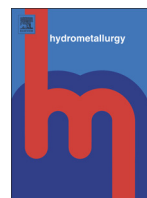




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Metal biorecovery in acid solutions from a copper smelter slag

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ABSTRACT

Slags from metallurgical processes represent a potential resource of metals but also waste materials that have not been successfully beneficiated to date. For this study, a bulk slag sample from a copper smelter was evaluated under chemical and bacterial leaching conditions to test the solubilization of Cu and Zn in acidic, sulfate-rich solutions. Fayalite, magnetite and glassy silicates as well as Cu-sulfides and sphalerite were the major phases of the slag. The acid demand of the slag was satisfied with a 24 h contact time with sulfuric acid. A mixed mesophilic culture capable of oxidizing iron and sulfur and dominated by *Acidithiobacillus thiooxidans*, *A. ferrooxidans*, and *Leptospirillum ferriphilum* was used for bioleaching. The maximum extent of Zn leaching was 14%, contrasted with 83% Cu in experiments with an initial pH of 2.1–2.2, 10% pulp density, 10 g L⁻¹ S⁰ addition, 5% inoculum, and 25 d contact time. Biological S⁰ oxidation was an important source of acid in bioleaching experiments. Ferric iron did not enhance the solubilization of Cu and Zn appreciably.

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1. Introduction

Reclamation of metals from slag materials has been of interest for waste management purposes as well as for resource recovery. In the absence of sustainable technology of large-scale processing of slag waste streams, stockpiling in heaps and tailings is a common approach but is potentially riddled with environmental problems due to stormwater, wind and dust and accidental leakage of drainage water. The chemical and mineralogical composition of metallurgical slags vary considerably with the pyrometallurgical process and the mineral concentrate (Shen and Forsberg, 2003; Balakrishnan et al., 2014; Piatak et al., 2015). Approaches to slag processing for recovering metals have included chemical treatment systems such as dissolution with sulfuric acid, ferric sulfate, hydrochloric acid, ferric chloride, potassium dichromate, chlorate, and hydrogen peroxide (Zhang et al., 2010; Muravyov et al., 2012; Balakrishnan et al., 2014; Cappuyns et al., 2014; Piatak et al., 2015). For smelter slags, acid solutions are required for metal solubilization and the oxidant demand is quite variable. While the treatment efficiency can be upgraded by process adjustments, none of the chemical treatments can justify the economic aspects of the treatment. Use of

slag materials in construction materials and landscaping is also possible (Sánchez et al., 2004; González et al., 2005; Tossavainen, 2005; Gahan et al., 2009; Lee and Pandey, 2012) but seems to represent a very minor fraction in the slag management.

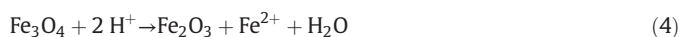
Pyrometallurgical processing of mineral concentrates leads to the formation of fayalite (2FeO·SiO₂, also represented as Fe₂SiO₄) and various other silicate phases as well as Fe-oxides and altered sulfide minerals. The dissolution of fayalite requires an acidic solution but the dissolution is not a redox reaction. Thus Fe³⁺ does not enhance the leaching of fayalite. Non-ferrous metals as well as trace metal impurities are usually distributed in multiple solid phases in slags, including oxides and sulfides, sometimes even elemental forms. As typical in other leaching processes, contact time, temperature, and decreasing particle size increase the extraction of metals from slags in acid solutions (Carranza et al., 2009a,b; Urosevic et al., 2015).

Low pH is one of the key parameters in slag dissolution. Acid demanding phases in slags include the formation of orthosilicic acid (H₄SiO₄) and metasilicic acid (H₂SiO₃) from fayalite (reactions 1–3) and hematite (Fe₂O₃) formation from magnetite (Fe₃O₄) (reaction 4) (Carranza et al., 2009b):



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Hematite is, however, usually formed at elevated temperatures including those in pressure leaching (Li et al. 2009) and its presence as an intermediate in magnetite dissolution or product of iron oxidation in sulfate-rich solutions at ambient temperatures is not clear.

Acid demand can be met in the bioleaching approach by the addition of appropriate reduced sulfur compounds that are oxidized to sulfuric acid (Vestola et al., 2010, 2012; Kaksonen et al., 2011). Elemental sulfur (S^0) is by far the most commonly used precursor to the biological formation of sulfuric acid. More recently, pyrite has been suggested as a source of lixiviant for the bioleaching of metal-containing waste materials (Bryan et al., 2015).

Microscopic fungi such as *Penicillium* and *Aspergillus* spp. have also been tested in slag leaching experiments (Sukla et al., 1992, 1995; Deng et al., 2013). Metals are dissolved due to organic acid production as part of fungal metabolism. Moreover, fungal mycelia sorb metals from the solution phase, which likely complicates the recovery because the metals are in two phases – dissolved in the solution and associated with the biomass. Biosorption of metals can be prevented if only the culture supernatant with organic acids is used. A two-stage biotreatment can also be envisaged: first, extraction of metals by supernatants containing organic acids produced by fungal fermentation, and second, sequestration of dissolved metals by fungal biomass recovered from the fermentation. The cost of processing and the handling, separation, and disposal of copious volumes of fungal cultures, supernatants, and biomass are not trivial in a large scale. Health risk due to exposure to fungal spores from mass cultures in air also increases with the scale. In general, fungi are not as resistant to dissolved metals if compared to acidophilic bacteria in bioleaching processes. In addition to fungi, heterotrophic bacteria (e.g., *Pseudomonas aeruginosa*) can also produce organic acids and sequester metals from slags (Cheng et al., 2009; Yin et al., 2014; Mirazimi et al., 2015) but their potential application for slag treatment is debatable.

A mixed culture of iron-oxidizing acidithiobacilli and *Alicyclobacillus* spp. was previously enriched from a smelter slag lagoon site and tested for the bioleaching of Cu and Zn from a smelter slag sample in a bioreactor system (Kaksonen et al., 2016). In the present study a mixed bacterial culture originally enriched from a polymetallic sulfide mine site was screened in shake flasks for the release of Cu and Zn from the slag matrix. The culture contained mesophilic Fe- and S-oxidizing bacteria and was dominated by *Acidithiobacillus thiooxidans*, *A. ferrooxidans*, and *Leptospirillum ferriphilum*. Chemical leaching of the slag sample in dilute sulfuric acid was used as a control system in efforts to estimate any incremental benefit from the use of bacterial cultures.

2. Materials and methods

2.1. Slag sample

The slag sample was collected from the copper flash smelting process at Boliden Harjavalta, Finland. Slag is formed as a by-product of sulfide concentrate smelting in a flash smelting furnace. Iron in the concentrate is oxidized in the process and fluxed with silica sand to form fayalite, $2\text{FeO} \cdot \text{SiO}_2$. Slag is periodically tapped into ladles where it slowly cools for approximately two days. Slow cooling enables the precipitation of valuable metals, and the growth of mineral crystals into recoverable size. After solidification and cooling, the slag is crushed, ground and treated at the slag concentrator. Copper bearing minerals are separated in the flotation cells. The slag concentrate containing the recovered metals is filtered and recycled back to the copper flash furnace. The remaining final slag tailings are discarded from the flotation

cells and stored in a dedicated tailings area at the Boliden-Harjavalta copper smelter plant.

For this study, a bulk sample of slag was collected from freshly produced final slag at the Boliden Harjavalta smelter. The sample was stored under water in a closed container at 4 °C to minimize air oxidation. An aliquot was dried at 105 °C to determine the water content in order to standardize the concentrations to dry weight basis. The particle size of the sample was 73% - 45 μm, with 45% within the 20–45 μm size fraction. Fe (40.9%) and SiO_2 (29.6%) accounted for approximately 70% of the chemical composition of the slag (Table 1). The distribution of Fe, Cu and Zn in various mineral phases of the untreated slag is shown in Fig. 1. Fayalite (48.8%) made up almost half of the matrix (Table 2), and fayalite and magnetite accounted for almost 95% of the total Fe carrier. Fe was also associated with glassy silicate phases (90% SiO_2 and the rest comprising Na-, K-, and Al-silicates). Some Cu- and Fe-arsenide grains and inclusions were also present. Zn was distributed in fayalite (58%), magnetite (20%), glassy silicates (16%) and sphalerite (6%). Cu was distributed in Fe-deficient Cu-sulfides (57%) and in fayalite (18%) and metallic Cu (16%), with minor amounts in glassy silicates and magnetite. The dominant Cu-sulfides were bornite and chalcocite. Metallic Cu was mostly in the +45 μm size fraction as free and occluded grains. The sample also contained 0.17% As, 0.05% Ni, 0.038% Co, and 0.17% C.

2.2. Test culture

A mesophilic bacterial consortium, designated PS, was used in the study. The consortium was originally enriched from water and sediment samples collected at the Pyhäsalmi Mine, in the south of Oulu Province, Finland. Based on analyses of 16S rRNA gene sequences, the consortium contained *A. thiooxidans*, *A. ferrooxidans*, and *L. ferriphilum* as the dominant bacteria (unpublished data). The culture was maintained in mineral salts solution containing (per liter): 0.5 g each of $(\text{NH}_4)_2\text{SO}_4$, K_2HPO_4 and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, acidified to pH 2.5 with sulfuric acid. Mineral salts solutions were supplemented with trace metals (Kaksonen et al., 2011) and 4.5 g $\text{Fe}^{2+} \text{L}^{-1}$ (added as $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and 10 g $\text{S}^0 \text{L}^{-1}$. The PS culture was incubated in shake flasks at 150 rpm and 27 °C.

2.3. Acid consumption

Immediate and 24 h acid consumption of the slag was measured at 5% pulp density at pH 2.0, 1.5, and 1.0. The slag sample was suspended in ultrapure H_2O and 1 M H_2SO_4 was added with a 719 S Titrimo titrator that was controlled with Metrohm TiNet 2.5 software.

2.4. Toxicity experiments

Initially, the potential toxicity of metals dissolved from the slag was tested by leaching 10% slag suspension chemically for 3 d at an initial pH of 1.0 in mineral salts solution, followed by filtration to remove the suspended solids. The filtrate was supplemented with 4.5 g $\text{L}^{-1} \text{Fe}^{2+}$, 10 g $\text{L}^{-1} \text{S}^0$, and 10 vol.% inoculum of the PS culture; initial pH was

Table 1
Partial elemental composition of the bulk smelter slag sample.

Element	Composition (%)
Fe	40.9
Zn	2.79
Cu	0.38
Ni	0.05
Co	0.038
As	0.16
Pb	0.60
Sb	0.04
S	0.14
SiO_2	29.6

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