



## Solid phase changes in chemically and biologically leached copper smelter slag



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### ABSTRACT

Pyrometallurgical processes for sulfide concentrates produce slag waste materials that contain multiple metals as carry-over impurities. Varied quantities of the metal content can be solubilized from the slag through chemical acid leaching or bioleaching. In this study, copper smelter slags were leached with and without iron- and sulfur-oxidizing bacteria in acid, sulfate-rich solutions and solid phase changes were determined. The samples (10% pulp density) were leached at 28 °C in stirred tanks at pH 2.5 and 3.0. The duration of the experiment was 37 d and the adjusted pH decreased to 2.3 in both sets of experiments. The primary metals of interest in the slag were Cu and Zn, with minor amounts of Ni and Co, and As, Sb, and Pb at trace levels. The metals in the slag were distributed in fayalite, glassy silicates and magnetite phases as well as minor amounts in oxides, metallic Cu and sulfides. Based on the solution analyses, the dissolution yields were 44% and 34% for Cu, 14% and 13% for Zn and Co, and 4.5% and 4.0% for Ni at initial pH values of 2.5 and 3.0, respectively. Fayalite was the most reactive mineral and Cu-sulfides were particularly refractory. The elemental composition of leached residues was matched with solid phase changes and the distribution of metals in the mineral phases.

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## 1. Introduction

Slags from smelting and other pyrometallurgical processes contain residues of the main metals as well as metal impurities originally present in the mineral concentrates. Slag waste management involves stockpiling in heaps or in tailings, and industrial uses of slag materials have been very limited to date although several applications have been proposed and tested with varying success and promise. Because copper smelters cannot recover the target metals quantitatively, chemical leaching of the residual metal content in smelter slags has been investigated quite extensively (Shen and Forssberg, 2003; Piatak et al., 2015; Potysz et al., 2015; Roy et al., 2016). Various chemical lixivants including strong oxidants and roasting at high temperatures have been tested for copper smelter slags in efforts to release residual metals and to lessen

the environmental impact during slag storage. Metal recovery from slag waste may produce revenue to help offset the cost of the process. The elemental and mineralogical content of slags vary with the ore and mineral processing as well as the smelting process (Schlesinger et al., 2011; Lee and Pandey, 2012; Panda et al., 2015; Piatak et al., 2015). For example, metallurgical slags from smelters are alkaline and not reactive in neutral environments. Their reactivity increases with acidity (Vítková et al., 2011; Ettler et al., 2016). Natural weathering processes may initiate alterations of the more susceptible phases as documented with slags from Pb-Zn smelters (Sobanska et al., 2016). Slags from Cu-, Ni-, and Zn-smelters may contain appreciable quantities of the main metals in addition to minor and trace impurities. In general, the acid demand can be prohibitively high for acid leaching and the oxidant demand must also be accounted for. Slags from steel production are relatively metal deficient, mostly comprising of Si and Al<sub>2</sub>O<sub>3</sub> from the ore, Ca- and Mg-oxides from the added flux, and dross (Gomes et al., 2016). Iron foundries produce slags that contain lime from the added flux and impurities. Thus there are great differences in the thermodynamic and chemical properties of slags and their reactivity in various solubilization tests (Stumpe et al., 2012;

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Engström et al., 2013; Piatak et al., 2015; Gomes et al., 2016). A requirement common to disposal of metallurgical slags is the compliance based on standard leaching tests using methods promulgated by national regulatory agencies, as outlined by Tiwari et al. (2015).

Fayalite, various other silicates, Fe-oxides and modified sulfide mineral phases are formed in pyrometallurgical processes for Cu-sulfides. Fayalite ( $\text{Fe}_2\text{SiO}_4$ , also written as  $2\text{FeO}\cdot\text{SiO}_2$ ) is an end member in the olivine group, which is relatively susceptible to weathering (Kobayashi et al., 2001; Mihailova and Mehandjiev, 2010). Substitution of Fe with Mg (e.g.,  $\text{Fe,MgSiO}_4$ ) is also common in this group. Fayalite dissolution occurs in acid solutions under oxygenated and anoxic conditions (Santelli et al., 2001).

For this study, a sample of copper smelter slag was leached under acidic, sulfate-rich conditions in the presence and absence of acidophilic bacteria. The yields for metal leaching reached 34–44% Cu, 13–14% Zn and 13–14% Co depending on the initial pH (Kaksonen et al., 2016). The bioleaching experiments employed a mixed culture of Fe- and S-oxidizing *Acidithiobacillus* and *Alicyclobacillus* spp. enriched from the slag lagoon site of the smelter (Kaksonen et al., 2016). The purpose of the present study was to examine changes in the solid phase of the slag before and after the contact with the leach solution and relate them to yields of metal dissolution and residual metals in leached solids.

## 2. Materials and methods

### 2.1. Slag sample description

The Boliden Harjavalta copper smelter uses a flash smelting and converter process to produce anode copper from Cu-sulfide concentrates. The slag that is formed in flash smelting furnace is lighter than the copper matte and rises to the surface. In the converter process, ground copper matte is converted to blister copper followed by fire refining for anode copper production. The slags from the flash furnace and converter processes are cooled, crushed, ground and Cu-bearing particles are separated through flotation in a slag concentrator. The Cu-rich slag concentrate is thickened, filtered, dried and recycled back to the copper flash furnace. The remaining slag from the flotation cells is discarded in a storage area.

For this study, the slag sample was collected from freshly produced slag of the slag concentrator of the Boliden Harjavalta smelter. The sample was ground to 98.2 w/w% finer than  $75\ \mu\text{m}$  and 28.3 w/w% finer than  $20\ \mu\text{m}$ . The 20–45  $\mu\text{m}$  fraction accounted for 44.7 w/w% of the sample weight. The sample was air dried before use in experiments.

### 2.2. Leaching experiments

The slag sample was initially strongly acid-consuming and this posed a problem for pH control. Therefore, the slag was chemically pre-leached for 24 h in mineral salts medium at the target pH before the bioleaching to satisfy the 24 h acid consumption of the slag by regular adjustment with sulfuric acid. The mineral salts medium contained (per liter) 0.5 g each of  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{K}_2\text{HPO}_4$  and  $\text{MgSO}_4\cdot 7\text{H}_2\text{O}$  (pH 2.5 or 3.0).

Slag bioleaching experiments were performed at initial pH values of 2.5 and 3.0 in continuously stirred 3-L bioreactors with a liquid volume of 1.5 L and 10 w/v% pulp density of slag. The bioreactors were equipped with water jackets to maintain the temperature at 28 °C. The suspensions in the bioreactors were mixed at 170 rpm with overhead stirrers and aerated at a rate of  $1.5\ \text{L}\ \text{min}^{-1}$ . Mineral salts medium was supplemented with  $10\ \text{g}\ \text{S}^0\ \text{L}^{-1}$  as an additional source of substrate for the bacteria. Bacterial oxidation

of sulfur also served to produce  $\text{H}_2\text{SO}_4$ , which helped to satisfy the acid demand. The bioreactors were inoculated with a mixed culture of bacteria enriched from the slag lagoon site of Boliden Harjavalta. The consortium was composed of *Acidithiobacillus ferrivorans* and *Alicyclobacillus* spp. (Kaksonen et al., 2016). The pH of the reactors was adjusted to target values using sulfuric acid or sodium hydroxide on weekdays until day 18. Water evaporation was compensated by adding ultrapure  $\text{H}_2\text{O}$ . The solution chemistry of the bioreactors has been previously described (Kaksonen et al., 2016). Solution samples were filtered ( $0.45\ \mu\text{m}$ ) before analysis of dissolved metals by atomic absorption spectroscopy (Perkin Elmer 1100, Waltham, MA). The solid residues were recovered after 37 d of bioleaching for elemental and mineralogical examination. The residues were rinsed twice in ultrapure  $\text{H}_2\text{O}$  and dried at 27 °C to avoid loss of water from crystal matrix and minimize any chemical changes such as oxide films that may occur at higher temperatures. Elemental analyses of the unleached slag and leach residues were carried out with X-ray fluorescence spectroscopy and mineral analyses were performed with X-ray diffraction (XRD), optical microscopy, and a JEOL 7000E field emission scanning electron microscopy (SEM) combined with energy dispersive X-ray spectroscopy and wavelength dispersive X-ray spectroscopy. Particle size analysis of the original slag was determined by sieving and the leach residues using a Malvern Mastersizer 2000.

## 3. Results and discussion

The slag sample was comprised of fayalite, glassy silicates, magnetite as well as sulfidic and metallic Cu, sphalerite, and galena. Fayalite, glassy silicates, and magnetite were the main mineral phases of the sample (Table 1). Based on XRD analysis, fayalite and magnetite were the most prominent defined mineral phases. The glassy silicate matrix contained 54.5%  $\text{SiO}_2$ , 11.6% FeO, 10.9%  $\text{Al}_2\text{O}_3$ , 5.88% CaO, 2.95%  $\text{K}_2\text{O}$ , and 1.28%  $\text{Na}_2\text{O}$  as the main constituents and minor and trace amounts of the other elements listed in Table 2.

The dominant Cu-sulfide phase was identified as bornite. Chalcocite and chalcopyrite were also present. Trace amounts of Cu- and Fe-arsenides were detected by SEM. The mineralogical composition of the slag is given in Table 1. Iron and  $\text{SiO}_2$  accounted for 70% of the elemental composition of the slag (Table 2), and 95% of the Fe was associated with fayalite and magnetite. Cu was mostly associated with Cu-sulfides, fayalite and metallic Cu (Fig. 1, Table 3). Zn was mostly distributed in fayalite, glassy silicates and magnetite. The slag also contained minor amounts of As, Sb, and Pb (Table 2).

The bioleaching experiments were carried out for 37 d in bioreactors at 10 w/v% pulp density and at initial pH 2.5 and 3.0 after chemical pre-leaching for 24 h in mineral salts medium by maintaining the target pH with sulfuric acid. During the bioleaching, the pH adjustment was continued for 18 days, after which the pH decreased to 2.3 in both reactors because of the bacterial oxidation of elemental sulfur (Kaksonen et al., 2016). Based on the solution analyses, the dissolution yields were 44% and 34% for Cu, 14% and 13% for Zn and Co, and 4.5% and 4.0% for Ni at initial pH values of 2.5 and 3.0, respectively, as previously reported (Kaksonen et al., 2016). The Cu leaching was lower but Zn leaching was higher than previously achieved by chemical leaching (68% for Cu and 3.7% for Zn) in shake flasks at pH 2.1–2.8 in 25 days (Tuovinen et al., 2015). The Cu- and Zn-contents of the leached solids were 37% and 9.7–14% lower, respectively, than those of the unleached slag (Table 2).

The relative amount of fayalite decreased during the leaching (Table 1). The data are insufficient for mass balance analysis. The relative amount of the glassy silicate phase increased during the leaching, indicating the recalcitrance of this silicate phase (Table 1).

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