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Chemical and bacterial leaching of metals from a smelter slag in acid solutions

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ABSTRACT

The purpose of this study was to assess the dissolution of Si, Fe, Cu and Zn from a smelter slag sample under acidic chemical and bacterial leaching conditions. The Cu-containing solid phases were Cu-sulfides (57% distribution), fayalite (18%) and metallic Cu (16%). Zn was mostly associated with fayalite, magnetite and Na-silicate phases (Σ94%). Two mixed cultures (HB1 and HB2) were enriched from samples taken from the slag lagoon site at the smelter location. Comparable results of metal dissolution were obtained with the two mixed cultures. The enrichment culture HB1 was characterized further by denaturing gradient gel electrophoresis (DGGE) of polymerase chain reaction amplified 16S rRNA genes. Based on the 16S rRNA gene sequences, culture HB1 contained at least *Acidithiobacillus ferrivorans* and *Alicyclobacillus cycloheptanicus*, with sequences of three DGGE bands matching distantly with *Alicyclobacillus tolerans* and *Alicyclobacillus herbarium* in the database. *Alicyclobacillus* spp. have not been previously associated with slag lagoons or slag bioleaching. Approximately 80% Cu and 25% Zn were dissolved from the slag (10% pulp) in shake flasks when S^0 was provided for the bacteria to produce H_2SO_4. Bioleaching in stirred tanks was conducted at controlled pH values and was practiced at pH levels promoting metal dissolution and suppressing iron and silicate solubilization from fayalite and Na-silicate. Chemical leaching at pH 2.3–4.0 did not yield substantial dissolution of valuable metals.

1. Introduction

Piatak et al. (2015) have recently provided an overview of mineralogical and chemical characteristics of slags from pyrometallurgical processes. The properties of slag waste are highly variable in mineralogy and metal content and are specific to the metallurgical process (Shen and Forssberg, 2003; Cappuyns et al., 2014; Piatak et al., 2015). Potentially beneficial applications of slag waste for instance in construction and land and environmental management have been discussed in the literature (Gorai et al., 2003; Sánchez et al., 2004; González et al., 2005; Gahan et al., 2009; Lee and Pandey, 2012; Piatak et al., 2015) but few efforts have been made to reduce concepts and experimental systems to practice. There are environmental concerns about long-term storage in landfills, dumps and lagoons due to potential solubilization of major or minor elements under ambient environmental conditions. Metals in slags also represent lost revenue since they are not recovered during the smelting process.

Slags are generally increasingly reactive in acid solutions. Acid dissolution at ambient temperatures enhances the solubilization of fayalite (Fe_2SiO_4) and other silicate phases and metal oxides including magnetite (Fe_3O_4) and maghemite (Fe_2O_3). Fayalite dissolution yields Fe^{2+}, which is slowly oxidized by molecular O_2 in acid solutions, but the

Table. 1
Partial elemental and mineralogical composition of the bulk slag sample.

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

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Table 2
Mineralogical composition of the smelter slag sample.

Mineral	Idealized formula	% Composition
Fayalite	Fe_2SiO_4	48.8
Na-silicate	$Na_2(SiO_2)_nO$, also Na_2SiO_3	23.7
Magnetite	Fe_2O_3	22.4
Cu-sulfides:		0.35
Bornite	Cu_5FeS_4	
Chalcocite	CuS	
Chalcopyrite	$CuFeS_2$	
Sphalerite	ZnS	0.23
Galena	PbS	0.16
Metallic Cu	Cu	0.07

rate is greatly accelerated by iron-oxidizing bacteria (Santelli et al., 2001) such as those found in bioleaching processes. The fayalite phase also usually contains other metals and its dissolution releases associated metals into the solution. Ferric iron has no direct role in fayalite and Fe-oxide dissolution but its hydrolysis to Fe(III)-oxyhydroxides and -hydroxysulfates are acid forming reactions. Ferric iron may also provide a redox shuttle in the oxidation of metal sulfide phases in the slag.

Mehta et al. (1999) tested the chemical and biological leaching of Cu, Co and Ni from a converter slag sample that contained fayalite and magnetite as major phases. At pH 2, up to 99% dissolution of Cu was achieved while Ni and Co recoveries were <30%. The bacterial action was attributed to iron oxidation and production of H_2SO_4. Carranza et al. (2009b) used ferric sulfate solutions (11.5 g Fe^{3+}/l) to treat a converter slag. Cu dissolution reached >90% at 2% pulp density at 60 °C. Muravyov et al. (2012) also reported rapid dissolution of Cu from a copper smelter slag using ferric sulfate–sulfuric acid as a lixiviant. In both studies, the process could potentially employ moderately thermophilic microorganisms to produce and regenerate ferric sulfate solutions. In general, fayalite and other silicate phases and occluded metals in smelter slags increasingly react in acid solutions with decreasing particle size and increasing temperature (Carranza et al., 2009a,b; Urosevic et al., 2015). Metallurgical slag waste materials are insufficient as substrates for bacteria and their bioleaching requires the addition of external S^0 or Fe^{2+} (Vestola et al., 2010; Kaksonen et al., 2011). Acid attack may be the most effective chemical leaching approach for slags because sulfides are usually minor mineral phases. Proton attack can be accomplished with H_2SO_4 that can also be produced through bacterial oxidation of S^0. Acid leaching also causes the dissolution of Fe-containing minerals, leading to the formation of acid ferric sulfate solution.

The present study was initiated to evaluate the dissolution of major and minor metals from a smelter slag. The emphasis of the study was on the acid bioleaching approach with iron- and sulfur-oxidizing bacteria in shake flasks and stirred tank reactors because the chemical leaching was known to be ineffective for metal release from this slag. With the premise that the local microbial community was already adapted to the chemical constituents in the slag, microbial cultures for this work were enriched from environmental samples collected from the slag lagoon area at the smelter site.

2. Materials and methods

2.1. Characterization of the slag sample

The sample of the smelter slag was collected from the smelting process at Boliden Harjavalta, Finland. The particle size of the sample was 73% −45 μm, with 45% within the +20 to −45 μm size fraction. Partial elemental composition was dominated by Fe (41.1%) and SiO_2 (29.6%) as listed in Table 1. Almost half of the matrix was fayalite (48.8%) (Table 2), which contains Fe in the reduced form. Structural examination with scanning electron microscopy indicated the presence of some Cu- and Fe-arsenide grains and occlusions. Fayalite and magnetite accounted for almost 95% of the total Fe, the rest being associated with the melted silicate phase. Zinc was distributed in fayalite (58%), magnetite (20%), Na-silicate (16%), and sphalerite (6%). Nickel was distributed in magnetite (56%) and fayalite (37%). Cobalt was associated with fayalite (66%), magnetite (25%), and Na-silicate (9%). Copper was mostly in Cu-sulfides (57%), and the rest in fayalite (18%) and as metallic Cu (16%) and with minor amounts in Na-silicate and magnetite. The dominant Cu-sulfide was bornite and the other Cu-phases were chalcocite and chalcopyrite. Metallic Cu was mostly in the +45 μm size fraction as free and occluded grains.

2.2. Bacteria and culture conditions

Acidophilic iron- and sulfur-oxidizing bacteria were enriched from samples of precipitates from the slag discharge pipe as well as water and sediment samples from the slag lagoon area at the smelter site. The samples were pooled in two combinations in Fe^{2+} and elemental S (S^0) media that contained (per liter) 0.5 g each of $(NH_4)_2SO_4$, K_2HPO_4 and $MgSO_4 \cdot 7H_2O$, pH 2.5. The media were supplemented with trace metals (per liter: 11.0 mg $FeCl_3 \cdot 6H_2O$, 0.5 mg $CuSO_4 \cdot 5H_2O$, 2.0 mg H_3BO_3, 2.0 mg $MnSO_4 \cdot H_2O$, 0.8 mg $Na_2MoO_4 \cdot 2H_2O$, 0.6 mg $CoCl_2 \cdot 6H_2O$, 0.9 mg $ZnSO_4 \cdot 7H_2O$ and 0.1 mg Na_2SeO_4). The cultures received 4.5 g/l Fe^{2+} (added as $FeSO_4 \cdot 7H_2O$) and 10 g/l S^0 and were grown in shake flasks at 150 rpm at 27 °C. Both combinations yielded mixed cultures, designated HB1 and HB2, which actively oxidized both substrates.

2.3. Molecular analysis of culture HB1

The bacterial community of culture HB1 was analyzed by denaturing gradient gel electrophoresis (DGGE) of PCR-amplified partial 16S rRNA gene sequences followed by sequencing. For the DNA analysis, cells were collected on 0.2 μm membrane filters (Schleicher & Schuell, Keene, NH) and washed with 0.9% NaCl (pH 1.8) followed by phosphate buffered saline-EDTA that contained per liter 390 mmol NaCl, 30 mmol Na_2HPO_4, 30 mmol NaH_2PO_4, 40 mmol Na-EDTA, pH 7.2). DNA was extracted from the washed filter using PowerSoil® DNA Isolation Kit according to the manufacturer's instructions (MO BIO Laboratories, Carlsbad, CA).

The bacterial 16S rRNA genes were amplified by PCR using primers Ba357F 5′-CCT ACG GGA GGC AGC AG-3′ (Muyzer et al., 1993) and

Table 3
Affiliations of partial 16S rRNA gene sequences of bands excised from DGGE gels of the mixed culture HB1.

Band	GenBank accession number	Sequence length (bp)	Closest related species (accession number)	16S rRNA gene similarity (%)
A	KP120617	532	*Acidithiobacillus ferrivorans* strain SS3-P1 (FN687888); previously classified as *A. ferrooxidans* (Amouric et al., 2011)	99
B	KP120618	356	*Alicyclobacillus tolerans* strain Feo-N4-15-CH (FN870324.1)	91
C	KP120619	380	*Al. cycloheptanicus* (X51928.1)	97
D	KP120620	523	*Al. tolerans* strain PCG-3 (KF940051) and *Al. tengchongensis* strain ACK006 (KF772795)	90
E	KP120621	522	*Al. herbarius* strain C-ZJB-12-61 (KC354679.1)	88