Leaching of metals from copper smelter flue dust (Mufulira, Zambian Copperbelt)

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ABSTRACT

The leaching behaviour of electrostatic precipitator dust from the Mufulira Cu smelter (Copperbelt, Zambia) was studied using a 48-h pH-static leaching experiment (CEN/TS 14997). The release of metals (Cd, Co, Cu, Ni, Pb and Zn) and changes in mineralogical composition using X-ray diffraction and PHREEQC-2 modelling were investigated in the pH range of 3–7. The highest concentrations of metals were released at pH 3–4.5, which encompasses the natural pH of the dust suspension (~4.3). About 40% of the total Cu was leached at pH 3, yielding 107 g/kg. Chalcantite (CuSO₄·5H₂O), magnetite (Fe₃O₄) and delafossite (CuFeO₂) represented the principal phases of the studied dust. In contact with water, chalcantite was dissolved and hydrated Cu sulphates precipitated at pH 4–7. Gypsum (CaSO₄·2H₂O) and secondary Fe or Al phases were observed in the leached residues. Serious environmental impact due to leaching may occur in dust-contaminated soil systems in the vicinity of the smelting plants.

1. Introduction

Dust and fly ashes produced during smelting processes represent a high potential risk of environmental contamination, depending particularly on the content and mobility of the metals contained. Residues of different origin vary in composition and thus exhibit different geochemical and environmental characteristics (Ettler et al., 2008; Ohmsen, 2001). The release of contaminants is mainly controlled by the stability of the mineral phases at specific pH values (Astrup et al., 2006; Vítková et al., 2009). Laboratory testing is, therefore, essential to understand the leaching behaviour and to assess the environmental risk represented by the residues.

This study was based on investigation of the flue dust trapped by an electrostatic precipitator (ESP dust) in the Mufulira Cu smelter in the Zambian Copperbelt. Although the residue is recycled in the smelting process (Ross and de Vries, 2005) handling of the residue in the Zambian Copperbelt. Although the residue is recycled by an electrostatic precipitator (ESP dust) in the Mufulira Cu smelter. The residues.

behaviour and to assess the environmental risk represented by the residues.

Investigation of solubility-controlling phases and to assess the potential release in combination with mineralogical/geochemical objectives were to determine the effect of pH on metal-contaminant release in combination with mineralogical/geochemical investigation of solubility-controlling phases and to assess the potential contamination by leaching of the ESP dust.

2. Materials and methods

The ESP dust was collected at the Mufulira Cu smelter situated in the Copperbelt Province, Zambia. Bulk chemical analysis, X-ray diffraction (XRD) and transmission electron microscopy (TEM) were used to characterise the chemical and mineralogical compositions.

The dust was subjected to a 48-h pH-static leaching experiment according to CEN/TS 14997 (2006). Based on preliminary determination of acid and base neutralisation capacities (ANC/BNC), the following pH values were selected: 3, 4, 4.5, 5, 5.5, 6 and 7. The experiment was carried out at L/S = 10; all the experiments were performed in triplicate and with procedural blanks. A mass of 15 g (dry matter) was placed in a glass bottle and the corresponding volume of demineralised water was added. Acid (HNO₃) or base
(NaOH) was used to adjust the predefined pH. Continuous pH control and titration followed. An experiment at the natural pH (i.e., without addition of acid/base) was also included. The physico-chemical parameters were measured in the leachates before filtration (0.45 μm). The concentrations of cations and anions were determined by ICP-OES and HPLC, respectively. The leached solid residues were dried (40 °C) and prepared for XRD analysis. The analytical results were combined with modelling of speciation and determination of possible solubility-controlling phases using PHREEQC-2 (Parkhurst and Appelo, 1999).

3. Results and discussion

3.1. Chemical and mineralogical characterization

The bulk chemical composition of the studied dust is given in Table 1. The main constituents were Cu (273 g/kg), Fe (194 g/kg) and S (85 g/kg). High concentrations of As, Bi, Pb and Zn were observed. Based on the XRD results, the principal primary phases were chalcocite (Cu2S04·5H2O), magnetite (Fe3O4) and delafossite (CuFeO2). The TEM investigation of the dust indicated Cu–Ca sulphates, delafossite and Cu sulphides (Fig. 1). The presence of SiO2 (both crystalline and amorphous) was detected. The mineralogical composition had a significant effect on the natural pH of the dust of ~4.3, which was much lower than that of the materials described by Astrup et al. (2006) and Vítková et al. (2009).

3.2. Leaching of metals

The leaching trends of selected metals are depicted in Fig. 2. The highest concentrations of metals were released at pH 3 with a gradual decrease towards pH 7. The values in the range of pH 5–7 decreased more rapidly. In contrast, a drop in Pb concentration at pH 4 was observed. The amounts released at natural pH ~ 4.3 were significantly high for all the metals, yielding 73,472 mg Cu/kg, 17,439 mg Zn/kg, 11,158 mg Co/kg, 4,762 mg Ni/kg and 4 mg Pb/kg. The leachable fraction of metals is illustrated by the pH-static leaching relative to the total concentration. Approximately 80% of the total Cd, 30–40% Cu, Zn and Co, 17% Ni and only 2% Pb were released at pH 3 (e.g., 153 mg Cd/kg and 107 g Cu/kg). Despite the high concentration of Bi (15 g/kg, Table 1), less than 1 mg Bi/kg was released at pH 3 (leaching data not shown). The extractable fraction of the metals is crucial for the assessment of potential contamination.

3.3. Speciation and solubility-controlling phases

The results of geochemical modelling using the PHREEQC-2 code showed that metallic elements were present mainly as uncharged sulphate complexes (MeSO42−) and as free ionic forms (Me2+) in the given pH range. The PHREEQC-2 predictions of possible solubility-controlling phases (Fig. 3) were in a good agreement with the mineralogical study using XRD. The dissolution of readily soluble chalcocite (Cu3S04·5H2O) resulted in high Cu concentrations in the leaches (with maximum at pH 3) and newly formed hydrated Cu sulphates at pH 4–7. The solution was oversaturated with respect to antlerite (Cu4(SO4)(OH)6) at pH 4–5.5 and to brochantite (Cu5(SO4)(OH)10) at pH 4.3–7. Based on XRD results, antlerite was detected in residues leached at pH 4–5.5, and brochantite was detected at pH 4.5, 6 and 7, indicating the stability of the latter phase under near-neutral conditions. All the leached phases were undersaturated with respect to anhydrite (CaSO4). Gypsum (CaSO4·2H2O) was identified by calculations within the given pH range and was also detected in all the samples by XRD. Chalcocite and gypsum were commonly observed in wastes from a Cu–Co chemical leaching plant in Zambia studied by Sracek et al. (2010). The presence of ferricyanide (Fe(OH)3) and/or lepidocrocite (FeOOH) at pH 3–5 and gibbsite (Al(OH)3) and boehmite (AlOOH) at pH 5.5–7 was predicted, but not confirmed by XRD. The leachates at pH 4.5 and 5 were also oversaturated with respect to maghemite (Fe2O3). The adsorption of metals onto Fe/Al oxyhydroxides may be responsible for their concentration decrease in the leachates (Pettersson and Ingri, 2001) and it is suggested that mainly amorphous secondary Fe oxyhydroxides can form in the leached Cu smelter residues and control the leaching of the metals. Primary magnetite (Fe3O4) and delafossite (CuFeO2) were also present in all the leached residues and can be partly responsible for metal attenuation. The metal solubility represents a high potential risk of soil contamination in the smelter area, especially during the rainy period when the washout of soluble phases may occur.

4. Conclusions

The pH-dependent leaching of metals from dust originating from the Cu smelter in Mufulira (Zambia) was demonstrated. Maximum concentrations were released at pH 3–4.5 with a gradual decrease towards pH 7. The leaching was controlled by dissolution/precipitation of several phases, particularly Cu- and/or Fe-bearing sulphates and oxides. Primary chalcocite, magnetite and delafossite dominated in the dust. Chalcocite was dissolved and secondary antlerite and brochantite were formed. Secondary Fe phases were observed in the leached residues. The leaching behaviour of the dust pointed to a serious environmental impact that may occur during the rainy season in the Copperbelt, when metals in soils highly contaminated by the smelter dust can be released.
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References


Fig. 2. Leaching of metals as a function of pH relative to the total concentrations of the individual elements.

Fig. 3. Saturation indices of selected solubility-controlling phases according to the PHREEQC-2 calculations.

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