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Research article

Characterization and pH-dependent environmental stability of arsenic trioxide-containing copper smelter flue dust

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ABSTRACT

Increasing amounts of impurities (especially As) in Cu ores have aggravated the problem of flue dust generation in recent years. As an example from a smelter processing As-rich Cu ores, we characterized a flue dust particularly rich in As (>50 wt%) to understand its mineralogy and pH-dependent leaching behavior, with special emphasis on binding, release and solubility controls of inorganic contaminants (As, Bi, Cd, Cu, Pb, Sb, Zn). Whereas arsenolite (As_2O_3) was the major host for As and Sb, other contaminants were bound in sulfides, arsenates, alloys and slag-like particles. The EU regulatory leaching test (EN 12457-2) indicated that leached As, Cd, Sb and Zn significantly exceeded the limit values for landfills accepting hazardous waste. The pH-dependent leaching test (CEN/TS 14997) revealed that As, Sb and Pb exhibited the greatest leaching at pH 11–12, whereas Cd, Cu and Zn were leached most under acidic condition (pH 3) and Bi leaching was pH-independent. Mineralogical investigation of leached residue coupled with geochemical modeling confirmed that newly formed Ca, Pb and Ca-Pb arsenates (mimetite, $Pb_5(AsO_4)_3Cl$) partly control the release of As and other contaminants under circumneutral and alkaline conditions and will be of key importance for the fate of smelter-derived contamination in soils or when stabilization technology is employed.

1. Introduction

Copper smelting generates large amounts of waste materials, especially slags (approximately 2.2 tonnes [t] for every t of Cu produced; Gorai et al., 2003) and dusts from flue gas cleaning. Production data for the latter are very scarce in the literature. For instance, in their early works, Dutré and Vandecasteele (1998) and Vandecasteele et al. (2002) noted that, in Belgium in the late 1990s, several thousand t of flue dust were generated by Cu smelters annually (Cu production in smelters in Belgium was 125,000 t in 2008; Schlesinger et al., 2011). Montenegro et al. (2008) estimated that, in 2008, about 36,000 t of dust accumulated in the Chuquicamata Cu smelter in Chile, where annual Cu production corresponded to 424,000 t (Schlesinger et al., 2011). Goonan (2005) studied material flows in 30 large-scale Cu smelters around the world and found that dust production varies between 20 and 480 kg for every t of Cu produced (the weighted average was 200 kg). As a result, taking into account an estimated Cu production of 19.4 Mt in 2016 (USGS, 2017a), roughly 3.9 Mt of flue dust could be generated annually by Cu smelters worldwide.

Copper smelter flue dusts generally consist of small particles of unreacted concentrate or flux, droplets of matte/slag that did not settle into the slag layer in the furnace and volatilized elements such as As, Sb, Bi and Pb, which either solidified as the gas cooled or reacted to form non-volatile compounds (Schlesinger et al., 2011). Given the fact that the dust exhibits high Cu contents (up to 40%), it is nearly always recycled to the smelting furnace (Goonan, 2005; Montenegro et al., 2008, 2013; Schlesinger et al., 2011). However, while this approach is suitable for Cu recovery, it also results in back-contamination of matte with deleterious impurities such as As, Bi, Pb, Sb and Zn (Montenegro et al., 2008, 2013). Eventually the high levels of impurities in blister copper then create difficulties during electrolytic refining (Schlesinger et al., 2011). Another option is hydrometallurgical processing of flue dust; this approach is designed to recover Cu and to stabilize impurities, mainly As, which is of the greatest environmental concern (Chen et al., 2012; Ha et al.,

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2015; Morales et al., 2010; Palumbo et al., 1985; Shibayama et al., 2010).

High levels of metal(loid) contaminants have been reported for Cu smelter flue dusts with up to 47 wt% As, 3.5 wt% Bi, 1.4 wt% Cd, 27 wt% Cu, 48 wt% Pb, 35 wt% Sb, 24 wt% Sn and 33 wt% Zn (Balladares et al., 2014; Chen et al., 2012; Dutré and Vandecasteele, 1995, 1998; Font et al., 2011; Ha et al., 2015; Montenegro et al., 2008, 2013; Morales et al., 2010; Oganigbe et al., 2016; Samuelsson and Carlsson, 1998, 2001; Shibayama et al., 2010; Skeaff et al., 2011; Vandecasteele et al., 2002; Vítková et al., 2011). The problem of dust generation in the copper industry has been aggravated in recent years by increasing amounts of impurities, especially As, in Cu ores (Chen et al., 2016; Ha et al., 2015). Arsenic-rich flue dusts can be treated by the technology of roasting at 750 °C in an oxygen-rich atmosphere to recover commercial-grade As_2O_3 after cooling the vapors. For decades As_2O_3 has been used for production of herbicides and pesticides or chromated copper arsenate (CCA) preservatives for wood and, more recently, for production of GaAs and other As-alloys used as semiconductors in the electronics industry (USGS, 2016; USGS, 2017b). However, given the fact that As compounds have been phased out of domestic use in a number of developed countries because of environmental restrictions (Chen et al., 2016; Villaescusa and Bollinger, 2008 and references therein), As-rich flue dusts produced in large quantities in Cu smelters are often not processed to recover As_2O_3 and must be stockpiled for future treatment or disposed in landfill sites (USGS, 2016). Stockpiling of flue dust in undisclosed locations and/or inefficient flue dust cleaning in a Cu smelter may lead to dispersal of flue dust particles in the surrounding environmental compartments such as soils or vegetation cover (Ettler et al., 2016; Kříbek et al., 2016; Shibayama et al., 2010).

The above factors emphasized the need for the present study. Taking into account the fact that detailed mineralogical and geochemical investigations of Cu smelter flue dusts are extremely rare in the literature (Samuelsson and Carlsson, 2001; Skeaff et al., 2011; Vítková et al., 2011), the main aim of this work was to develop a state-of-the-art characterization of a typical flue dust originating from a Cu smelter processing As-rich concentrates. We used a multi-method approach (bulk chemistry, X-ray diffraction, electron microscopy, electron microprobe, Raman microspectrometry) to determine the major host of As and other contaminants in this waste. This knowledge was then combined with investigation of the pH-dependent leaching behavior of the flue dust and thermodynamic speciation-solubility determination of major solubility controls affecting the release of metal(loid) contaminants under various environmental and/or technological conditions.

2. Materials and methods

2.1. Sampling of copper smelter flue dust

The flue dust originated from a Cu smelter, where As-rich concentrates composed of Cu-bearing pyrite (FeS_2), chalcopyrite ($CuFeS_2$), and Cu-As sulfosalts such as enargite (Cu_3AsS_4) and/or tennantite ($Cu_{12}As_4S_{13}$) were processed. The concentrate is smelted at temperatures around 1200 °C in reverbatory and/or Ausmelt furnaces to produce matte (as the intermediate product), which is then transformed into blister copper (98.5% Cu) in a Peirce-Smith converter. Waste slags from furnaces and converters are granulated and stored at interim disposal sites within the smelter facility and re-processed by milling and flotation (Jarošíková et al., 2017). Blister copper, corresponding to the final product, is subsequently delivered to refineries for final processing. The flue gas from the furnaces is cleaned in a bag-house unit. Trapped flue dust is partially roasted in an arsenic plant, where As is fumed into a vapor phase, which is subsequently cooled and pure As_2O_3 is recovered. Arsenic trioxide can then be sold to third-party customers. The surplus flue dust is packed in bags and stockpiled at an open-air disposal site outside the smelter. We received approximately 3 kg of fresh flue dust as a composite sample collected from plastic storage bags at an interim disposal site located near the bag-house facility.

2.2. Physical, chemical and mineralogical characterization

The granulometry of the flue dust was determined using a Sympatec particle size analyzer equipped with a HELOS laser diffraction sensor and ultrasound sample treatment (Sympatec GmbH, Germany) and yielded the following particle-size distribution: <1 μm (4.1%), 1–2.5 μm (8.1%), 2.5–5 μm (16.3%), 5–10 μm (31.9%), >10 μm (39.6%) (Fig. S1 in the Supplementary Material).

An aliquot part of the flue dust was pulverized in an agate mortar (Fritsch Pulverisette, Germany). Based on the best element recoveries, the bulk chemistry of the smelter dust was determined after digestion of a 0.1 g sample in 10 ml of a 3:1 mixture of concentrated HNO_3 and HCl (called inverted or Lefort *aqua regia*; Dulski, 1996) on a hot plate, dilution to 50 ml and analysis by inductively coupled plasma optical emission spectrometry (ICP-OES; ThermoScientific iCap 6500; ThermoScientific, USA). The contents of total sulfur and total carbon were determined using an ELTRA CS 530 instrument (combustion with infrared detection analyzer; ELTRA, Germany). The accuracies of the digestion procedure and subsequent analytical determinations were controlled by parallel analysis of the following certified reference materials: SU-1b nickel-copper-cobalt ore, CPB-2 lead concentrate and CCU-1e copper concentrate (certified by CCRMP-Canadian Certified Reference Materials project, CANMET, Canada). The quality control/quality assurance (QC/QA) results are reported in Table S1 and indicate good agreement between the measured and certified values.

The phase composition of the flue dust was determined by X-ray diffraction analysis (XRD) using a PANalytical X'Pert Pro diffractometer (PANalytical, the Netherlands), equipped with an X'Celerator detector (analytical conditions: CuKα radiation at 40 kV and 30 mA, 2-theta range 2–80°, step 0.02°, counting time 150 s per step). X'Pert HighScore Plus 3.0 software coupled to the Crystallography Open Database (COD) (Gražulis et al., 2012) was used for analysis of the obtained XRD patterns. For the microscopic observations, flue dust was embedded in epoxy resin and prepared as polished sections. The specimens were first examined under a Leica DM LP polarizing microscope (Leica, Germany). Flue dust powders, mounted on double-sided conductive tape, were studied in the back-scattered electron (BSE) and secondary electron (SE) modes by a TESCAN VEGA3 XM scanning electron microscope (SEM; Tescan, Czech Republic) equipped with an energy dispersion spectrometer (EDS; Quantax 200 X-Flash 5010, Bruker, Germany). Polished sections were further examined using an electron probe microanalyzer (EPMA; JEOL JXA-8530F, Japan) equipped with a field emission gun electron source (FEG) for SEM imaging and an EDS analysis (spectrometer JEOL JED-2300F). The same instrument was used for quantitative chemical analysis of the individual phases and X-ray elemental mapping. The analytical conditions, standards and detection limits for EPMA analyses are given in Table S2. A Renishaw InVia Reflex Raman microspectrometer was used for the Raman spectroscopic analyses. Excitation was provided by the 514.5 nm line of an argon laser. The scanning parameters were as follows: 20-second exposure time and 10–20 accumulations were recorded in order to provide improved signal-to-noise ratios. The spectra were recorded at a nominal spectral resolution of 2 cm^{-1} in