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Antimony smelting process generating solid wastes and dust: Characterization and leaching behaviors

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ABSTRACT

A large amount of solid waste has been produced by the antimony smelting process in the "World Capital of Antimony", Xikuangshan area in China. This study comprehensively investigated the physical and chemical characteristics of the various solid wastes, as well as the leaching behavior of the solid wastes, which included water-quenched slag, arsenic-alkali residue, desulfurized slag and blast furnace dust. These four types of waste were enriched in a variety of heavy metals and metalloids and more specifically with As and Sb levels up to 8.6×10^4 and 3.16×10^5 mg/kg, respectively, in arsenic-alkali residue. For desulfurized slag and water-quenched slag, the leaching concentration of Sb significantly exceeded the acceptable limits during the leaching tests using the toxicity characteristic leaching procedure and the synthetic precipitation leaching procedure. In addition, As leaching in arsenic-alkali residue was extraordinarily hazardous, being three orders of magnitude higher than the regulatory level of As. According to the results of the extraction tests, all the tested wastes were classified as hazardous waste.

Introduction

Elevated levels of heavy metals in the aquatic and soil systems can be caused by the weathering of mineralized rocks. This enrichment is often considerably enlarged by historical and current mining and smelting activities. The metalliferous ore mining and smelting industries have been the main source of heavy metal pollution over the past hundreds of years (Aleksander-Kwaterczak and Helios-Rybicka, 2009; Douay et al., 2007).

Antimony mineral is a common non-ferrous metal mineral resource, especially in China (Anderson, 2012). Possessing 56% of the basic world reserves of antimony, China has the most abundant Sb resources in the world (Lei, 2009). Eighty percent of the world total output of Sb is from China, with an average yield of 1.50×10^5 tons of antimony per year from 2005 to 2010 (He et al., 2012; Wang, 2002). In China, the Hunan Province produces 75% of the countrywide production of antimony. The Xikuangshan Sb mine, located to the west of the Hunan Province, is the largest antimony mine in the world. Being famous for its high output and long history, the Xikuangshan mine is considered as the "World Capital of Antimony".

A large amount of solid waste has been produced by the smelting processes in the Xikuangshan area. Specifically, the antimony smelting activities have historically produced 2×10^5 tons of arsenic-alkali residue (AAR), the majority of which has not yet been properly handled (Li and Liang, 2010). Currently, the amount of AAR in the Xikuangshan area is increasing by 5×10^3–6×10^3 tons each year, in addition to thousands of tons of other smelting slags (Li and Liang, 2010). If the waste is discharged into the environment, a variety of metallic contaminants associated with these wastes will be released into the environment. According to previous reports, the concentrations of heavy metals, such as Sb, As, Pb and Hg, in the soils, waters, plants and even human hair around the Xikuangshan antimony mine are much higher than the concentrations in the non-mining areas (He, 2007; He and Yun, 2003; Zhu et al., 2009; Liu et al., 2009). For example, the Sb contents in soils near this area ranged

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from 100 to 5.05 × 10^3 mg/kg (He, 2007). A geochemical study in Xikuangshan Sb mine area showed that the streams flowing through tailing piles contained high dissolved Sb concentrations of 4580–29,000 μg/L, which exceeded the World Health Organization (WHO) drinking water guidelines for 900–5800 times (Zhu et al., 2009). These metallic contaminants, especially As compounds and Sb compounds, are carcinogenic and hazardous to human health (Fowler and Goering, 1991; Gebel, 1997).

Obtaining a comprehensive picture of the composition and properties of the solid wastes is essentially important for assessing the pollution load and potential environmental risk of these wastes. Therefore, this study focused on the characterization of the physical and chemical properties and the leaching behavior of the solid wastes produced during the antimony smelting process.

1. Experiments

1.1. Origin of the wastes and their sampling

Xikuangshan Flash-Antimony Industry Limited Liability Company is a smelting plant in the Xikuangshan area with an annual production of 4 × 10^4 tons of antimony. The wastes produced in the smelting processes in the Xikuangshan area mainly include water-quenched slag (WQS), desulfurized slag (DS), arsenic-alkali residue (AAR) and blast furnace dust (BFD). The Xikuangshan Flash-Antimony Industry Company currently performs melting by blast furnaces and refining using reverberatory furnaces. More specifically, pelletized antimony concentrates combined with coal are placed into a blast furnace, being smelted at 1300–1400°C in an oxidization environment. The resulting antimony oxide products are volatilized and collected by a bag-type dust collector, which are subsequently placed into a reverberatory furnace for additional refinement. WQS is produced when the remaining worthless fraction of the products generated in the blast furnace is poured out and quenched by water. The dust generated in the blast furnace is a significant dust source which can be released into the atmosphere. Metallic antimony with a purity of 99.4% is obtained when the antimony oxide is reduced in a reverberatory furnace at 1200°C by reducing coal. During the refining process in a reverberatory furnace, any As accompanying the antimony oxide is removed by the addition of sodium hydroxide. AAR is generated during the As removal process. DS is produced during the desulfurization of the smelting off-gas using limewater. The quenching water and cooling water are both reused. Thus, the primary heavy metal sources discharged into the environment are from slags and dust.

The WQS, DS, and AAR were freshly collected from the heaps of slag at different regions. BFD was collected from the smoke channel. The fresh DS was a white, wet and pasty solid, which turned into white powder after drying. WQS was found as a granulated black material with particle sizes ranging from 3 to 5 mm and with a surface sheen. AAR was found as large fragments with size ranging from 5 to 12 cm of a massive and heavy material with a yellow and gray color and a hard texture. The BFD from the blast furnace was a fine powder with a dark brown color.

After being broken and grinded, the massive slag was sieved to <2 mm and subsequently homogenized. The dust was directly homogenized due to its powder form. All of the samples were oven-dried at 50°C for 24 hr to a constant weight. After drying, an aliquot of 20 g for each waste was chosen for pulverization in an agate mortar. All the aliquots were sieved to <147 μm through a nylon sieve. The <2 mm fraction was used for the sequential extraction procedure and leaching tests. The <147 μm fraction was used to analyze the bulk chemical composition, phase and mineralogical composition.

1.2. Bulk chemical analyses

Two analytical methods were used to determine the chemical composition of the solid waste. An X-ray Fluorescence Spectrometer (S4-Explorer, Bruker, Germany) produced a detailed mapping of the major elements of the slag particles. Inductively coupled plasma atomic emission spectrometry (ICP-AES) (Spectro Arcos EOP, Spectro, Germany) was applied to measure the metal concentrations in the wastes after the total digestion. The digestion of the solid was performed using the method of ISO11466.3, as described in the following steps. One gram of slag was accurately weighed and placed in a 250 mL Pyrex Erlenmeyer flask. The slag was first conditioned with a 40-mL acid mixture of concentrated HCl and concentrated HNO_3 with the volume ratio of 3:1 at room temperature for 24 hr. Next, the suspension was digested on a hot plate at 130°C for 15 min. The obtained suspension was cooled to room temperature, and subsequently filtered through a glass fiber filter. Finally, the solution was stored in a volumetric flask after dilution to 25 mL with 0.17 mol/L of HNO_3. The digested solution was diluted to a proper concentration range before the analysis by ICP-AES.

1.3. Phase and mineralogical characterization

After pulverizing the slag samples, the X-ray diffraction (XRD) analysis was performed on an X'Pert PRO MPD diffractometer (PANalytical, Holland) with Cu-Kα radiation. The interpretation of diffraction patterns was conducted with the assistance of the X'Pert HighScore software. The micro-structure of the three slags and the dust was observed by field-emission scanning electron microscope (S-4800, JEOL, Japan) using an accelerating voltage of 10 kV. The oxidation state of antimony in the dust was measured by analyzing X-ray photoelectron spectra (XPS), which was performed at an ESCALAB 250 Spectrometer (ThemoFisher Scientific, UK) with a step width of 0.1 eV.

1.4. Sequential extraction and leaching test

The adopted sequential extraction test was an improvement over the sequential extraction procedure proposed by the Community Bureau of Reference (BCR) three-step. Details of the experimental protocol were introduced by Rauret et al. (1999). Briefly, the acid-soluble fraction was first extracted by 0.11 mol/L of CH_3COOH. The reducible fraction was then extracted by 0.5 mol/L of $NH_2OH{\cdot}HCl$. Next, the oxidizable fraction was extracted using 1.0 mol/L of CH_3COONH_4 after oxidization by 8.8 mol/L of H_2O_2. The concentrations of heavy metals in the extracts were analyzed by ICP-AES.

The toxicity characteristic leaching procedure (TCLP) was developed by the US EPA (1992). The solid wastes were extracted for 18 hr with an extraction of CH_3COOH at a pH of