Journal of Geochemical Exploration 176 (2017) 76–84

Contents lists available at ScienceDirect

Journal of Geochemical Exploration

journal homepage: www.elsevier.com/locate/gexplo

The leaching characteristics and changes in the leached layer of antimony-bearing ores from China

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ARTICLE INFO

Article history:
Received 24 April 2015
Revised 23 December 2015
Accepted 12 January 2016
Available online 14 January 2016

Keywords:
Antimony-bearing ores
Leaching
Antimony
Arsenic
Leached surface

ABSTRACT

China has the most abundant antimony (Sb) resources of any country in the world. Large quantities of Sb have been released from mining and smelting processes, causing serious Sb contamination in the mine or nearby areas. To understand the leaching characteristics of hazardous Sb, As, Pb and Cr from antimony minerals, 12 samples of antimony-bearing ores from eight large mines from China distributed in Hunan, Yunnan, Guizhou and Guangxi provinces were studied. The main compositions of these minerals are Sb_2S_3, SiO_2 or $CaCO_3$. The pH changes during the leaching indicated that some minerals themselves are alkaline, providing sufficient acid neutralizing capacity during leaching. However, some alkaline minerals release much more Sb, As, Pb and Cr than others. Inconsistencies between totals amounts and the released content of Sb, As, Pb and Cr were also found. The surface topography of an antimony sulfide mineral and the species changes of Sb and sulfur (S) on its leached surface were also characterized by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS), respectively. It is the oxidation dissolution of Sb_2S_3 that releases Sb. Sb(III) and S^{2-} on the surface of the fresh mineral were oxidized to Sb(V) and $S_2O_3^{2-}$ and SO_4^{2-}, respectively, and finally, an equilibrium of dissolution was reached over time. The release of Sb, As, Pb and Cr from typical antimony ores is a source of Sb, As, Pb and Cr in the weathering zone; with this in mind, it is easier to understand the geochemical processes and the pollution accidents involving Sb and As within the mining areas and their surroundings.

1. Introduction

Antimony (Sb) is widely utilized for a variety of purposes, including flame retardants, brake linings, polyethylene glycol terephthalate, lead-acid batteries and alloys (Amarasiriwardena and Wu, 2011; Takahashi et al., 2008). Previous reports have shown that like lead (Pb), arsenic (As) and mercury (Hg), Sb is a toxic element of global concern. The majority of Sb pollution appears to originate from mining and industrial emission sources (Adriano, 1986; Guo et al., 2014; Telford et al., 2009; Wilson et al., 2010) because very high levels of pollution have been detected around smelter sites (Ainsworth et al., 1990; Baroni et al., 2000; Filella et al., 2002; Ragaini et al., 1977; Wilson et al., 2010). China has the most abundant Sb resources of any country in the world. It has been responsible for approximately 90% of all antimony metal produced globally over the past decade (Carlin and James, 2012). Serious Sb pollution in China had been reported (He et al., 2012). For example, high Sb concentration in water (up to 29.4 mg/L), sediments (up to 1163 mg/kg) and soils (up to 5045 mg/kg) were found nearby Xikuangshan mining and smelting areas in China (He, 2007; He et al., 2012; Li et al., 2014). Antimony pollution in the aquatic environment results from rock weathering, soil runoff and anthropogenic activities (Filella et al., 2002). Some studies showed that the dissolution of Sb-bearing ore minerals is thought to contribute significantly to the Sb pollution in waters draining zones. The kinetics of the mobilization of Sb from stibnite, Sb_3O_6OH and Sb_2O_3 under environmental conditions has been studied in detail by Biver and Shotyk (2012, 2013). Hu et al. (2014, 2015) studied the release kinetics and mechanisms of Sb from stibnite and Sb_2O_3 under the irradiation of light. As we know, in the natural environment the oxidative dissolution of abundant sulfide ore leads to the net release of protons, a phenomenon known as acid mine or acid rock drainage (Kwong et al., 2009; Verplanck et al., 2009). Subsequent leaching of ores by acidic drainage waters causes elevated concentrations of a broad range of potentially toxic elements, especially the chalcophile elements such as cadmium (Cd) and Pb, which are enriched in metal sulfides. The elevated concentrations of these “heavy metals” and the predominance of their generally more harmful cationic forms at low pH present serious risks to all forms of life in receiving water bodies (Asta et al., 2010; Domènech et al., 2002; Edwards et al., 2000; Moncur et al., 2005; Moncur et al., 2009). In the majority of mine districts, acid drainage is a serious environmental geochemical issue. Thus, serious Sb pollution in waters and soils in China may be concerned with leaching raw ores, tailings and waste rock by acid drainage as a result of the mining activity.

Therefore, 12 samples of antimony-bearing ores from 8 different mines distributed in Hunan (Banxi, Xikuangshan, Zhazixi and Chenzhou

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http://dx.doi.org/10.1016/j.gexplo.2016.01.009
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antimony mines), Yunnan (Muli antimony mine), Guizhou (Xinghua antimony mine) and Guangxi (Chehe and Dachang antimony-bearing pollymetallic mines) provinces in China were sampled. The release characteristics of Sb and other heavy metals were determined. Through comparing the release of hazardous heavy metals from different mines, we hope to obtain background information for heavy metals contamination remediation and management and implementation of reduction programs.

2. Materials and methods

2.1. Sample collection and pretreatment

Origins of 12 samples of antimony-bearing ores, which were named by their sites and grades (e.g. Banxi high-grade and low-grade antimony ores from Banxi antimony mines, North of Xikuangshan and two South of Xikuangshan antimony ores from Xikuangshan antimony mine, Muli high-grade and low-grade antimony ores from Muli antimony mines, and Zhazixi, Xinghua, Chenzhou, Dachang and Chehe antimony-bearing ores from their corresponding mines) and their corresponding antimony deposit types (Wu, 1993) are listed in Table 1. Large bulk ores were broken crushed with a steel hammer and then crushed in a steel percussion mortar and ground to powder in an agate mortar. The powder was sieved, and the fraction between 0.15 and 0.075 mm was retained for elemental analysis. Individual samples of 0.1000 g were digested in 9 mL of concentrated nitric acid, 3 mL of hydrochloric acid and usually 3 mL hydrofluoric acid for 30 min using microwave heating (180 ± 5 °C) (Refer to USA EPA METHOD 3052). After cooling, the vessel contents were filtered, decanted and diluted to volume. The total digestions were performed in triplicate for each sample. The analytical accuracy was checked by triplicate digestions/measurements of standard reference material CRM/RM information center of China GBW07174 (Sb = 1.1 ± 0.11% by weight) and GBW07176 (Sb = 39.7 ± 0.49% by weight) (antimony ore). All reagents used were analytical pure grade or better.

2.2. Experimental methods

Leaching experiments were conducted in the series of 100-mL propene polymer (PP) batch reactors. One reactor was used for one sampling time to ensure the same solid–liquid ratio after sampling. For every run, 50 mL of sulfuric acid aqueous solution with an initial pH of 2 (1 mol/L sulfuric acid was used to adjust pH) and an accurately weighed mass of approximately 0.5000 ± 0.0002 g ores were introduced into the reactor. These reactors were put in a vapor-bathing constant temperature (25 °C) vibrator at 120 rpm. At every interval (one or two days, please see the x-coordinate of Figs. 2–5), 10 mL leached solution was taken, filtered using disposable PP/PE syringes (Shanghai Zhiyu medical equipment Co., LTD, China) with CME 0.45 μm hydrophilic syringe filters. The solution pH was determined using PB-10 pH probes (Sartorius (Shanghai) Trading Co., LTD, China). The concentration of metals (Sb, As, Pb, Cd and Cr) in the leached solution was measured over time. The remaining solid was decanted into plastic tubes and then rinsed with clean acid solution to prevent contamination of the surface. The samples were frozen in liquid N_2 and stored in a freezer until immediately prior to surface analysis. This procedure has been shown to inhibit significant surface speciation alteration (Smart, 1991).

2.3. Analytical methods

Digestion and leached solution were analyzed by ULTIMA inductively coupled plasma atomic emission spectrometry (ICP-AES) (HORIBA JobinYvon S.A.S., France) according to the water and sludge analysis standard EN ISO 11885:1997.

The main composition of the ore samples was analyzed by X-ray diffraction (XRD) (PANalytical B. V., Holland). The XRD patterns were recorded on an X'Pert Pro diffractometer. Conditions: Cu K_λ radiation, 40 kV and 40 mA, 2 theta range 10–70° with a scan rate step of 0.05°/s, using an X'Celerator detector. The qualitative analysis of the XRD patterns was performed using MDI Jade software (version 6.5), plus the ICDD PDF-2 database.

The scanning electron microscope (SEM) micrographs collected from fresh particles and particles leached for 12 days and 16 days were obtained on a Hitachi S-4800 field emission scanning electron microscope (Hitachi Ltd., Japan).

The species changes of Sb and S on the leached surface at different times were determined by ESCALAB MK II X-ray photoelectron spectroscopy (XPS) (VG Scientific Ltd. UK) analysis with a monochromatic Al $K\alpha$ source and a charge neutralizer. Carbon cloth (C 1 s binding

Table 1
Abstract summary of typical antimony deposit in China.

Antimony ores	Mines	Type	Primary minerals	Wall rock alteration
Xikuangshan antimony deposit, Hunan	South of Xikuangshan, North of Xikuangshan	Carbonate stratiform and stratoid deposit	Stibnite (Sb_2S_3), Valentinite(Sb_2O_3), Germanite (Sb_2O_4), Cervantite (Sb_3O_6OH)	Silicification (major) carbonatation, baratization, pyritization, fluoritization, sericitization
Banxi antimony deposit, Hunan	Banxi antimony mine	Quartz vein-type deposit	Stibinite (Sb_2S_3)	Arsenopyritization, pyritization, Silicification, sericitization, carbonatation,
Zhazixi antimony- deposit, Hunan	Zhazixi antimony mine	Filling-metasomatic vein deposit	Stibinite (Sb_2S_3)	
Dachang antimony-polymetallic deposit, Guangxi	Dachang antimony mine	Stratoid integrated Sb, Pb sulfosalt deposit	Jamesonite ($Pb_4FeSb_6S_{14}$), Cassiterite (SnO_2), Arsenopyrite (FeAsS), Pyrrhotite (FeS), Pyrite (FeS_2), Marcasite (FeS_2), etc.	Bleaching, weak silicification, Recrystallization
	Chehe antimony mine	Vein staggered Sb–W deposit	Stibnite (Sb_2S_3), Berthierite ($SbFeS_3$)	Skarnization, Silicification and Carbonatization.
Banpo antimony deposit, Guizhou	Xinghua antimony mine	Clastic sedimentary-modified hydrothermal deposit	Stibnite (Sb_2S_3), Pyrite (FeS_2), Valentinite (Sb_2O_3), Germanite (Sb_2O_4)	Silicification, Carbonatization, Recrystallization, Pyritization and Sericitization
Muli antimony deposit, Yunnan	Muli antimony mine	Carbonatite Sedimentary-modified deposit	Stibnite (Sb_2S_3), Pyrite (FeS_2), Germanite (Sb_2O_4), Cervanite (Sb_3O_6OH), Valentinite (Sb_2O_3)	Silicification, Carbonatization, Recrystallization, Pyritization, Calcilization,