Full Length Article

The role of S(II) and Pb(II) in xanthate flotation of smithsonite: Surface properties and mechanism

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ABSTRACT

Smithsonite is a readily dissolvable carbonate mineral that is naturally hydrophilic, making recovery of this ore by flotation difficult. The flotation results showed that conditioning with only sodium sulfide (Na_2S) did not successfully allow the smithsonite samples to float, whereas treatment with a combination of S(II), Pb(II) and xanthate (with Na_2S as the sulfurizing reagent, lead ions (Pb(II)) as the activator, and xanthate as the collector) improved the flotation of smithsonite, achieving a mass recovery of 95.8%. A combination of analytical techniques, including X-ray diffraction (XRD), atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS), in conjunction with depth profiling, was used to investigate the chemical nature of the sulfur and lead species on the smithsonite surface. For S(II)-conditioned smithsonite, a layer of ZnS formed on the smithsonite ($ZnCO_3$) substrates; this newly formed ZnS coating was amorphous or poorly crystallized. For smithsonite samples conditioned with S(II) and Pb(II), the microstructures and the phase constituents, obtained by AFM and XRD analyses, confirmed the formation of the PbS species with a cubic galena structure on the surface. XPS depth profiling showed that the PbS layer was 18-nm thick, which corresponds to 30 PbS molecular layers. This study presents direct evidence that the coating of the activation product, PbS, on the smithsonite surface was similar to a relatively thick galena layer, which led to successful flotation.

1. Introduction

The oxidized ores in mineral processing, which are generally related to sulfide ores, are mainly ores containing oxidized base metals, including silicate and carbonate minerals of metals such as lead, copper, and zinc. Currently, the oxidized ores are difficult to recover through beneficiation operations; hence, enormous amounts of these ore resources are either unexplored, stacked in open-air mines, or drained into tailing reservoirs, resulting in massive waste [1–8]. Additionally, a stack of refractory ores (some of which are oxidized ores) is a source of heavy metal pollution that causes the deterioration of regional ambient air and water quality. The gradual depletion of sulfide ore, which can easily be recovered through flotation, as well as stricter emission standards for sulfur oxides (SO_x) and the rational exploitation and utilization of these ores, urgently needs to be addressed [9]. The mineral dressing of oxidized ores serves to pre-enrich the valuable oxidized base metal minerals to improve the concentrate grade and greatly reduce the metallurgical operating cost. Because of its high efficiency and low costs, flotation is currently the most important and widely used method in mineral processing [10]. The flotation of sulfide ore is primarily based on the semiconductor properties of the ores, which enable achieving effective chemical adsorption with xanthate collectors through an electrochemical reaction. Currently, however, it is difficult to obtain satisfactory results for the flotation of the oxidized ores [11,12].

Because the valuable minerals and gangue slime in oxidized ores have similar structures and physicochemical properties, the related flotation selectivity is very poor. To increase the differences in the properties of the valuable oxidized base metal minerals and those of the gangue minerals, sulfurizing agents such as sodium sulfide (Na_2S) have been used to selectively pre-sulfurize the oxidized ore to create a metal sulfide layer on the surface of the valuable minerals. This surface layer allows the use of a flotation separation process based on the differences in the surface properties [13].

Smithsonite is a zinc carbonate mineral with the chemical formula $ZnCO_3$ and forms trigonal crystals belonging to the R3c space group. In smithsonite crushing, the surface breakage usually occurs at the Zn—O bond; the C—O bonds in the CO_3 groups are much

stronger and are rarely broken. The cleavage of the Zn—O bond exposes large amounts of Zn^{2+} and CO_3^{2-} ions on the mineral surface, and the charge-polarized surface results in an electrostatic attraction to water molecules. Thus, smithsonite particles are naturally hydrophilic [14–17]. Smithsonite is the most important zinc oxide ore and is a major potential source of zinc. Sulfidation-flotation technology is one of the most widely used methods for processing oxide ores. Currently, there are two kinds of sulfurizing flotation processes for zinc oxide ores: sulfidization followed by amine collection and sulfidization followed by xanthate collection [17–19]. Most studies focus on sulfidization followed by the use of amine collectors [20]. However, since amine collectors are more sensitive to slime, it is necessary to add a desliming step to the process [21,22]. The zinc oxide ores tend to contain a large amount of zinc-rich mud, rendering this technology unsuitable for smithsonite flotation.

The process of sulfidization followed by using xanthate collectors has been widely applied in the flotation of copper and lead oxide ores; particularly, the flotation of malachite and cerussite with this technique has been very successful [23–25]. In contrast to sulfidization followed by the use of amine collectors, processes that use sulfidization followed by the use of xanthate collectors are more demanding, possibly due to the electrostatic repulsion between the negative S^{2-} ions and the anionic collector, xanthate [23,26]. The sulfidization of smithsonite ($ZnCO_3$) is more difficult than that of other minerals (such as lead and copper carbonate minerals) due to the high solubility of ZnS.

However, to date, research on the sulfurization-xanthate process for smithsonite flotation has been limited. Hamid et al. [27,28] explored smithsonite flotation using a combination of sulfurization followed by Cu(II) and xanthate application. They concluded that the xanthate collector species adsorbed onto the surface of the mineral in the form of zinc xanthate. Wu et al. [29] studied the interaction between Na_2S and smithsonite and concluded that the sulfidization product formed on the surface of the smithsonite was ZnS. Feng et al. [30] demonstrated that other than zinc monosulfide (ZnS), the newly generated zinc sulfide on the smithsonite surface was zinc polysulfide, which greatly promoted the flotation of sulfidized smithsonite.

This work focuses on the properties of the products of activation on the surface of smithsonite that are involved in flotation when using a combination of sulfurization, heavy metal ion activation, and xanthate collection for flotation. The main objectives of this study were (i) to describe the influence of Na_2S and Pb(II) on the flotation behavior of smithsonite when using xanthate as the collector; (ii) to examine the morphology, composition and structural characteristics of the activation products during the process; and (iii) to understand the activation mechanism. A combination of advanced surface characterization techniques, including X-ray diffraction (XRD), atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS), were used to monitor the chemical and physical changes on the surface of the smithsonite during conditioning. In particular, XPS depth profile measurements were used to characterize the depth distribution of the chemical components of the corresponding activation products on the smithsonite surface.

Our motivation for this study was to develop a new flotation technology for the industrial processing of large quantities of zinc oxide ores.

2. Experimental

2.1. Materials and reagents

High-purity smithsonite samples were obtained from the mining district of Lanping (Yunnan, China). Some larger pieces of smithsonite were acquired for contact angle measurements, AFM and XPS, and other samples were dry-ground using a porcelain mortar to produce the $-74\,\mu m$ fraction for microflotation and the $-5\,\mu m$ fraction for XRD measurements. XRD analysis showed that the main phase in the samples was smithsonite. The results of the chemical composition analysis of the smithsonite samples by X-ray fluorescence (XRF) are presented in Table 1.

Hydrochloric acid (HCl) and sodium hydroxide (NaOH) obtained from Aladdin Reagent Co. Ltd. (Shanghai, China) were used to adjust the pH. Sodium sulfide ($Na_2S \cdot 9H_2O$) obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China) was used as the sulfidization agent. Lead nitrate ($Pb(NO_3)_2$) was purchased from Kemiou Chemical Reagent Co. Ltd., Tianjin, China. All the abovementioned chemicals were of analytical grade. Commercial sodium n-butyl xanthate (SBX, Zhuzhou Flotation Reagents Ltd., China) was purified by repeated recrystallization from acetone and petroleum ether as described earlier. All experiments were conducted at room temperature (approximately 22 °C). Ultra-pure water (18.2 MΩ/cm) was used to prepare the solutions.

2.2. Methods

2.2.1. Microflotation

Microflotation tests were performed on an XFG flotation machine with a 40 mL capacity cell at an agitation rate of 2700 rpm. A 2 g sample of the -74 μm fraction of smithsonite was subjected to ultrasonication and then was mixed with 30 mL of ultra-pure water and conditioned for 2 min. Then, the sulfidization agent (Na_2S, 2×10^{-3} mol/L), metal ion ($Pb(NO_3)_2$, 2×10^{-3} mol/L) and collector (SBX, 3×10^{-3} mol/L) were added in succession with 5 min of conditioning between additions. After adding solutions of NaOH or HCl as necessary to adjust the pH to the required value, the frother (MIBC, 0.1×10^{-3} mol/L) was added, and the sample was conditioned for another 1 min. Finally, the flotation was conducted for 5 min. The resulting foam product was dried, and the flotation recovery of the smithsonite was calculated after weighing.

2.2.2. Contact angle measurements

To measure the contact angles, bulk specimens were selected and cut into $20 \times 20 \times 5$ mm pieces. Each sample was sequentially polished with #800, #2000 and #3000 emery papers and a fine polishing cloth mounted on a semiautomatic polishing machine (Tegramin-25, Struers) using 3 μm and 1 μm diamond polishing powder. The polished samples were cleaned with ethyl alcohol, rinsed with deionized water, and then conditioned in the desired solution for 5 min. A schematic diagram of the sample preparation for the contact angle measurements is given in Fig. 1. Finally, the conditioned samples were gently washed with ultra-pure water and dried in a vacuum desiccator for contact angle measurements.

The contact angle measurements were performed with a DIGIDROP-DS goniometer (GBX Instruments, Romans) using the classical sessile drop method. Measurements were conducted by settling 4 μL droplets with a precision syringe on the mineral surface (polished side). The drop images were recorded by a high-speed camera, and the contact angle was determined automatically by Windrop++ software. For each sample, 6 replicate tests were conducted at different locations, and the reported result is an average of those replicates.

2.2.3. AFM measurements

To study the mineral morphology before and after activation, an AFM instrument (Innova, Veeco) was used. The sample preparation method used for the AFM samples was a slightly altered version of the procedure used for the contact angle samples (see 2.2.3). To precisely image the topography of the samples, the samples were cleaned by soaking them in ultra-pure water several times instead