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Understanding the roles of Na_2S and Pb(II)in the flotation of hemimorphite

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ABSTRACT

The mechanisms involved in hemimorphite flotation using the "Na_2S-Pb(II)-xanthate" process, including pre-sulfurization using sodium sulfide, activation by lead cations and subsequent flotation using a butyl xanthate collector, were studied. X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) coupled with energy dispersive spectrometry (EDS), and X-ray diffraction (XRD) characterization were conducted to identify the mechanism of interaction of Na_2S and Pb(II) with hemimorphite particles. The results indicated that the "Na_2S-Pb(II)-xanthate" process is an effective method for the flotation of hemimorphite, and the maximum recovery of the hemimorphite concentrate increased from 40% to 90%. Hydrosulfide ions were chemisorbed or participated on the hemimorphite ore surface, and a layer of ZnS was formed. The XRD results indicated that the ZnS layer was amorphous or poorly crystallized. PbS was generated by the interaction of Pb(II) with ZnS through an ion-exchange mechanism, which was verified by XPS, SEM-EDS and XRD. The XRD study indicated that the new PbS phase formed on the hemimorphite ore surface was well-crystallized "synthetic galena" with good floatability, which is critical for the potential application of hemimorphite flotation using the "Na_2S-Pb(II)-xanthate" process.

1. Introduction

Zinc is the fourth most commonly used metal, following only iron, aluminum, and copper, with an annual production of approximately 13 million tonnes (USGS, 2016). Zinc is widely used as a raw material in industries such as electroplating, batteries, and alloy manufacturing (Sethurajan et al., 2016). Worldwide, 95% of new zinc is made from zinc sulfide mineral, which can be easily concentrated using flotation with thiol-compounds as collectors due to its natural hydrophobicity and semiconductor-like properties (Mikhlin et al., 2016; Porter, 1991). However, due to continuous exploitation, the easy-floating sphalerite will soon be exhausted (Ejtemaei et al., 2011; Kashani and Rashchi, 2008). It has already become an urgent task to identify alternative zinc minerals.

Zinc oxide ores are the second largest sources of zinc mineral and normally occur as silicate or carbonate forms (Irannajad et al., 2009; Srdjan, 2007). Hemimorphite ($Zn_4Si_2O_7(OH)_2{\cdot}H_2O$) is the main native zinc silicate mineral, and it exists in different places around the world (Chen et al., 2009). There are several disadvantages in the processing of low-grade zinc oxidized ore using hydrometallurgy, such as the consumption of a large quantity of acid and energy, environmental pollution and low stability (De Wet and Singleton, 2008). In contrast, conventional flotation has the advantages of lower cost, good controllability, and simple operation, making it a promising technology for hemimorphite enrichment (Kashani and Rashchi, 2008).

However, flotation of hemimorphite has not been achieved because it is highly hydrophilic (Ejtemaei et al., 2014). There is little research on the flotation of hemimorphite, and most of the existing studies have focused on the amine flotation process, i.e., sulfidization using sodium sulfide, and flotation with amines as collectors (Ejtemaei et al., 2014; Salum et al., 1992). Salum found that hemimorphite had maximum floatability at pH 9.5–10.0 when conducting flotation tests in Hallimond tubes using this method. Their results indicated that the flotation performance of hemimorphite was worse than that of willemite, and they ascribed this difference to the chemical and structural differences between the minerals (Salum et al., 1992). The authors proposed that RNH_2 reacted with the zinc atom, which existed as ZnS on the surface of hemimorphite through chelation. However, because this method is sensitive to slime and soluble salts, desliming is required to improve the concentrate grade, which may result in a significant loss of zinc metal (Fleming, 1959).

In the flotation of sphalerite with short-chain xanthates as collectors, flotation can be achieved only after activation by heavy-metal ions, such as Cu(II), Pb(II), Zn(II), and Ag(I) (Mcfadzean et al., 2014). Many relevant studies have been conducted (Pattrick et al., 1999; Popov et al., 1989a,b; Rashchi et al., 2002). In this article, we assume

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that the sulfurized hemimorphite has properties similar to sphalerite. Heavy-metal ions were introduced to improve the flotation of hemimorphite. $Pb(NO_3)_2$ was selected as an activator, and Pb(II) was the focus of this study.

The "Na_2S-Metal ions-xanthate" flotation process, which can be broken into three sub-processes, (i) pre-sulfuration by sodium sulfide, (ii) activation by heavy-metal ions and (iii) flotation using xanthate as collectors, has been successfully applied to industrial flotation of lead and copper oxide ores (Fuerstenau et al., 1985; Herrera-Urbina et al., 1999; Kongolo et al., 2003; Popov and Vučinić, 1992). In this work, the activation mechanism for hemimorphite flotation using the "Na_2S-Pb (II)-xanthate" process was studied by analyzing the reaction products. The first aims were to determine the interaction mechanisms of S(II) and Pb(II) in aqueous solutions with hemimorphite and to identify the new phase generated on the mineral. X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) coupled with energy dispersive spectrometry (EDS) analysis were used to determine the S(II) and Pb(II) adsorption products on hemimorphite and to characterize the changes to hemimorphite samples during the activation process. The crystalline states of the minerals are key to flotation, as such, the X-ray diffraction (XRD) patterns were studied to confirm the formation of the new phase and to estimate the crystalline state. To the best of our knowledge, this is the first report on hemimorphite under the "Na_2S-Pb (II)-xanthate" process.

2. Experimental

2.1. Materials

High-quality hemimorphite samples (Lanping, Yunnan Province, China) were used throughout the research. The elemental composition of the hemimorphite samples is shown in Table 1, and the petrographic analysis showed that the percentage of hemimorphite in the samples was 99.1%. The samples were ground and sieved to collect the -106 + 38 μm fraction for the microflotation tests. XRF, XRD, and XPS were conducted using the minus 5 μm fraction.

Sodium sulfide ($Na_2S{\cdot}9H_2O$) was used as the sulfurizing agent, and lead nitrate ($Pb(NO_3)_2$) was used as the ion activator. Commercial-grade sodium butyl xanthate (SBX) was purified by repeated crystallization from acetone and ethyl alcohol. SBX solutions were prepared daily. Methyl isobutyl carbonyl (MIBC) was used as the flotation frother. The chemicals used in this study were of analytical grade unless otherwise specified, and solutions were prepared with Milli-Q water. The pH of the solutions in this study was adjusted to the desired value by adding NaOH or HCl.

2.2. Methods

2.2.1. Microflotation

Flotation tests were conducted using an XFG flotation machine with a rotational speed of 1900 r/min. For each test, a 2.0 g hemimorphite sample was placed in the flotation cell with 30 ml of 1 mM KNO_3 solution, and the suspension was mixed for 1 min, followed by the sequential addition of Na_2S (1 mM), $Pb(NO_3)_2$ (1 mM), SBX (2 mM) and MIBC (0.01 mM). The conditioning time for the sample in the Na_2S, Pb $(NO_3)_2$ and SBX solution was 3 min (after each addition). After adding MIBC, the pulp was conditioned for an additional 1 min; then, the flotation was conducted immediately for 5 min. The floating and non-floating products were collected, filtered, and dried, and the recovery was determined based on the mass ratios.

Table 1
Chemical analysis of the studied hemimorphite mineral sample (Lanping, Yunnan Province, China).

Element	O	Si	P	S	Zn	Pb	Other
Weight (%)	27.88	11.27	0.15	0.05	57.98	0.10	2.57

2.2.2. X-ray photoelectron spectroscopy measurements

In the preparation of the sulfurized samples, a 5 g ultrasound-treated sample was conditioned in 2 mM Na_2S solution for 10 min, and then the suspension was centrifuged in a tube at 9000 rpm for 5 min followed by a decantation of the supernatant. This procedure was repeated for 3–5 times until the pH of the supernatant was approximately neutral (to ensure that no residual divalent sulfur ions and newly-formed ZnS precipitate interfered with the XPS detection). The sulfurized samples were then immediately transferred to a vacuum oven. Lead ion activation was conducted by conditioning the sulfurized samples with 2 mM $Pb(NO_3)_2$ solution for 10 min and then using the same sample preparation procedure as above. To avoid the oxidation of the newly generated surface, all procedures were performed in a nitrogen-rich atmosphere.

XPS was performed using a Thermo Fisher K-Alpha1063 photoelectron spectrometer equipped with a micro-focused monochromatic Al Ka X-ray source (hν 1486.6 eV; 75 W). The parameter settings were: 400 μm wide X-ray spot size, 12 kV working voltage, 6.0 mA working current, 1 eV energy step size for the survey scan and 0.1 eV energy step size for the high-resolution scan. The peaks were fitted using XPSPeak 4.1 software with Gaussian-Lorentzian symmetric peak profiles after Shirley background subtraction (Plackowski et al., 2014). The binding energies in the XPS spectra were calibrated against the adventitious carbon C 1s peak at 284.6 eV, as in previous publications (Bertóti et al., 2000).

2.2.3. SEM measurements

The hemimorphite ore samples, before and after the activation process, were identified using a scanning electron microscope (JSM 5600LV, Japan) equipped with a Noran Vantage 4105X energy dispersive X-ray detection (EDX). The sample preparation methods were the same as for the XPS tests in Section 2.2.2.

2.2.4. XRD measurements

The crystalline nature of the films grown on the activated hemimorphite substrate is one of the keys to the successful separation of the zinc oxide ore by flotation. The sample phase and crystallinity were analyzed using a Bruker D8 Advanced X-ray diffractometer with a one-dimensional detector(Baither et al., 2008; Yoon et al., 2008) and a Cu Kα irradiation source (λ = 1.5406 Å) at 40 kV, 40 mA and room temperature. The sample preparation methods were the same as in Section 2.2.2. Due to the detection limit of the XRD method: (i) The concentrations of sodium sulfide and lead nitrate were increased to 0.2 M, (ii) Hemimorphite samples with much finer granularity (−5 μm) were used, (iii) The scanning speed was slowed down, and (iv) The sample was ensured to be aligned to the optical path and the receiving slit was moderately reduced(Rafaja et al., 1997; Watanabe et al., 2013). The samples were scanned in reflection mode in the 2θ range from 5° to 75°.

3. Results and discussion

3.1. Flotation tests

The flotation results are presented in Fig. 1. Hemimorphite displayed very poor floatability in the absence of Na_2S or lead ions, as shown in Fig. 1A. Furthermore, the addition of Na_2S had little or no effect on the flotation of hemimorphite (Fig. 1B). There was a significant increase in the maximum recovery from 33% to 90% after adding $Pb(NO_3)_2$ and Na_2S (Fig. 1C). The increase in recovery was due to the interaction of xanthate and the newly formed PbS film at the surface of the hemimorphite particles. The flotation results indicate that it is theoretically possible to float hemimorphite using the "Na_2S-Pb(II)-SBX" process.