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Activation mechanism of Fe (III) ions in cassiterite flotation with benzohydroxamic acid collector

Mengjie Tian, Runqing Liu, Zhiyong Gao, Pan Chen, Haisheng Han, Li Wang, Chenyang Zhang, Wei Sun*, Yuehua Hu*

School of Minerals Processing and Bioengineering, Central South University, Changsha, Hunan 410083, China

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ABSTRACT

Pb^{2+} ions are commonly used as the activator in the flotation of cassiterite. However, lead pollution of surface water has attracted more concern and attention. In this study, the effect of Fe^{3+} ions as an activator on the flotation performance of cassiterite using benzohydroxamic acid (BHA) as the collector was investigated by the micro-flotation tests. The results of the flotation experiments showed that the addition of Fe^{3+} ions significantly increased the recovery of cassiterite in the presence of BHA collector. In the BHA flotation of cassiterite, there was a direct relationship between the recovery of cassiterite and the adsorption amount of BHA on the cassiterite surface. The adsorption mechanism of BHA on un-activated and Fe-activated cassiterite surfaces was studied by the adsorption experiments, zeta potential measurements, and X-ray photoelectron spectroscopy (XPS) analysis. The results of the adsorption and zeta potential experiments indicated that the adsorption amount of BHA on the cassiterite surface increased significantly in the presence of Fe^{3+} ions. The XPS analysis also revealed that terminal hydroxyl group oxygen atoms of the cassiterite surface were the dominant reactive sites for Fe^{3+} ion adsorption. Furthermore, BHA anions can react with Fe atoms adsorbed on the cassiterite surface to form Fe-BHA complexes, thus improving the hydrophobicity of the cassiterite surface.

1. Introduction

Tin has many essential properties, including malleability, electrical conductivity, plasticity, and corrosion resistance. Accordingly, tin has been applied extensively in gas sensors (Spencer, 2012; Xu et al., 2015; Bechthold et al., 2015), catalytic chemistry (Zhao et al., 2006; Niu et al., 2010), electrochemical detection of heavy metal ions (Wei et al., 2012; Bhanjana et al., 2015; Jin et al., 2017), tin plating, and plumbing (Chakrabarti and Lahiri, 1996). As a result, tin metal resources are continuously consumed in the world. Cassiterite (SnO_2) is an abundant tin mineral of economic importance. In general, the flowsheet for cassiterite beneficiation includes a combination of gravity and flotation units (Angadi et al., 2015). Gravity separation is an age-old approach used in mineral processing plants because of its low cost and environmental friendliness. However, gravity separation is sensitive to the particle size, and highly inefficient for recovering fine-sized minerals (Bulatovic and Silvio, 2000). The cassiterite in hard-rock deposits is highly disseminated and intimately associated with other minerals. The disseminated nature of cassiterite occurrence in hard-rock deposits necessitates fine grinding to liberate mineral values from the host rock. The inherent brittle nature of cassiterite leads to the generation of undue fines not only during grinding but also during various other processes. For the recovery of fine cassiterite particles, as an alternative technique, flotation has been proved to be a more attractive method (Zhou et al., 2014; Leistner et al., 2016).

Froth flotation is an attractive method for separating valuable minerals from gangue minerals depending on their surface chemistry differences in physicochemical properties. Regarding the flotation of cassiterite, more attention has been paid to the development of selective and powerful collectors. Aryl or alkyl hydroxamic acids, RCONHOH (R, aryl or alkyl), are extensively used as collectors in mineral flotation because of their excellent selectivity (Sreenivas and Padmanabhan, 2002; Qin et al., 2011; Griffith et al., 2011). Benzohydroxamic acid (BHA), as a well-known hydroxamic acid, shows a pronounced selectivity in flotation separation (Wu and Zhu, 2006; Sun et al., 2016; Tian et al., 2017b, 2017a). The poor solubility of cassiterite results in the deficiency of active sites on mineral surface, which leads to the inadequate adsorption quantity of BHA. In order to increase the number of active sites on the mineral surface, lead nitrate has been applied successfully as the activator in wolframite, scheelite, and cassiterite flotation in the presence of BHA collector (Zhao et al., 2015; Tian et al., 2017b, 2017a; Han et al., 2017). However, lead poisoning is

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* Corresponding authors.
E-mail addresses: sunmenghu@csu.edu.cn (W. Sun), huyuehuacsu@126.com (Y. Hu).

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still a serious public health problem. Drinking water is a possible source of lead exposure, and flotation is a water-intensive process. Leakage of waste water contaminated with lead ions can damage the ecological environment and threaten human health. Therefore, it is necessary to explore substitutes for Pb^{2+} ions in order to reduce environmental pollution.

Jin et al. (2016) found that the addition of Fe^{3+} ions can significantly increase the flotation recovery of quartz in the presence of sodium petroleum sulfonate collector. In addition, Fe^{3+} ions are usually used as the activator in the flotation recovery of spodumene in the presence of sodium oleate collector (Zhang et al., 2014). Inspired by this, our group has found that the addition of Fe^{3+} ions can significantly increase the adsorption amount of BHA on the cassiterite surface; this is the first time that Fe^{3+} ions have been used as the activator in cassiterite flotation.

This work aimed to investigate the potential application of Fe^{3+} ions to replace Pb^{2+} ions for cassiterite flotation in the presence of BHA collector through the flotation experiments. The effect of Fe^{3+} ions on the adsorption of BHA on the cassiterite surface was studied by the adsorption tests and zeta-potential measurements, and X-ray photoelectron spectroscopy (XPS) analysis. XPS was used to detect the mineral surface after Fe^{3+} ion activation and subsequent BHA adsorption. According to the results of XPS, the adsorption mechanism of Fe^{3+} ions from aqueous solution on the cassiterite surface is discussed in detail.

2. Experimental

2.1. Minerals and chemicals

Pure cassiterite crystals were obtained from Hunan province in China. X-ray powder diffraction (XRD) data confirmed that the purity of the cassiterite was 99%. The mineral samples were ground in a porcelain mortar. $-74 + 38\,\mu m$ particle sizes were used for the flotation and adsorption experiments. The sample was further ground to less than 5 µm in an agate mortar for the zeta potential measurements.

BHA used as the collector was obtained from Tokyo Chemical Industry. Lead nitrate ($PbNO_3$) and iron (III) chloride hexahydrate ($FeCl_3{\cdot}6H_2O$) used as the activator were purchased from the Tianjin Kermil Chemical Reagents Development Centre. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were used as pH regulators. All reagents were of analytical grade. Deionized water with a resistivity of 18 MΩ × cm, produced by a Medium-Q800 laboratory water purification system (HITECH, Taiwan, China), was used in the experiments.

2.2. Flotation tests

Flotation tests were conducted on an XFG flotation machine (Exploring Machinery Plant, Changchun, China) with a 40-mL cell, shown in Fig. S1 in the supporting information. In each test, the flotation pulp was prepared by adding 2 g of mineral samples to 40 mL of deionized water. The pH of the mineral suspensions was first adjusted to the desired value by adding pH regulators for 2 min. Then, the collector was added into the pulp with a conditioning time of 5 min. Total flotation time was 6 min. The froth was scraped manually by using a plastic blade. The froth products and tails were dried and then weighed after filtration to calculate the flotation recovery under various flotation conditions.

2.3. Adsorption experiments

For adsorption tests, 2 g of mineral powder was taken and made up to 40 mL after the addition of desired amounts of flotation reagents in a flotation cell. The sample was prepared at the same conditions as the flotation tests. After a pre-defined conditioning period, the solids were separated out using a high-speed centrifuge for 30 min, operated at 9000 rpm. The residual concentration of BHA in the supernatant was determined by a Shimadzu TOC-L CPH analyser. All of the experiments were repeated three times, and the reproducibility of the data was checked. The adsorption amount of BHA on the mineral particles was calculated from the difference between the initial and residual BHA concentrations.

2.4. Zeta potential measurements

Zeta potential measurements for cassiterite particles were carried out using a JS94H micro-electrophoresis instrument (Shanghai Zhongchen Digital Technic Apparatus Co., China). Cassiterite sample (16 mg) was added to 80 mL 10^{-2} mol/L KNO_3 solution in a 100-mL beaker with or without flotation reagents. The mixture suspension was agitated for 10 min with a magnetic stirrer, and then the suspension was allowed to stand for 6 min until coarse particles settled down. Prior to the zeta potential measurements of cassiterite, the pH of the suspension was adjusted to the desired value. The reported zeta potential was averaged from at least three measurements.

2.5. XPS analysis

A Thermo Fisher Scientific K-Alpha 1063 XPS spectrometer was used for the X-ray photoelectron spectroscopy (XPS) measurements. The instrument uses Al Kα as the sputtering source at 12 kV and 6 mA with pressure in the analytical chamber at 1.0×10^{-7} Pa. The data were collected and processed using Thermo Scientific Advantage software.

2.6. Foaming by bubbling

The foam was produced by placing the foaming solution (40 mL) in the bottom of a glass column, and a constant air flow of 1 L/min was bubbled into the solution through porous glass plates. The constant air flow was produced by a Model HP-1116 Electromagnetic Vibrating Air Pump (Morrison Group Co., Ltd.), and air flow rate was measured by a Model LZB-3WB Glass Rotor Flowmeter (Revitalization). The half-life time, $t_{1/2}$ (the time required for the foam volume to decrease to 50% of its maximum volume), was used to characterize the foam stability (Anokhina et al., 2005).

3. Results and discussion

3.1. Micro-flotation experiments

In order to determine if the combination of Fe^{3+} and BHA behaves similarly to that of Pb^{2+} and BHA, a series of single-mineral flotation experiments using lead nitrate and BHA as the activator and collector, respectively, were conducted. Fig. S2 in the supplementary material shows the flotation recovery of cassiterite as a function of BHA concentration at 10 mg/L lead nitrate. As shown in Fig. S2, in the presence of lead nitrate, the recovery of cassiterite increased rapidly with an increase in BHA concentration from 10 mg/L to 80 mg/L, and remained nearly constant at approximately 85% in the BHA concentration range of 80–100 mg/L.

Fig. 1 shows the flotation recovery of cassiterite as a function of pH. In the absence of ferric chloride, the recovery of cassiterite increased with an increase in pH from 4 to 7, and then declined with pH increasing after reaching a maximum. The highest recovery of cassiterite in the presence of BHA alone was only 30% at pH 7. This indicates the weak collecting ability of BHA. In the presence of ferric chloride, the recovery of cassiterite increased with pH increasing until 8, and then decreased slightly with an increase in pH. The highest recovery in the presence of ferric chloride activator was 80% higher than that in the presence of BHA alone. This indicates that the floatability of cassiterite can be greatly improved by the presence of ferric chloride.

Fig. 2 shows the flotation recovery of cassiterite as a function of