Novel insights into adsorption mechanism of benzohydroxamic acid on lead (II)-activated cassiterite surface: An integrated experimental and computational study

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ABSTRACT

Using microflotation experiments, this study investigated the effect of Pb^{2+} ions on flotation performance of cassiterite (SnO_2) by using benzohydroxamic acid (BHA) as collector. Flotation results showed that floatability of cassiterite significantly improved after addition of Pb^{2+} ion to the process. Adsorption behaviour and mechanism of BHA on the inactivated and Pb-activated cassiterite surface were further explored by adsorption experiments, zeta potential measurements, X-ray photoelectron spectroscopy analysis and first-principle density functional theory calculations. Experimental and computational results consistently suggested that the adsorbed Pb atoms can coordinate with two O atoms of the two hydroxyl groups on the cassiterite surface. BHA molecules can form two coordination bonds with one Pb ion adsorbed on the cassiterite surface, resulting in a five-membered chelating ring. The proposed adsorption mechanism can be extended to the vast majority of interface assembly systems.

1. Introduction

Tin is one of the five most famous metals (gold, silver, copper, iron and tin). Given its antioxidant effect, electrical conductivity and malleability, tin has been applied extensively in various fields, such as in gas sensors (Xu et al., 2015), catalytic chemistry (Zhao et al., 2005) and environmental protection (Jin et al., 2017). Cassiterite (SnO_2) is the main source of tin. Gravity separation is one of the main processing method to recover cassiterite from its ore due to its high specific gravity, while, recovery of fine-grained cassiterite is remarkably low. Owing to the brittleness of the material, certain amounts of fine cassiterite particles are invariably generated as severe and excessive combinations of crushing and grinding can occur frequently in crushing–grinding circuits (Angadi et al., 2015). Flotation is the most widely used beneficiation technology for processing fine particles, and it mainly takes advantage of the distinction of mineral surface according to physical and chemical characteristics by using flotation reagents to have selective separation of useful minerals from the associated gangues. Flotation also plays an essential role in recovery of ultrafine cassiterite from refractory ores (Angadi et al., 2015; Leistner et al.,

2016; Zhou et al., 2014). Refractory ores with low grade and mineralogical complexity require reasonable exploitation and utilisation due to limited mineral resources and increasing demands. Thus, the mechanism of improving cassiterite flotation performance has become an essential issue.

Floatability of cassiterite majorly depends on the development and utilisation of flotation collectors. Fatty acid collectors, such as oleic acid and its derivatives, have been applied extensively in flotation of cassiterite (Baldauf et al., 1985; Liu et al., 2017). However, the related industrial application is limited due to lack of selectivity and poor solubility of fatty acid collectors at low temperatures (Angadi et al., 2015; Liu et al., 2012; Peng et al., 2017; Tan et al., 2016). As cassiterite collectors, alkyl sulphates suffer from low selectivity for the separation of cassiterite from its gangue minerals (Angadi et al., 2015; Li et al., 2015). Alkyl sulphates only exhibit strong collecting capacity for cassiterite in acidic media, and this condition will result in serious causticity of the flotation equipment. Arsenic acids exhibit both superior collecting ability and selectivity towards cassiterite. However, arsenic acids production was ceased due to its severe toxicity (Angadi et al., 2015; Liu et al., 2012). Phosphonic acids have been widely used in

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cassiterite flotation (Li et al., 2015). However, microflotation studies indicated that maximum cassiterite recovery with phosphonic acids collectors is obtained from pH of 2 to 3; this condition will cause severe corrosion to metal equipment (Angadi et al., 2015; Senior et al., 1989). Compared with other collectors, amide sulfosuccinates exhibit considerable benefits, such as nontoxicity, strong collecting ability, low dosage and insensitivity to multivalent cations (Khangaonkar and Kamarudin, 1994). However, the major weakness of these reagents is their ultrastrong frothing capacity (Angadi et al., 2015; Khangaonkar and Kamarudin, 1994). In recent years, hydroxamic acids have been used widely in cassiterite flotation (Qin et al., 2011; Sreenivas and Padmanabhan, 2002; Tian et al., 2018). Among these collectors, benzohydroxamic acid (BHA) stands out as it shows a limited collecting ability but excellent selectivity (Tian et al., 2017a,b; Wu and Zhu, 2006) due to the good balance between its hydrophobic group (benzene ring) and ore-affinity group (hydroxamic acid, $-(C{=}O){-}NH{-}OH$).

Lead nitrate has been widely used as activator reagent in flotation to increase mineral recovery. For example, although quartz possesses hydrophilic surface properties, it can still be completely floated out with lead nitrate as activator reagent in the presence of amyl xanthate collector (Liu et al., 2016a). After lead nitrate treatment, rutile and hemimorphite floatability significantly improves in the presence of salicylhydroxamic acid and sodium oleate, respectively (Li et al., 2016; Liu et al., 2016b). Addition of lead nitrate can distinctly enhance the recovery of scheelite (Han et al., 2017) and wolframite (Zhao et al., 2015b) in the presence of hydroxamic acids. As it was reported, the possible mechanism which is involved in the process is, Pb^{2+} ions are preferably adsorbed on terminal hydroxyl oxygen (O_{term}) atoms of mineral surfaces (Chen et al., 2017; Feng et al., 2017). Although considerable works have been carried out to investigate the effect of Pb^{2+} ions on flotation separation of target minerals, adsorption and activation mechanisms of Pb^{2+} ions on target minerals remain unclear and must be explored. This lack of information should be ascribed to the complexity of mineral–water interface structure. Furthermore, metal ion solvation has not been fully considered in previous reports.

This work aims to thoroughly understand the adsorption behaviour of solvated Pb ions on the cassiterite surface at the atomic level and their interaction mechanism with BHA anions via various experimental and computational methods, including flotation experiments, adsorption tests, zeta potential measurements, X-ray photoelectron spectroscopy (XPS) analysis and first-principle calculations based on density functional theory. Accordingly, floatability of cassiterite, utilizing BHA as collector in the absence and presence of lead nitrate activator, was investigated using microflotation experiments. Then, the effect of Pb^{2+} ions on adsorption of BHA on the cassiterite surface was systematically explored using adsorption experiments, zeta potential measurements and XPS analysis. First-principle calculation was adopted to gain insight into hydration of Pb ions and adsorption behaviour of water molecules, solvated Pb ions and BHA anions on the cassiterite surface.

2. Methodology

2.1. Materials and reagents

High-purity cassiterite crystal samples were obtained from Hunan province, China. Fig. 1 shows the X-ray diffraction (XRD) patterns of cassiterite samples. The diffraction peaks recorded for cassiterite matched well the pattern of standard diffraction peaks (Peng et al., 2017; Qin et al., 2012). According to results and as shown in Fig. 1, few impure peaks were recorded, indicating that the cassiterite samples had high purity. Purity of cassiterite was over 97% according to X-ray fluorescence results. The minerals were ground in a porcelain mortar and then sieved. A portion of the fraction ($-38\,\mu m$) was further ground using an agate mortar and then microsieved to obtain a particle size of less than $5\,\mu m$. Samples with size $38–74\,\mu m$ were used in microflotation and adsorption experiments. Samples with sizes below $5\,\mu m$ were used
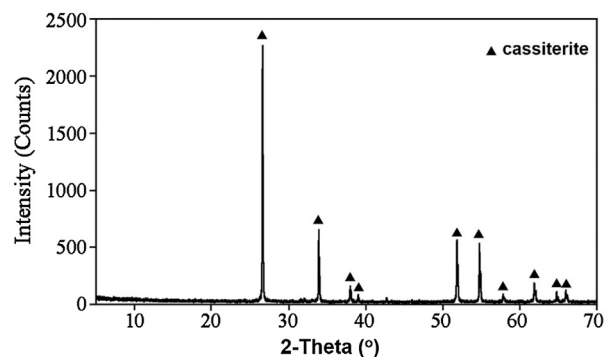

Fig. 1. XRD of cassiterite.

in zeta potential measurements and XPS analysis. BHA, which was used as a collector, was purchased from Tokyo Chemical Industry. Lead nitrate was used as an activator and was obtained from Tianjin Kermil Chemical Reagents Development Centre. For pH modification, NaOH and HCl were used. All reagents employed in this study were of analytical grade. Deionised water with a resistivity of $18\,M\Omega \times cm$ was produced by a Medium-Q800 laboratory water purification system (HITECH, Taiwan, China) and was used in the experiments.

2.2. Flotation experiments

All flotation tests were carried out using a 40 mL XFG flotation cell operated at 1600 rpm. The flotation pulp for single minerals was prepared by adding 2.0 g mineral samples to 40 mL of deionised water in the cell. pH modifier was firstly added to adjust the pulp pH value with stirring time of 2 min. Subsequently, the mineral suspension was conditioned with lead nitrate for 3 min. Afterwards, a desired amount of the flotation collector was added into the cell with 5 min conditioning time. Flotation lasted for 6 min, and concentrates were recovered by skimming the overflow froth. The float froth and pulp fraction were collected and dried separately, and recovery was calculated based on solid weight distributions between the two products. All flotation tests were repeated three times and their average was reported.

2.3. Adsorption tests

In each test, after addition of desired amounts of flotation reagents in the flotation cell, 2.0 g cassiterite powder was obtained and used to prepare a 40 mL solution. Agitation times of different flotation reagents were in accordance with those of the flotation tests. Afterwards, the suspension was centrifuged for 30 min with an agitation speed of 9000 rpm. Residual concentration of BHA in the supernatant was determined by TOC-L CPH/CN (Shimadzu Corporation). The amount of BHA adsorbed on minerals was calculated from the differences between initial and residual BHA concentrations. All adsorption test results were obtained from three separate experiments and their average was considered.

2.4. Zeta potential measurements

Zeta potential measurements were performed in $1\,mol/L\ KNO_3$ background electrolyte solution using a JS94H microelectrophoresis instrument (Shanghai Zhongchen Digital Technic Apparatus Co., China). A total of 40 mg of $-5\,\mu m$ mineral samples were added into 40 mL aqueous solution in a 100 mL beaker in the absence or presence of flotation reagents. pH value was adjusted with NaOH or HNO_3. Zeta potential of the obtained pulp was determined. A small amount of pulp was injected through a syringe into the test electrophoresis tube for zeta potential tests. Each sample was measured thrice, and average zeta potential was recorded.