Activation mechanism of lead ions in cassiterite flotation with salicylhydroxamic acid as collector

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A B S T R A C T

The effect of lead ions on cassiterite flotation with salicylhydroxamic acid as collector was assessed by a combination of microflotation tests, adsorption experiments, zeta-potential determinations, and X-ray photoelectron spectroscopy (XPS) analysis in this work. Microflotation tests confirmed the contribution of lead ions to cassiterite flotation at an increased floatability of 12.12% compared with that in the absence of lead ions. The adsorption experiments demonstrated that the adsorbed amount of SHA onto cassiterite surfaces was greatly increased after treatment with lead ions. The results of zeta-potential determinations indicated that the cassiterite surface was activated by the adsorption of lead species in the form of $Pb(OH)^+$, and the higher adsorption capacity of SHA onto the mineral surface was obtained after modifying with lead ions. XPS analysis revealed that lead ions adsorbed onto the mineral surface through the interaction between lead species and oxygen sites of cassiterite surfaces. This occurrence increased the number of active sites on the mineral surface and improved the collector attachment. These results consistently indicated that the activity of the cassiterite surface increased after pretreatment with lead ions and enhanced the flotation behavior.

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1. Introduction

Tin is an important metal with extensive applications, such as in soldering, plating, alloy production, chemistry, and metallurgy. In nature, the metal mainly exists in the form of cassiterite (SnO_2). In the past, gravity-separation technology has been utilized to enrich tin minerals from ores, and flotation method is employed to remove sulfide minerals from tin concentrations to further increase tin grade [1–3]. With the progressive exploitation and exhaustion of rich tin resources, low-grade, and refractory ores are processed and considered for tin-mineral extraction. Tin minerals in such ore body type are finely disseminated. Given the brittle nature of cassiterite, the recovery of fine and ultrafine cassiterite particles should be the core of work. However, the gravity concentration technique is restricted by the exceedingly fine particle sizes of cassiterite [4–6]. For these reasons, the froth flotation method has been given increased attention for the recovery of fine and

ultrafine cassiterite particles from low-grade tin ores and gravity tailings [7–9].

Froth flotation is an effective method for separating target minerals from gangue minerals depending on their surface differences in physicochemical properties. The selection and application of an appropriate collector are vital to the mineral flotation process. Numerous collectors have been developed and employed to examine the flotation performance of cassiterite minerals. Xu and Qin [10] investigated the interaction between cassiterite and sodium oleate using flotation experiments, solution measurements, and surface analysis. Alkane dicarboxylic acids were found as a suitable collector for effectively floating cassiterite particles at a low dosage of reagents [11]. The finely disseminated tin minerals could be recovered with a high-grade tin concentration using styrene phosphonic acid as a collector, and the collection was confirmed through laboratory and plant tests [12]. Li et al. [13] demonstrated that α-hydroxyoctyl phosphinic acid showed a collection ability and selectivity for cassiterite superior to those of styrene phosphonic acid. The involved interaction mechanism was studied by surface analysis techniques. Sulfosuccinamate was introduced to serve as collector for cassiterite flotation, and chemical bonding occurred between sulfosuccinamate and cassiterite surfaces [14,15]. Janczuk et al. [16] studied the wettability of cassiterite

conditioned with sodium dodecyl sulfate and found that cassiterite particles were suitable for flotation at acidic pH. Besides fatty acid, phosphonic acid, sulfosuccinamate, and dodecyl sulfate, various hydroxamic acid collectors were also utilized to float cassiterite [17–20]. Among these hydroxamic acid collectors, salicylhydroxamic acid (SHA) was considered as an effective and selective collector for cassiterite flotation, and the flotation mechanism was systematically studied [21,22].

However, the individual usage of SHA did not attain the desired floatability despite the presence of increased collector dosages. The potential reason may be the deficiency of active sites on the cassiterite surface, which led to the inadequate adsorption quantity of SHA onto the mineral surface. A commonly used method to increase the number of active sites is to introduce additional active metal ions onto the mineral surface [23–25]. When benzohydroxamic acid was employed as a collector, lead nitrate served as an activator to improve the recovery of fine cassiterite particles from tin tailing [8]. Choi et al. [15] also found that lead ions could activate mineral surfaces to increase cassiterite recovery wherein sulfosuccinamate was employed as collector. Lead ions were also used to activate rare earth [26], wolframite [27], hemimorphite [28], rutile [29], and quartz [30] to enhance collector adsorption onto the mineral surface. Nevertheless, minimal information is available in published literature as regards the activation mechanism of lead ion in the cassiterite flotation with SHA as collector.

In the present work, the positive influence of lead ions on cassiterite flotation with SHA as collector was exhibited using microflotation experiments. The activation mechanism was investigated by solution measurements, zeta-potential determinations, and XPS analysis.

2. Experimental

2.1. Materials and reagents

Cassiterite sample used in all the experiments was derived from Yunnan Province, China. For microflotation experiments and adsorption measurements, the cassiterite sample was crushed and dry ground in an agate torsion mortar. The ground products were sieved using a standard screen to achieve a particle fraction of −38 + 20 μm cassiterite. The rest of the samples were ground continuously and received a proportion finer than 5 μm for zeta-potential determination. The X-ray diffraction (XRD) pattern of the representative sample in Fig. 1 demonstrates that only the diffraction peak of cassiterite is detected. The measured result of
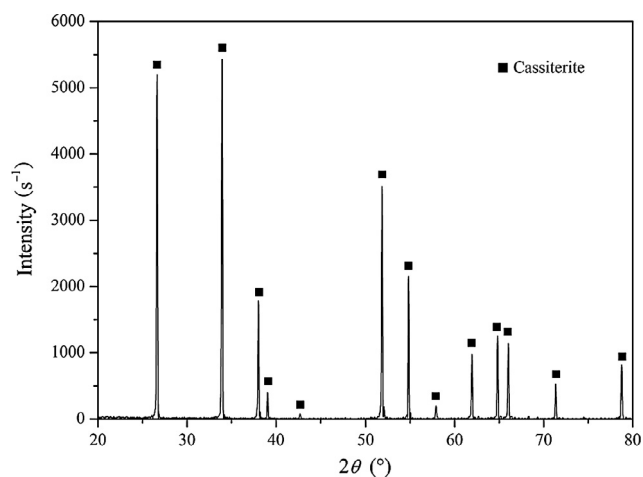

Fig. 1. XRD pattern of the pure cassiterite samples.

X-ray fluorescence (XRF) analysis indicates that 97.33% SnO_2 was included in the cassiterite sample, which further confirmed that the sample used was of high purity with a small quantity of mineral impurities.

SHA was employed as a collector, and lead nitrate ($Pb(NO_3)_2$) was supplied with a lead-ion source. Potassium nitrate (KNO_3) was obtained as background solution to guarantee the ionic strength of measured solution during zeta-potential determination. Solution pH values were regulated using 0.1 mol/L hydrochloric acid and 0.1 mol/L sodium hydroxide stock solutions. All reagents employed in the present study were of analytical grade, and pure deionized water was used throughout testing.

2.2. Flotation studies

Flotation experiment was conducted at room temperature in a small-scale flotation machine, and 2.0 g of pure cassiterite samples were added into a 40 mL flotation cell. The mineral suspension was first conditioned with 1×10^{-4} mol/L $Pb(NO_3)_2$ stock solution before SHA was added as necessary. Subsequently, various concentrations of SHA solutions were poured into the pulp suspension and subjected to flotation before the pulp pH was regulated to pH 7.5. After the collected products were filtered and dried, the weight distribution between the floated and unfloated cassiterite particles was calculated to determine the corresponding floatability.

2.3. Adsorption experiments

The adsorption experiments of SHA onto the cassiterite surfaces treated and not treated with lead ions were conducted in a thermostatic water bath at 298 K. Pure cassiterite particles (2 g) were dispersed into 100 mL of aqueous phase in the absence and presence of 1×10^{-4} mol/L lead ions. After the mineral suspensions were conditioned for 30 min, the SHA stock solution of a desired concentration was injected to interact with the mineral surface, and the mixture was stirred for another 30 min. The resultant suspension was immediately subjected to solid–liquid separation using a centrifuge, and the separated liquid was collected to quantitatively analyze the SHA concentration using a UV–Vis spectrophotometer (UV-2700, Shimadzu, Japan). The adsorbed amount of SHA on the cassiterite surface was calculated using the following equation:

$$\Gamma = \frac{(C_0 - C) \cdot V}{m} \tag{1}$$

where Γ is the adsorbed amount of SHA on the cassiterite surface in the absence and presence of lead ions; C_0 and C are the concentrations of SHA in the pulp suspension before and after the SHA interacts with the mineral surface, respectively, for the desired time; V is the volume of the resultant solution; and m is the weight of cassiterite particles.

2.4. Zeta-potential determination

The zeta potential of the cassiterite samples was determined using a Brookhaven ZetaPlus instrument. The ionic strength of the cassiterite suspension in all the measurements was maintained using 5×10^{-3} mol/L KNO_3 background solutions. The mineral suspension (0.01% mass fraction) was dispersed in electrolyte solutions and magnetically stirred for a desired time by a magnetic stirring apparatus. This step was performed in the presence of desired reagent concentrations at a determined pH regulated through HCl or NaOH stock solutions. After 10 min of settling of the resultant suspensions, the pH was measured and recorded, and the fine mineral particles were transferred to the measurement vessel for zeta-potential determination at room temperature.