



Effect of calcium ions on adsorption of sodium oleate onto cassiterite and quartz surfaces and implications for their flotation separation



Qicheng Feng^{a,b}, Shuming Wen^{a,b,*}, Wenjuan Zhao^{b,*}, Yu Chen^b

^a State Key Laboratory of Complex Nonferrous Metal Resources Clean Utilization, Kunming University of Science and Technology, Kunming 650093, PR China

^b Faculty of Land Resource Engineering, Kunming University of Science and Technology, Kunming 650093, PR China

ARTICLE INFO

Keywords:

Cassiterite

Quartz

Calcium ions

Flotation separation

Sodium oleate

ABSTRACT

The effect of calcium ions on the adsorption of sodium oleate on the mineral surfaces and flotation separation of cassiterite from quartz were studied in this work through micro-flotation tests, zeta potential measurements, solution chemistry calculation, surface adsorption experiments, and X-ray photoelectron spectroscopy (XPS) analysis. The micro-flotation tests showed that calcium species had little effect on the floatability of cassiterite and quartz at acidic pH, but the effect significantly changed at pH higher than 9.1. Cassiterite had good floatability at pH 8.2 and was less affected by calcium species. Quartz exhibited poor floatability in the absence and presence of calcium ions around pH 8.2, which facilitated its flotation separation from cassiterite. Zeta potential and surface adsorption results indicated that the adsorption of sodium oleate on the mineral surface was minimally influenced by calcium ions at acidic pH but was greatly affected at strong alkaline pH because of the specific adsorption of hydrated $\text{Ca}(\text{OH})^+$ and $\text{Ca}(\text{OH})_2$ on the mineral surface. The adsorption mechanism was identified by XPS analysis, demonstrating that calcium species were adsorbed onto the mineral surface through the interaction with O sites of cassiterite and quartz particles.

1. Introduction

Cassiterite (SnO_2) is a primary tin-bearing mineral that is universally upgraded based on its relatively high specific gravity through gravity separation [1–3]. The application of gravity separation is restricted when tin minerals exist in the form of fine and ultrafine particles. In this case, flotation is an alternative and effective method used to concentrate tin minerals [4–6]. Flotation is a physico-chemical separation technology that depends on the surface characteristics of both targeted and gangue minerals. As such, flotation is combined with advanced modern analysis and testing techniques, solution chemistry calculation, and density functional theory calculation to thoroughly understand the interaction mechanism between mineral surfaces and flotation reagents [7–11]. The flotation pulp environment, a complex system, may refer to the dissolution of various minerals, addition of flotation reagents, and utilization of water and may increase the difficulty in flotation separation of valuable minerals from gangue minerals. Collector is an important flotation reagent, and its adsorption is associated with the flotation recovery of cassiterite. Fatty acids and their salts can respond well with cassiterite, and their interaction mechanism has been studied in detail [12,13]. Styrene phosphonic acid [14], α -hydroxyoctyl phosphonic acid [15], sulfosuccinamate [16], sodium

dodecyl sulfate [17], and hydroxamic acid [18–20] have been also employed as collector in laboratory and actual plants to alter the hydrophobicity of cassiterite surfaces and improve its floatability. Among them, sodium oleate is an excellent collector with strong collection power and has been successfully applied to industrial production [12,21].

Quartz, a primary gangue mineral associated with tin minerals, adversely affects the quality of tin concentrates, so the flotation separation of cassiterite from quartz must be investigated. The floatability of quartz is very weak across the entire pH range when individual sodium oleate is employed as collector. However, quartz can be activated after treatment with multivalent metal ions, such as calcium, copper, lead, zinc, and ferric ions, and the underlying mechanism has been studied by means of solution measurement and surface analysis techniques [22–25]. Calcium ion, one of ubiquitous and unavoidable species in pulp solution, may be derived from the dissolution of calcium-bearing minerals (i.e., calcite, dolomite and fluorite) [26–28]. In addition, calcium-containing flotation reagents, such as lime and calcium chloride, are added into the pulp solution to condition the pulp environment and modify the surface property of targeted minerals [29,30]. Water used in flotation contains certain concentration of calcium ions, which will influence the flotation performance [31,32].

* Corresponding authors.

E-mail addresses: fqckmust@126.com (Q. Feng), shmwen@126.com (S. Wen), zwjkust@126.com (W. Zhao).

Several mechanisms, including electrostatic interactions, hydrogen bonding and chemisorption, have been proposed to account for the activation of calcium ions to quartz. The flotation recovery of cassiterite is influenced by metal cations [33]. Peng et al. [21] reported the adverse influence of Fe^{3+} on cassiterite flotation by using sodium oleate as collector. Feng et al. [34] systematically studied the activation mechanism of lead ions in cassiterite flotation with salicylhydroxamic acid as collector through flotation tests, adsorption experiments, zeta potential measurement, and XPS analysis. However, few studies were conducted to determine the effect of calcium ions on cassiterite flotation separation from quartz by using sodium oleate as collector.

This work aims to investigate the effect of calcium ions on the adsorption of sodium oleate on cassiterite and quartz surfaces and their floatability. Micro-flotation tests, zeta potential measurements, solution chemistry calculation, surface adsorption experiments, and XPS studies were performed to ascertain the adsorption behavior and mechanism of calcium ions and sodium oleate onto the mineral surfaces and identify the implications for their flotation separation.

2. Experimental

2.1. Materials

Pure samples of cassiterite and quartz minerals were purchased from Yunnan Province, China. X-ray diffraction and X-ray fluorescence analyses showed that the cassiterite and quartz samples were of high purity. The mineral samples were manually crushed and ground using an agate mortar. The ground products were dry sieved to prepare samples with particle size ranging from $-38\ \mu\text{m}$ to $20\ \mu\text{m}$. The samples were used for microflotation tests and adsorption studies of calcium ions and sodium oleate on cassiterite and quartz surfaces. The remaining samples ($-20\ \mu\text{m}$) were ground in the agate mortar to produce a fraction with particle sizes less than $5\ \mu\text{m}$ for zeta potential measurements.

2.2. Reagents

Sodium oleate was used as anionic collector to interact with cassiterite and quartz surfaces. Calcium chloride was employed as source of calcium species. Potassium nitrate was used to prepare background solution to adjust the ionic strength of the mineral suspensions during the zeta potential measurement. In brief, 0.1 mol/L hydrochloric acid and 0.1 mol/L sodium hydroxide stock solutions were used to adjust the solution pH in the experiments. All reagents used were of analytical grade. Pure deionized water was used in the experiments.

2.3. Micro-flotation tests

Micro-flotation tests on pure minerals were performed using varied pH levels in a small-scale flotation machine (mechanical agitation), with a volume capacity of 40 mL. In brief, 2.0 g of mineral samples were placed into the flotation cell and added with a certain amount of pure deionized water. The pulp pH was adjusted by adding 0.1 mol/L hydrochloric acid and 0.1 mol/L sodium hydroxide stock solutions. The mixture was added with 5×10^{-4} mol/L calcium chloride solutions and conditioned for 3 min as necessary. 4×10^{-4} mol/L sodium oleate was then added to the pulp suspension and subjected to flotation. The froth and sink products were separately filtered, dried, and weighed. Data from weighing was used to calculate the flotation recovery, and each test was repeated three times.

2.4. Measurements of zeta potentials

Zeta potentials of cassiterite and quartz samples were measured in 5×10^{-3} mol/L KNO_3 background electrolyte solutions by using a Brookhaven ZetaPlus instrument. The suspensions with 0.01%

concentration (mass fraction) of the minerals were conditioned in a beaker for a desired time in the presence of desired reagent concentrations. The pH of the resulting suspension was adjusted by adding 0.1 mol/L hydrochloric acid and 0.1 mol/L sodium hydroxide stock solutions. After the resultant suspensions were set for 10 min, fine mineral particles at the top of the suspension were collected to determine zeta potential at room temperature. At least three measurements were conducted for each pH condition, and their averages were taken as the final result.

2.5. Adsorption experiments

The adsorption experiments of sodium oleate onto the mineral surfaces as a function of pulp pH were carried out in a thermostatic water bath at 298 K. First, 2.0 g of mineral samples were dispersed into 100 mL of aqueous solution. The solution was then added with 0.1 mol/L hydrochloric acid and 0.1 mol/L sodium hydroxide stock solutions to adjust the pulp pH. 5×10^{-4} mol/L calcium chloride was added to the solution as necessary and conditioned for 30 min. 4×10^{-4} mol/L sodium oleate stock solutions were then added to the solution and stirred for another 30 min. After completing the adsorption process, the solid particles were separated by a centrifuge. The concentration of sodium oleate in the supernatant was analyzed by UV-vis spectrophotometer (UV-2700, Shimadzu, Japan). The adsorbed amount of sodium oleate on the mineral surface (Γ) was calculated according to the following equation:

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

where C_0 and C are the initial and supernatant concentrations of sodium oleate in the solution, respectively; V is the solution volume; and m is the weight of pure mineral particles.

2.6. XPS studies

The XPS spectra of the mineral particles were recorded under ultra-high vacuum conditions by using a PHI5000 Versa Probe II (PHI5000, ULVAC-PHI, Japan) with an Al K_{α} X-ray source. All elements in the measured samples were detected by a survey scan, and the high-resolution XPS spectra of a targeted element were then collected. All spectra were calibrated according to the C1s spectrum at binding energy of 284.8 eV for charge compensation.

Samples for XPS measurements were prepared as follows: 2.0 g of mineral samples were dispersed into 100 mL of the aqueous solution. The pulp pH was adjusted by adding 0.1 mol/L hydrochloric acid and 0.1 mol/L sodium hydroxide stock solutions. 5×10^{-4} mol/L calcium chloride was then added to the solution as necessary and conditioned for 30 min. The samples were collected, dried, and stored for XPS analysis.

3. Results and discussion

3.1. Flotation study

Fig. 1 shows the plots of the flotation recovery of cassiterite and quartz as a function of pulp pH in the absence and presence of calcium chloride with sodium oleate as collector. The flotation recovery of cassiterite significantly increased with increasing pH until pH 8.1 and then decreased in the absence of calcium species prior to the addition of sodium oleate. At acidic pH, oleate species exists in the form of oleic acid molecules and exhibits weak floatability because it is difficult to be adsorbed on the cassiterite surface [12]. Cassiterite could not be well floated at high pH due to the competitive adsorption of hydroxyl ions with oleate species. In the absence of calcium ions, quartz could not be floated across the entire pH range because of its weak interaction with oleate species as a result of the deficiency of active sites on the mineral

Download English Version:

<https://daneshyari.com/en/article/7043824>

Download Persian Version:

<https://daneshyari.com/article/7043824>

[Daneshyari.com](https://daneshyari.com)