Adsorption behavior of calcium ions and its effect on cassiterite flotation

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Abstract: Naturally, most of the cassiterite co-exists with sparingly soluble calcite, which makes it difficult to be fully utilized. Due to the adsorption of calcium ions dissolved from calcite, surface properties of cassiterite and its floatability can be influenced. Adsorption tests show calcium ions can adsorb on cassiterite surface. In the presence of Ca^{2+}, the zeta potentials of cassiterite shift to more positive values and the isoelectric point of cassiterite increases from pH 4.4 to pH 4.9. XPS results show that after calcium ions treatment, a strong calcium spectral peak at 347.65 eV is detected on the cassiterite surface and the chemical circumstance of oxygen atoms is changed. The presence of Ca^{2+} can significantly depressed the flotation behavior of cassiterite with salicylhydroxamic acid (SHA) as collector. Its recovery is decreased by 26.03% compared to that without Ca^{2+} at SHA dosage of 8.0×10^{-4} mol/dm³. When increasing SHA concentration to 9.0×10^{-4} mol/dm³ and above, the depression effect is partly compensated and the recovery rises by about 20%. Contact angle values of cassiterite measured by the bubble method correspond well to the flotation performance. Hence the depression mechanism of Ca^{2+} in cassiterite flotation can be interpreted in two aspects: 1) the consumption of SHA due to complexation reactions in pulp; 2) a decrease of effective adsorption site for SHA on cassiterite because of the adsorption of Ca^{2+}.

Keywords: cassiterite, calcium ions, adsorption, flotation, salicylhydroxamic acid

1.   Introduction

Tin and its compounds can be applied in many industries, such as soldering, plating, alloy, chemistry, and metallurgy (Angadi et al., 2015). Cassiterite (SnO_2) is the main resource of tin metal and usually co-exists with calcite ($CaCO_3$) (Tian et al., 2017). In industrial utilization, cassiterite should be separated from calcite to improve its purity. For fine cassiterite, flotation is an effective method and has been extensively employed for many decades (Cheng et al., 1993; Wu and Zhu, 2006). In flotation process, target minerals are separated from gangue minerals depending on their differences in surface hydrophobicity, which can be characterized and quantified by contact angle (Chau, 2009). However, the contact angle of natural cassiterite is around 35° as reported, which is not sufficient to float by itself (Ren et al., 2017). To acquire successful flotation, an effective collector should be selected to enhance its hydrophobicity. Salicylhydroxamic acid (SHA) has been proved to display excellent selectivity and widely used as collector for cassiterite flotation (Feng et al., 2017; Qin et al., 2011; Sun et al., 2016). In addition, ionic environment in pulp is quite complicated, and the existence of metal ions could influence the flotation recovery of target minerals. Feng, et al (Feng et al., 2017) proposed that flotation behavior of cassiterite was improved after treating by lead ions. The cassiterite surface formed complex Sn-O-Pb⁺, which could increase the adsorption amount of SHA on cassiterite surface.

   Many studies have been focused on the interaction mechanism of calcium ions with different kinds of minerals. Zhang et al. (Zhang et al., 2017) investigated the depression effect of calcium ions on monazite flotation with hydroxamic acid as collector. For the phosphate-oxygen active sites on the monazite surface, they discovered specially adsorbed $CaOH^+$ via hydrogen bonding, which can

decrease the hydrophobicity of monazite. They also proposed an interaction model between monazite, hydroxamic acid and calcium ions. Chen et al. (Chen et al., 2017) found calcium ions depressed the flotation behavior of sillimanite in the pH range of 2.0-9.0 using dodecylammonium chloride as collector, since the binding energy of RNH^{3+} on sillimanite surface was reduced in the presence of calcium ions. In another case, Liu et al. (Liu et al., 2015) claimed calcium ions could improve the flotation performance of spodumene using sodium oleate as collector in strongly alkaline solutions. They found that the $CaOH^+$ and $Ca(OH)_2$ contributed to the formation of oleate complexes, thus increasing the adsorption amount of sodium oleate. Although these studies demonstrated the influence of calcium ions on flotation, the interaction mechanism is complicated because it involves the mineral characteristics, calcium ions concentration, collector type, solution pH values, etc (Santos et al., 2010; Scott and Smith, 1993). The behavior of calcium ions in cassiterite flotation has not been studied systematically. Whether calcium ions can adsorb on cassiterite surface has not been reported, and how it affects the cassiterite flotation has not been revealed yet.

This paper is to investigate the adsorption behavior of calcium ions and its effect on the cassiterite flotation with SHA as collector. Dissolution experiment was performed to acquire the concentration of Ca^{2+} that dissolved from calcite surface. Adsorption tests, zeta potential measurements and XPS analysis were carried out to reveal the adsorption mechanism of calcium ions on cassiterite surface. Micro-flotation tests were performed to study the effect of calcium ions on the floatability of cassiterite. Contact angle measurements were implemented using the bubble method to analyse the influence of calcium ions on the hydrophobicity of cassiterite under different conditions. Then a rational model is presented to elucidate the depression mechanism of Ca^{2+} in cassiterite flotation.

2. Materials and methods

2.1. Materials and reagents

Pure cassiterite and calcite were obtained from the YiLiang mine and the Dulong mine in Yunnan province, China. The X-ray powder diffraction (XRD) patterns of them were illustrated in Fig. 1, indicating a high purity of cassiterite and calcite. The results of X-ray fluorescence (XRF) analysis indicated that cassiterite sample contained 97.89% SnO_2 and calcite sample contained 98.86% $CaCO_3$. The bulk crystals of cassiterite were polished to form a flat surface, which was later cleaned and used for contact angle measurements. Other samples were crushed and ground with an agate mortar and then screened to the size -38 μm for dissolution tests, adsorption tests and flotation tests. Some were further ground to -5 μm for XPS analysis and zeta potential measurements.

Salicylhydroxamic acid (SHA, 98% analytical purity) was purchased from Yika bio-technology company, Shanghai, China. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) were used to adjust the pH values. Fresh deionized water, with electrical resistivity >0.18 MΩm, was used in all experiments.
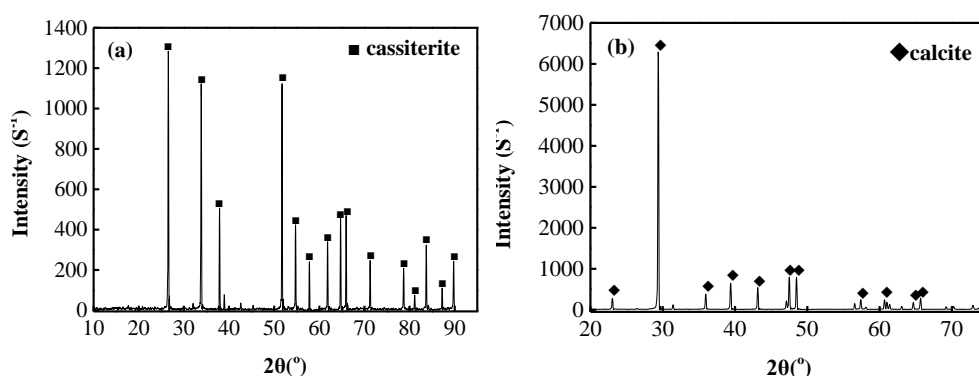

Fig. 1. XRD patterns of samples: (a) cassiterite, (b) calcite

2.2. Dissolution and adsorption tests

The dissolution and adsorption tests were carried out in a temperature-controlled water bath at 298 (±1) K. The solution containing calcium ions was prepared by dissolution of calcite. The concentration of

calcium ions was measured using inductively couple plasma-mass spectrometry (ICP-MS, XSERIES2, Thermos Fisher scientific, Germany). In the dissolution tests, 2.0 g of calcite was added to 25 cm³ solution and the suspensions was agitated with a magnetic stirrer for different time. After stirring, the suspension was immediately subjected to solid-liquid separation using a centrifuge, and the separated liquid was collected to quantify the calcium ions concentration. The maximum dissolution concentration of calcium ions was determined. The saturated calcium carbonate solutions were used for zeta potential measurements, XPS analysis and contact angle measurements.

In the adsorption tests, 2.0 g of cassiterite sample was added to 25 cm³ solution with different concentrations of calcium ions. The adsorption tests were conducted with a magnetic stirrer for 5 min. The adsorption time was consistent with that of flotation processes. And the suspension was also separated with a centrifuge to obtain the liquid and the concentration of calcium ions was measured.

2.3. Zeta potential measurements

The zeta potentials of the mineral were measured using a DELSA micro electrophoresis instrument (DELSA-440SX, Brookhaven, USA). The suspension was prepared by adding 0.01 g cassiterite (-5 μm) to the 25 cm³ deionized water or saturated calcium carbonate solutions. After magnetic stirring for 5 min, the pH of the suspension was adjusted to desirable values by adding HCl or NaOH solution. The tests were repeated three times.

2.4. XPS measurements

The XPS measurements were performed using a PHI5000 Versa Probe II (PHI5000, ULVAC-PHI, Japan) with an Al Kα X-ray source. Pure cassiterite (-5 μm) was washed by deionized water and dried in a vacuum oven at 298 K for 24 h. The other sample was prepared by adding 2.0 g pure cassiterite into 25 cm³ saturated calcium carbonate solutions and agitated for 30 min. The treated cassiterite sample was filtered, washed twice with deionized water and dried. A survey scan of the samples was first conducted to detect elemental compositions, and then high-resolution scans were used to measure the elements of Ca, Sn and O. The MultiPak spectrum software was used to calculate and analyze the results.

2.5. Micro-flotation tests

The micro-flotation tests were performed using a 25 cm³ cell (XFG II). The impeller speed was fixed at 1800 rpm. The micro-flotation tests involved three groups of tests: (1) Flotation tests were conducted within different concentrations of SHA and pH values. The optimum condition of SHA dosage and pH value was determined; (2) Under this condition, micro-flotation tests within different concentrations of Ca^{2+} solution were carried out; (3) Flotation tests were proceeded in saturated calcium carbonate solutions with higher dosage of SHA. In each test, 2.0 g of cassiterite sample was placed into the cell with 20 cm³ deionized water or Ca^{2+} solutions of different concentration. After adding the required amount of SHA, the suspension was agitated for 3 min, and pH was adjusted to a desired value by using HCl or NaOH solution. Then flotation was conducted for another 2 min. And floated cassiterite particles were filtered, dried and calculated to determine the corresponding flotation recovery. Each test was repeated three times. The average recovery of three flotation experimental results was reported.

2.6. Contact angle measurements

Contact angle measurements were implemented using the bubble method. The first three group measurements were conducted in solutions without Ca^{2+} ions, i.e., water and SHA solution ($8.0×10^{-4}$ mol/dm³ & $12.0×10^{-4}$ mol/dm³, respectively). The next three groups were carried out sequentially after adding Ca^{2+} ($1.6×10^{-4}$ mol/dm³). The cassiterite samples were treated for 30 min in designed solutions. Then the treated sample was placed on two stable supports with the polished surface facing downward in a rectangular glass chamber which was filled with the desired solution. A small bubble was produced by a specially designed U-shaped needle connecting with a microsyringe. The bubble was then released from the needle tip at a fixed distance (0.8 cm) below the submerged specimen surface. The rising bubble

was captured by the solid surface due to buoyant transportation. After the air bubble attached to the solid surface, images were recorded by a microscopic camera. Contact angle was calculated automatically after processed with a Matlab program. This procedure was repeated 10 times for each set of solution.

3. Results and discussions

3.1. Dissolution and adsorption tests

Mineral dissolution rate is defined as the quantity of lattice ions dissolved in solution at a fixed time. It is proposed that the mineral dissolution rate correlates with the particle size of mineral, the environmental temperature, the pH of solution, and so on (Shi et al., 2013; Subhas et al., 2015). Pure cassiterite is almost chemically inert and highly insoluble. As a result, the concentration of constituent ions in solution is negligible (Angadi et al., 2015). However, calcite is a sparingly soluble mineral, in which the lattice ions such as calcium ions can be dissolved in solution. Fig. 2 presents the concentration of calcium ions dissolved from calcite surface as a function of time at pH 7.0. The concentration of calcium ions rapidly increases within the time range of 5-40 min. It reaches equilibrium beyond this moment at around $1.6×10^{-4}$ mol/dm^3.
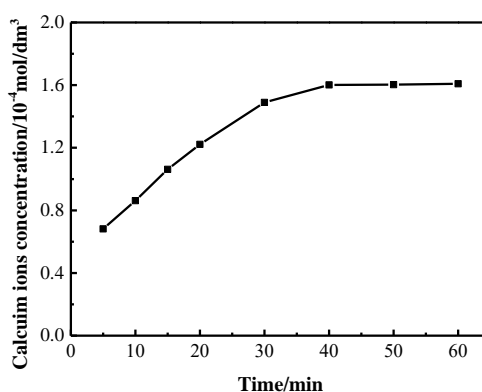
Fig. 2. Concentration of dissolved calcium ions from calcite as a function of time at pH 7.0
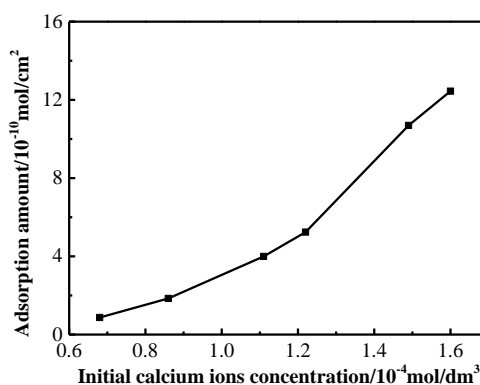
Fig. 3. Adsorption amount of calcium on cassiterite surface as a function of initial concentration

To verify whether calcium ions can adsorb on cassiterite surface, adsorption tests were performed with Ca^{2+} solution of different concentrations. As shown in Fig. 3, calcium ions can adsorb on cassiterite surface, and the adsorption amount of calcium ions increases along with the increase of the initial concentration of calcium ions. The adsorption amount reaches approximately $12.4×10^{-10}$ mol/cm^2 with an initial concentration $1.6×10^{-4}$ mol/dm^3.

3.2. Effect of calcium ions on Zeta potential of cassiterite

In order to investigate the adsorption mechanism of calcium ions on the cassiterite surface, cassiterite zeta potentials were measured as a function of pH before and after adding Ca^{2+}. The adsorption

mechanism is investigated using electro-kinetic tests based on the fact that the isoelectric point (IEP) of mineral particles typically shift when specific adsorption occurs in the stern layer. As shown in Fig. 4, the IEP of the untreated cassiterite is achieved at about pH 4.4, which agrees with values reported in previous studies (Li et al., 2015; Tan et al., 2016). After adding calcium ions 1.6×10^{-4} mol/dm³, the zeta potentials of cassiterite positively shift across the entire pH range, and the IEP increases from pH 4.4 to pH 4.9. This shift can be attributed to the coverage of calcium ions on cassiterite surface.
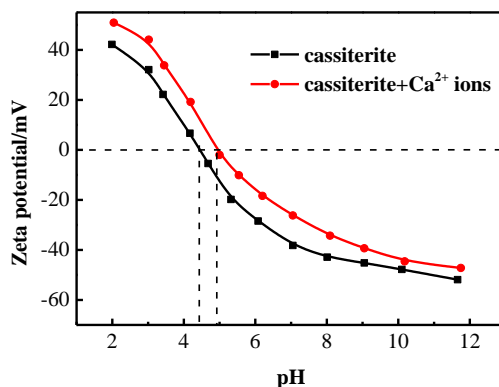
Fig. 4. Zeta potential of pure cassiterite (square line) and cassiterite treated with calcium ions 1.6×10^{-4} mol/dm³ (dot line) as a function of pH

As shown in Fig. 5, the distribution diagram of calcium species is calculated using Visual MINTEQ 3.1 software as the function of pH at the concentration of 1.6×10^{-4} mol/dm³. The solution contains various calcium species, of which Ca^{2+} is the main species at pH values below 9.0. After the pH exceeds 9.0, the species of $CaCO_3$ (aq) start to appear. The species of $CaOH^+$ come into existence in the pH range of 10.0 -12.0. There are also few species of $CaHCO_3^+$ across the entire pH range. Fig. 4 and Fig. 5 signify that the increase in the zeta potential is caused by adsorption of Ca^{2+} below pH 9.0. After the solution pH excessed 9.0, the uncharged or unicharged calcium species, e.g. $CaCO_3$, $CaOH^+$ and $CaHCO_3^+$, caused the shift on the cassiterite surface become relatively weak.
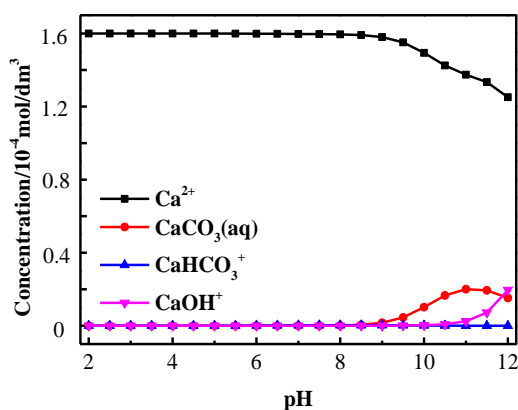

Fig. 5. Distribution diagram of calcium species as the function of pH at total calcium concentration of 1.6×10^{-4} mol/dm³

3.3. Adsorption mechanism of calcium ions on cassiterite surface

XPS measurements are applied to further reveal the effect of calcium ions on surface properties of cassiterite. Fig. 6a shows XPS survey spectra of untreated cassiterite. As expected, C, Sn and O are the major constituents and there is no evidence of other elements or impurities. Fig. 6b illustrates XPS survey spectra of cassiterite treated by calcium ions. An obvious Ca spectral peak appears at 347.65 eV, which confirms the adsorption of calcium species on the cassiterite surface.

The high-resolution XPS spectra of Ca, Sn and O are presented in Figs. 7-9. The Ca signal is not detected on pure cassiterite surface (Fig. 7a). For treated cassiterite, the Ca2p spectra are presented in

Fig. 7b, which is fitted by two spin-orbit split peaks, with binding energies of 347.65 eV for the Ca2p3/2 level and 351.22 eV for the Ca2p1/2 level. These peaks are ascribed to the Ca species from calcite (Zhang et al., 2018). Fig. 8a shows the Sn3d spectra of the pure cassiterite, and a double structure is obtained with a binding energy of 495.07 eV for the Sn3d3/2 level and 486.59 eV for the Sn3d5/2 level, respectively (Li et al., 2015). As shown in Fig. 8b, after calcium ions treatment, almost no change is found in the binding energy of Sn3d spectra. This result indicates that there are weakly interactions between calcium ions and Sn sites on the cassiterite surface. To further explore the interaction of calcium ions on the mineral surface, the O1s XPS spectra are analyzed. Fig. 9a illustrates that the O1s XPS peaks of pure cassiterite are composed of two components, 530.43 eV for Sn-O and 532.12 eV for O-H (Nowak et al., 2000). The O1s XPS peaks of treated cassiterite are shifted to higher binding energies at 530.70 eV and 532.71 eV, indicating that chemical circumstance of oxygen atoms has been changed (Fig. 9b). Based on XPS analysis, it can be concluded that Ca^{2+} can attach on cassiterite surface, resulting the change of chemical circumstance of O atoms.
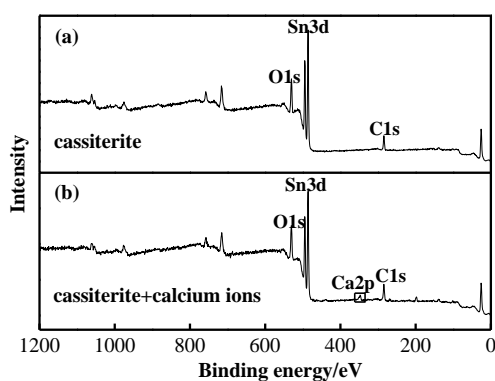

Fig. 6. XPS survey spectra: (a) pure cassiterite; (b) cassiterite treated with 1.6×10^{-4} mol/dm³ calcium ions at pH 7.0
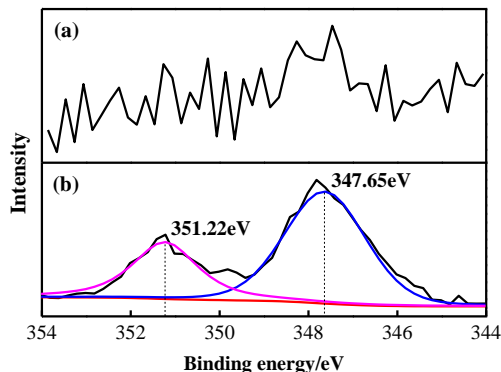

Fig. 7. Ca2p XPS spectra: (a) pure cassiterite; (b) cassiterite treated with 1.6×10^{-4} mol/dm³ calcium ions at pH 7.0
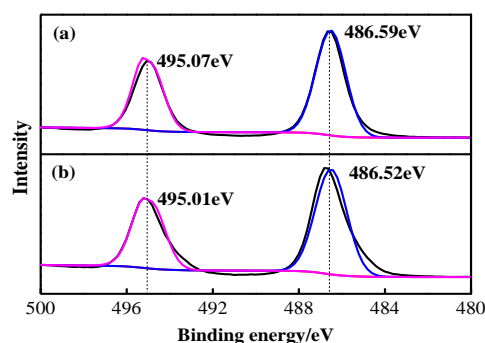

Fig. 8. Sn3d XPS spectra: (a) pure cassiterite; (b) cassiterite treated with 1.6×10^{-4} mol/dm³ calcium ions at pH 7.0
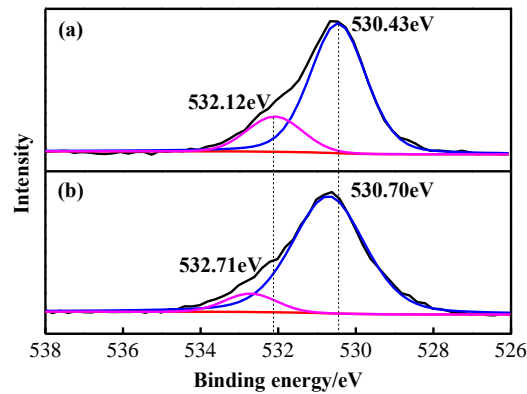
Fig. 9. O1s XPS spectra: (a) pure cassiterite; (b) cassiterite treated with 1.6×10^{-4} mol/ dm^3 calcium ions at pH 7.0

3.4. Effect of calcium ions on cassiterite floatability

Fig. 10 shows the recovery of cassiterite conditioned with different SHA dosages and pH values. At pH 7.0, the recovery of cassiterite gradually increases as SHA dosages increase from 2.0×10^{-4} mol/dm^3 to 8.0×10^{-4} mol/dm^3 (Fig. 10a), reaching 72.15%. No significant increase in the recovery is observed at higher concentrations. Fig. 10b shows the recovery of cassiterite with 8.0×10^{-4} mol/dm^3 SHA as a function of pH. The recovery increases with increasing pH, while it decreases after pH over 7.0. Thus, the optimum condition is 8.0×10^{-4} mol/dm^3 SHA solution at pH 7.0 for flotation of pure cassiterite. In the following section, flotation tests were performed under this condition to explore the effect of Ca^{2+} concentration on cassiterite flotation.
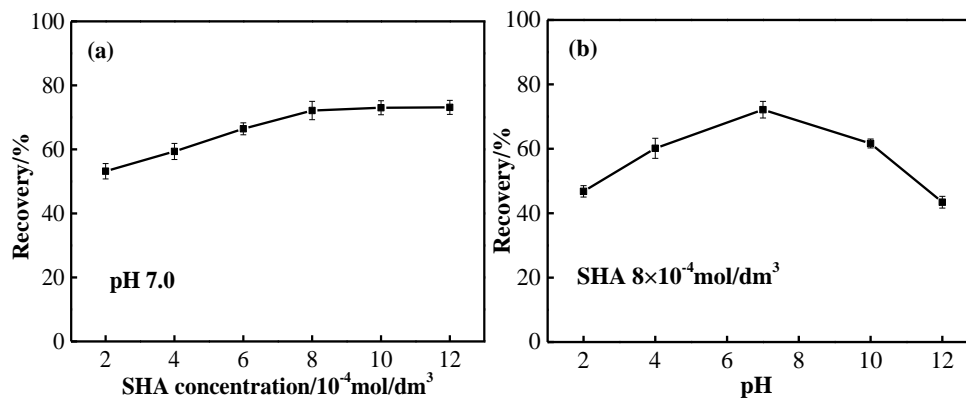

Fig. 10. Effect of (a) salicylhydroxamic acid dosages and (b) pH values on the flotation recovery of cassiterite

Fig. 11 demonstrates the recovery of cassiterite in presence of calcium ions. The recovery of cassiterite decreases from 72.15% (no Ca^{2+}) to 67.26% at Ca^{2+} concentration of 0.68×10^{-4} mol/dm^3. It gradually decreases along with the increase of Ca^{2+} concentration. The cassiterite shows fairly low floatability and the recovery is only 46.12% when Ca^{2+} reaches the saturated concentration of 1.6×10^{-4} mol/dm^3. This phenomenon clearly shows a significant depression impact of Ca^{2+} on cassiterite flotation.

3.5. Discussion

To uncover the depression mechanism of Ca^{2+} in cassiterite flotation, more micro-flotation tests with higher dosage of SHA and contact angle measurements were conducted. According to the literature, there exists complexation reactions between SHA and Ca^{2+} in solution (Zhao et al., 2013). Thus, part of SHA will be consumed by Ca^{2+} in pulp, resulting insufficient amount to interact with cassiterite surface and consequently, leading to a lower recovery rate. To quantify how much SHA is consumed by Ca^{2+} in our case, flotation tests with higher SHA concentration are further performed. Fig. 12 shows the recovery of cassiterite as a function of SHA concentration in saturated calcium carbonate solutions (1.6×10^{-4} mol/dm^3). When the concentration of SHA increases from 8.0×10^{-4} mol/dm^3 to 9.0×10^{-4} mol/dm^3, the recovery of cassiterite remarkably increases from 46.12% to 63.25%. Above this

concentration, the recovery of cassiterite increases slightly. The maximum recovery of cassiterite is around 65% at the SHA concentration of 12.0×10^{-4} mol/dm^3, which is still lower than that without Ca^{2+} (72.15%). This evidence indicates that the supplement of SHA could offset part of the depression impact of Ca^{2+} as recovery increases from 46.12% to about 65%, while the other part of depression effect could not be compensated (65% vs. 72.15%). It implies that the adsorption of Ca^{2+} on cassiterite surface inevitably contributes to this depression effect. To further excavate the interaction mechanism and explain it explicitly, contact angle measurements were conducted to quantify the change of surface hydrophobicity under different conditions.
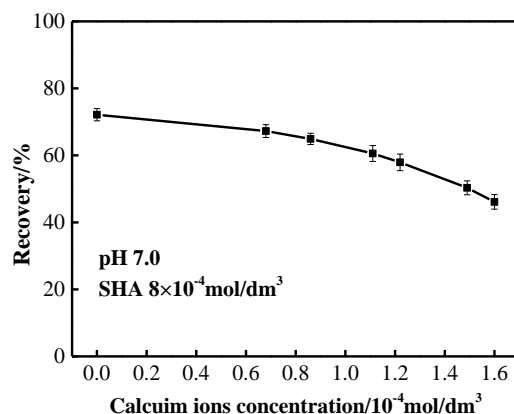

Fig. 11. Effect of calcium ions concentration on the flotation recovery of cassiterite
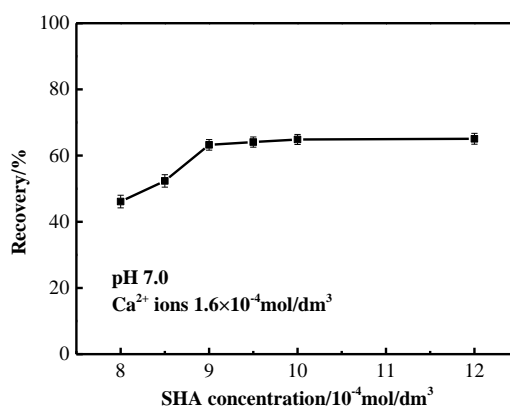

Fig. 12. Effect of salicylhydroxamic acid dosages on the flotation recovery of cassiterite in the presence of 1.6×10^{-4} mol/dm^3 calcium ions at pH 7.0

Contact angle of cassiterite in different solutions is shown in Fig. 13: (a) & (d) contact angles within deionized water and Ca^{2+} 1.6×10^{-4} mol/dm^3 solution are around 33.7°; (b) & (c) contact angles within SHA solution of 8.0×10^{-4} mol/dm^3 & 12.0×10^{-4} mol/dm^3 are almost the same about 45°; (e) & (f) in presence of Ca^{2+} 1.6×10^{-4} mol/dm^3, contact angles are 40.41° and 43.12° with SHA 8.0×10^{-4} mol/dm^3 and 12.0×10^{-4} mol/dm^3, respectively. These results corresponding to the flotation behavior of cassiterite under different conditions. Specifically, with existence of Ca^{2+}, contact angle decreases from 45.08° to 40.41° as shown in (b) & (e), declaring that Ca^{2+} impedes the hydrophobization process in SHA solution. After increasing the SHA concentration to 12.0×10^{-4} mol/dm^3, average contact angle ascends to 43.12° as shown in (f), indicating that higher SHA concentration can partly compensate the depression effect due to complexation of Ca^{2+} and SHA. Therefore, it is concluded that the adsorption of Ca^{2+} account for the irreversible part of depression effect.

According to above results, the presence of calcium ions has negative effect on the flotation recovery of cassiterite with SHA as collector. As is known, there exists complexation reactions between Ca^{2+} and SHA. This complex has a stability constant of about 2.4 (Wang and Hu, 1988), which means it is not stable and will dissociate in solution. The adsorption mechanism of SHA on cassiterite surface has been well studied, and a recommended adsorption model of SHA on cassiterite surface has been presented

(Qin et al., 2012). Based on the knowledge and discovery in this work, a reasonable model to explain the depression mechanism of calcium ions in cassiterite flotation with SHA as collector was illustrated as is seen in Fig. 14. It can be interpreted in two aspects: 1) the explicit one is the consumption of SHA by complexation reactions with Ca^{2+}, which can be offset through adding considerable amount of SHA; 2) the adsorption of Ca^{2+} on cassiterite surface, which is confirmed by adsorption tests, zeta potential measurements and XPS analysis, can occupy the effective interaction sites of SHA and Sn^{4+}. Though Ca^{2+} can combine with SHA through complexation, its instability results in a less adsorption of SHA on cassiterite in total.

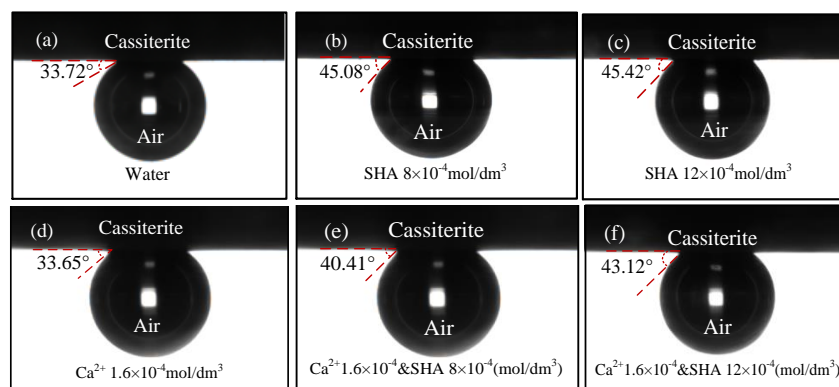Fig. 13. The contact angle of cassiterite in different solutions: (a) water; (b) salicylhydroxamic acid solution of 8.0×10^{-4} mol/dm³; (c) salicylhydroxamic acid solution of 12.0×10^{-4} mol/dm³; (d) calcium ions solution of 1.6×10^{-4} mol/dm³; (e) mixture of calcium ions and salicylhydroxamic acid solution (1.6×10^{-4} mol/dm³ and 8.0×10^{-4} mol/dm³, respectively); (f) mixture of calcium ions and salicylhydroxamic acid solution (1.6×10^{-4} mol/dm³ and 12.0×10^{-4} mol/dm³, respectively)

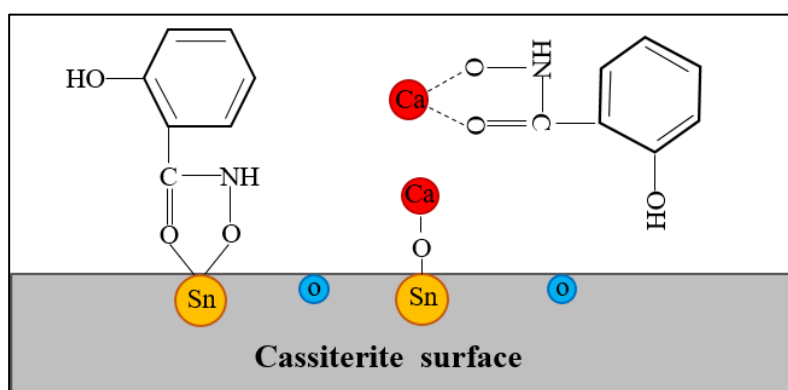

Fig. 14. A reasonable interaction model of salicylhydroxamic acid and Ca^{2+} in cassiterite flotation

4.   Conclusions

The present work confirms that the calcium ions dissolved from calcite can adsorb on cassiterite surface, and negatively influences the flotation behavior of cassiterite with SHA as collector. The flotation recovery of cassiterite can be decreased by as much as 26.03% compared to that without calcium ions. The complexation reactions in solution and adsorption of Ca^{2+} on cassiterite surface are main troubles accounting for this depression effect, which is verified by flotation tests with higher concentration SHA and contact angle measurements. This study provides a fundamental understanding of Ca^{2+} behavior in cassiterite flotation with SHA as collector. It is of great importance to avoid this depression effect through adjusting the reagent regimes in cassiterite flotation.

Acknowledgments

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