

Article

Selective Flotation of Cassiterite from Calcite with Salicylhydroxamic Acid Collector and Carboxymethyl Cellulose Depressant

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Received: 18 June 2018; Accepted: 24 July 2018; Published: 26 July 2018



Abstract: Cassiterite is the most common and important tin-bearing mineral, and calcite, a primary gangue mineral is generally found in tin deposit. The flotation separation of cassiterite from calcite remains a challenge due to their similar response to traditional reagents. In cassiterite flotation, sodium oleate (NaOL) and sodium silicate (SS) have been widely used as a collector and a depressant, respectively. However, the low selectivity of NaOL and the large amount of SS required (which leads to serious problems in wastewater treatment) remain a difficult issue. In this study, a novel reagent scheme using lead nitrate as the activator, salicylhydroxamic acid (SHA) as the collector and carboxymethyl cellulose as the depressant was employed to improve the separation selectivity of cassiterite from calcite. Results of the flotation experiment using this new reagent scheme showed that compared with the previously reported scheme using benzohydroxamic acid (BHA) as the collector, the separation of cassiterite from calcite exhibited a higher selectivity and selectivity index (SI). The mechanism of the selective separation was investigated by zeta potential measurements, Fourier transform infrared and X-ray photoelectron spectroscopy analysis.

Keywords: cassiterite; calcite; separation; salicylhydroxamic acid; carboxymethyl cellulose

1. Introduction

Tin and its compounds have a broad range of applications due to their special properties such as malleability, ductility and corrosion resistance [1–4]. Cassiterite (SnO_2), the primary ore mineral for tin, is related to the granitic host rock in hard-rock deposits [5]. Traditionally, cassiterite was mainly recovered from tin ore by gravity separation using equipment including jigs, spiral chutes and shaking tables, at a relatively coarse particle size [6,7]. In recent years, due to the increasing fine-grained dissemination of cassiterite with gangue minerals, flotation has become a supplementary and/or alternative method for comprehensive cassiterite recovery. However, the flotation separation of cassiterite from gangue minerals (especially calcite (CaCO_3)) remains a challenge due to their similar response to traditional reagents. Therefore, increasing importance has been attached to selective reagents due to their dominant roles in high quality and high recovery concentration.

The development of selective collectors for cassiterite flotation is a relatively popular field [8]. Oleic acid and its derivatives are the most widely used collectors in oxidized ore flotation [9–12]. The downside of this fatty acid collector is its low selectivity and poor solubility at low temperatures [5].

P-tolyl arsonic acid was proved to be a selective collector for cassiterite, yet due to its high cost and environmental concerns, the commercial production of this reagent ceased after 1975 [5]. Phosphonic acids exhibit a strong collecting capacity for cassiterite in acidic media but can cause severe equipment corrosion. More recently, hydroxamic acids or their salts have been extensively used as a chelating type of chemical reagent in mineral flotation due to their strong selective complexation with various metal ions [13–15], among which, benzohydroxamic acid (BHA) shows excellent selectivity but limited collecting ability in cassiterite flotation [14]. Thus, BHA and metal ions (such as Pb^{2+} and Fe^{3+}) are used as the collector and activators, respectively, to float cassiterite and enhance its recovery [16–19]. Recently, it has been reported that octanol, as an auxiliary collector, promotes the adsorption of BHA on the surface of cassiterite and reduces the consumption of BHA [20]. Inspired by these reports, salicylhydroxamic acid (SHA) is considered to be a candidate collector for cassiterite flotation through the addition of a hydroxyl group to the BHA benzene ring [15,21]. Qin et al. [15] reported that SHA can be physically and chemically adsorbed on the cassiterite surface. Besides, Feng et al. [15,21] reported that the addition of lead ions can improve the adsorption of SHA on cassiterite. Unfortunately, they did not investigate the function of SHA, with or without lead ion, in separating cassiterite from its main gangue minerals, such as calcite.

Calcite is the primary gangue mineral for cassiterite flotation and it needs to be selectively depressed [14]. Sodium silicate (or water glass) is an industrial depressant widely used for calcite flotation [22–24]. Its biggest drawback lies in the huge dosage (as much as 6–10 kg per ton of run-of-mine), which not only reduces the cassiterite recovery [25–27], but also makes it more difficult to treat the wastewater due to its slow sedimentation rate [22,28]. Therefore, an alternative depressant should be identified to replace sodium silicate. Carboxymethyl cellulose (CMC) is a commonly used polymer depressant for talc flotation [29–33]. Furthermore, the prior addition of calcium ions can enhance the depression effect of CMC on talc flotation [29–33] due to its stronger interaction between calcium ion species such as $\text{Ca}(\text{OH})^+$ and CMC. Inspired by these reports, we hypothesized that CMC could be a potential depressant for calcite. However, few studies have reported CMC as a depressant for calcite [34,35].

In this work, a novel reagent scheme for cassiterite flotation from calcite was evaluated by experiments of a single mineral sample flotation test using lead nitrate as the activator, SHA as the collector and CMC as the depressant. This new reagent scheme was further evaluated in the flotation experiments using mixed binary mineral samples. The mechanism of selective separation was investigated through zeta potential measurement, Fourier transform infrared and X-ray photoelectron spectroscopy analysis.

2. Materials and Methods

2.1. Materials and Reagents

Natural cassiterite and calcite crystals were obtained from Yunnan Province, China. The high purity of the cassiterite and calcite was confirmed by X-ray diffraction (XRD) data as shown in Figure 1. Initially, the crystal samples were ground in a porcelain ball mill and wet sieved to produce a particle size fraction of $-74 + 38 \mu\text{m}$ for flotation experiments. Then, samples were further ground to $-5 \mu\text{m}$ in an agate mortar for zeta potential measurements, Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS) analysis.

Analytically pure salicylhydroxamic acid ($\text{C}_7\text{H}_7\text{NO}_3$, SHA) with 99% purity was purchased from Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China), lead nitrate (LN) with 99% purity from Tianjin Kermil Chemical Reagents Development Centre (Tianjin, China), chemically pure sodium carboxymethyl cellulose (CMC) (degree of substitution (DS) = 1.2, molecular weight = 250,000, viscosity = 1500–3100 mpa·s) from Sinopharm Chemical Reagent Co., Ltd., Beijing, China, and Terpeneol with 95% purity from Guangdong Xilong Chemical Co., Ltd., Guangdong, China, which were used as the

collector, activator, depressant and frother, respectively. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were used for pH modification.

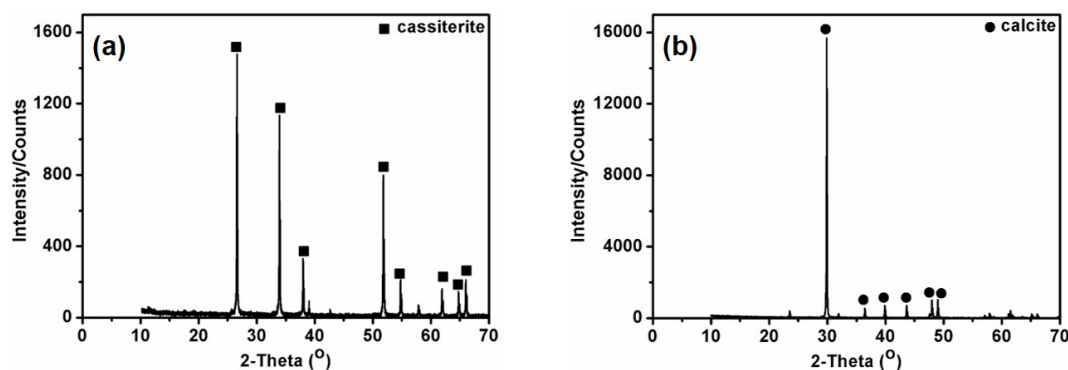


Figure 1. XRD spectrum of cassiterite (a) and calcite (b) minerals.

2.2. Flotation Tests

As described in previous publications, flotation tests of single mineral and mixed binary minerals were performed in an XFG-type flotation machine at a spindle speed of 1600 rpm [16–18,34]. In each test, the mineral suspension was prepared by adding 2.0 g of single mineral samples (1 g cassiterite and 1 g calcite for mixed binary minerals flotation) and 40 mL of deionized water to the cell. After the sequential addition of LN activator, CMC depressant and SHA collector in a desired dosage, the pulp was conditioned for 3, 5 and 5 min, respectively. Then, the pH value was adjusted by pH regulators (NaOH and HCl) and recorded. Finally, terpeneol (1 μ L) was introduced with 1 min conditioning time followed by collecting floated products for 6 min. For single mineral flotation, both floated and unfloated particles were collected, dried and weighted to calculate the recovery rate. For mixed binary minerals, the SnO_2 and CaCO_3 grade of the concentrates and tailings were analysed. Each test was repeated at least three times.

2.3. Zeta Potential Measurements

Zeta potential measurements were conducted in 0.01 mol/L KNO_3 background electrolyte solution using a JS94H microelectrophoresis instrument (Shanghai Zhongchen Digital Technic Apparatus Co., Shanghai, China). The mineral samples were suspended in water or flotation reagent (Pb^{2+} and SHA) solution at 16 mg per 80 mL before being agitated with a magnetic stirrer for 10 min prior to each measurement. After the resultant suspension was settled for 6 min, the supernatant liquid was collected for measurement. At least three measurements were conducted for each pH condition, and the average value as well as the standard deviation was calculated. The cassiterite suspension was conditioned using reagents within the pH range of 2–12. Due to the dissolution of calcite mineral, it was so difficult to adjust the pH of the calcite-contained suspension to $\text{pH} < 7$ that the pH range tested for calcite was limited to a range from neutral to basic pH values.

2.4. FTIR Spectroscopy Measurements

The FTIR transmission spectra were recorded at room temperature by a Bruker Alpha (Thermo Fisher, Waltham, MA, USA) Spectrophotometer, ranging from 400 to 4000 cm^{-1} . The mineral sample (2.0 g) with a size of $\sim 5 \mu\text{m}$ was placed in solution (40 mL) with or without the flotation reagents, at concentrations that were used in the flotation experiments. In the preparation of test samples, extra attention was paid to the removal of excess flotation reagents by filtering the suspension and repeatedly washing the residues with DI water. The test samples were dried and vacuum stored. The spectra of the samples were taken with KBr pellets.

2.5. XPS Analysis

XPS data was acquired using a K-Alpha 1063 XPS spectrometer (Thermo Fisher, Waltham, MA, USA). Al K α was used as the sputtering source in the analytical chamber (12 kV, 6 mA and 1.0×10^{-7} Pa).

3. Results and Discussion

3.1. Single Mineral Flotation Experiments

Figure 2a shows the recovery of cassiterite and calcite as a function of SHA concentration in the absence of LN. As SHA concentration increased from 10 mg/L to 30 mg/L, cassiterite recovery gradually rose to a maximum value of 36.51%, and when SHA concentration reached 30 mg/L, calcite recovery stood at 25.81%. Thus, 30 mg/L of SHA was adopted in the following flotation experiments.

Figure 2b shows the recovery of cassiterite and calcite as a function of LN concentration in the presence of 30 mg/L SHA. As LN concentration increased to 5 mg/L, cassiterite recovery gradually climbed to 92.21% and then remained stable despite further increases in LN concentration. Thus, 5 mg/L of LN was employed in the following flotation experiments.

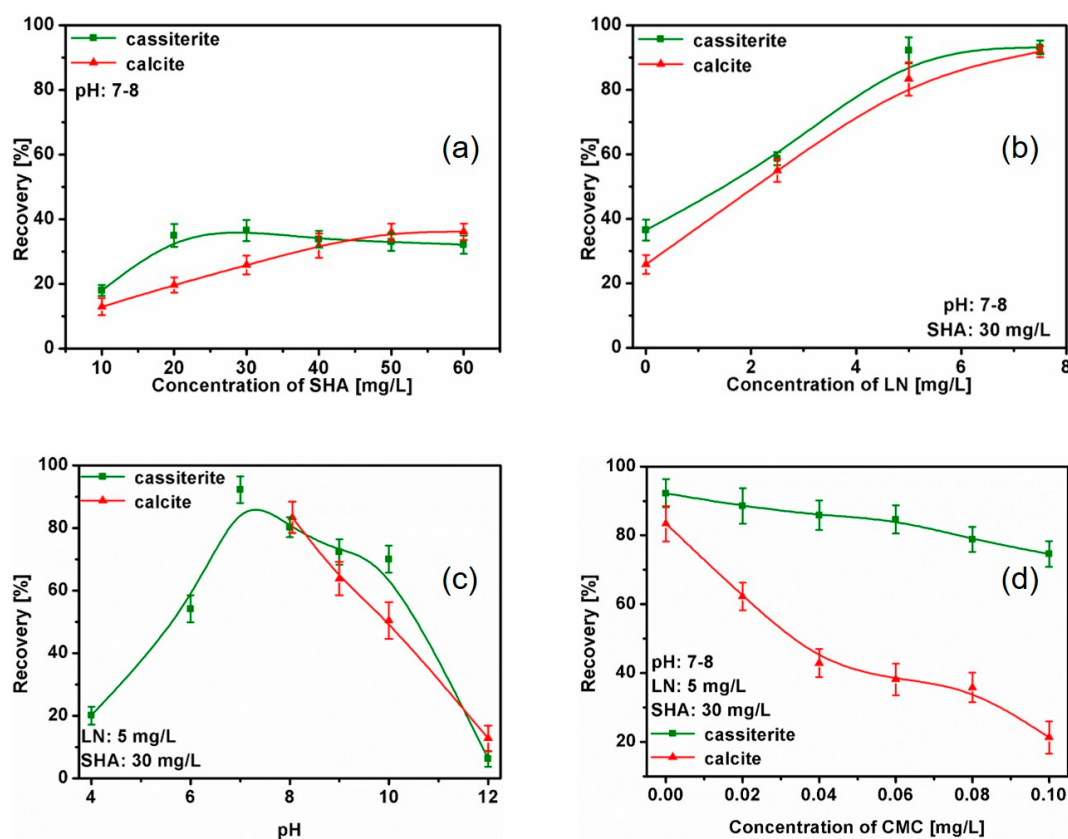


Figure 2. Recovery of cassiterite and calcite as a function of salicylhydroxamic acid (SHA) concentration (a), lead nitrate (LN) concentration (b), solution pH (c) and carboxymethyl cellulose (CMC) concentration (d).

Figure 2c demonstrates the flotation recovery of cassiterite and calcite as a function of pH in the presence of LN and SHA. As the value of pH increased from 4 to 7, cassiterite recovery gradually rose to a maximum value of 92.21% before it slowly decreased as the pH values continued to rise. Due to the dissolution effect of calcite mineral, it was very difficult to adjust the pH of the calcite-contained suspension to pH < 7. Hence, the pH tested for calcite flotation experiments was limited to a range

from neutral to basic pH values. As shown in Figure 2c, calcite recovery dropped from 83.37% to 12.75% as the pH value increased from 8 to 12. In a bid to improve cassiterite recovery, the desirable pH values for separating cassiterite from calcite was set within the neutral pH range, i.e., probably the natural pH of the suspension. Thus, pH 7–8 was selected for the following flotation experiments.

Figure 2d depicts the flotation recovery of cassiterite and calcite as a function of carboxymethyl cellulose (CMC) concentration. As CMC concentration rose to 0.1 mg/L, cassiterite recovery remained almost unchanged at around 80% whereas for calcite recovery, there was a dramatic decrease from 83.27% to 21.26%. In the presence of CMC, this distinct recovery difference shows that it is possible to separate cassiterite and calcite.

When BHA was used as the collector in the flotation of cassiterite and calcite, calcite recovery plummeted to 26.73% as CMC concentration increased to 4 mg/L, while that of cassiterite declined slowly to 50% [34]. The extensive use of CMC will depress cassiterite to some extent and affect the separation efficiency. This result indicates that compared with BHA, SHA exhibits much better selectivity and collecting ability, which helps to reduce the consumption of CMC depressant and facilitate the cassiterite recovery.

Figure 3 shows the recovery of cassiterite and calcite as a function of flotation time in the presence of 5 mg/L of LN and 30 mg/L of SHA. As the most widely accepted flotation model, the classical first-order model was used here to calculate the proposed rate constant (k). The k value can be calculated according to the Equation (1),

$$\varepsilon = \varepsilon_{\infty}[1 - \exp(-kt)] \quad (1)$$

where ε represents the recovery at time (%); ε_{∞} is the ultimate recovery (%); t is the flotation time and k is the first-order rate constant (s^{-1}). According to Equation (1), the ultimate recovery of cassiterite and calcite were $93.61 \pm 2.06\%$ and $19.61 \pm 0.79\%$, respectively. The flotation rate constants of cassiterite and calcite were $0.03784 \pm 0.00283 s^{-1}$ and $0.01961 \pm 0.00141 s^{-1}$, respectively.

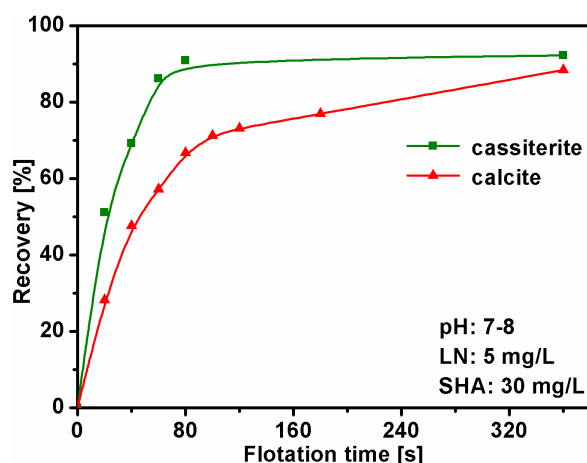


Figure 3. Recovery of cassiterite and calcite as a function of flotation time in the presence of 5 mg/L of LN and 30 mg/L of SHA.

3.2. Mixed Binary Mineral Flotation Experiments

Based on the above single mineral flotation experiment results, flotation experiments were conducted to separate cassiterite from mixed binary minerals which were prepared by mixing cassiterite and calcite at a mass ratio of 1 to 1, namely, the mixtures contained approximately 50% SnO_2 . Figure 4 shows the grade and recovery of SnO_2 in mixed binary minerals in the presence of 2.5 mg/L LN and 15 mg/L SHA at pH 7–8 as a function of CMC concentration. As CMC concentration increased from 0 to 0.05 mg/L, the SnO_2 grade also presented an upward trend, increasing from

81.91% to 97.90% whereas for SnO₂ recovery, there was a drop from 83.78% to 54.39%. To strike a balance between the grade and recovery of cassiterite, a so-called “trade-off domain” where CMC concentration was set at 0.01–0.02 mg/L was found. Under good control, the recovery and grade of SnO₂ reached approximately 90% and 75%, respectively.

It is interesting to note that in the absence of CMC, the recovery of SnO₂ and CaCO₃ stood at 81.91% and 20.66%, respectively, indicating the excellent selectivity of the SHA collector in the separation of cassiterite from binary mixed minerals. Although the results seemed to be inconsistent with those of the single mineral flotation, as shown in Figure 2d, this seeming inconsistency can be explained by the competitive adsorption of LN and SHA as well as the different flotation rate (*k*) of two minerals using a reagent scheme (2.5 mg/L LN, 15 mg/L SHA and 0 mg/L CMC) in binary mineral flotation. Figure 2a,b indicates that there is stronger adsorption of LN and SHA on cassiterite than calcite. According to Equation (1), the cassiterite flotation rate is almost twice that of calcite. Figure 5a shows that at the initial stage of flotation (0 min), the cassiterite particles tended to float to the flotation pulp surface, forming stable mineralized froths. Figure 5b shows that after 3 min of flotation, the stable mineralized froths disappeared as the floated cassiterite particles were scraped from the pulp surface, leading to significant consumption of LN, SHA and terpineol frother. Thus, the lower the calcite flotation rate and flotation reagent dosage left in the pulp, the lower the calcite recovery became. The results also indicate good selectivity of the novel reagent scheme for the separation of cassiterite from calcite.

Gaudin’s selectivity index (*SI*) was calculated based on Equation (2) [36]. By definition, *SI* is selected as the criterion to evaluate the separation performance, and the larger the *SI* value is, the better the separation performance becomes.

$$SI = \sqrt{\frac{R_a \times J_b}{(100 - R_a) \times (100 - J_b)}} \quad (2)$$

R_a represents the recovery of cassiterite in flotation concentrate and J_b represents the recovery of calcite in the flotation tailing.

As shown in Table 1, when SHA was used as the collector, the *SI* value in the presence of CMC was a bit lower than that without CMC, indicating that CMC has a good selective depressing effect on calcite. The *SI* value with SHA was almost doubled compared to that of BHA, indicating that the selectivity of SHA is much better than BHA.

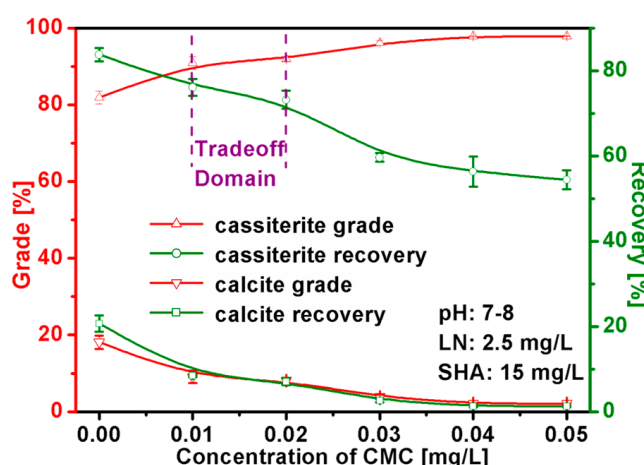


Figure 4. Grade and recovery of cassiterite in mixed binary minerals as a function of CMC concentration.

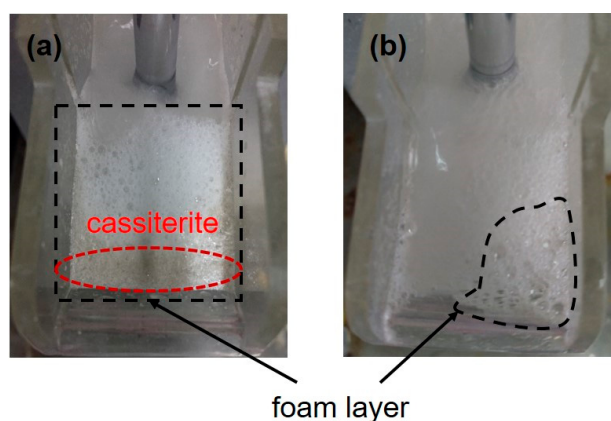


Figure 5. Froth phase images of mixed binary mineral flotation experiments after 0 (a) and 3 min (b) flotation.

Table 1. Selectivity index (SI) values in different flotation reagent schedules.

Reagent Schedule	Salicylhydroxamic Acid		Benzohydroxamic Acid	
	Without CMC	With CMC	Without CMC	with CMC
Selectivity index (SI)	5.19	4.68	-	2.79 [34]

3.3. Zeta Potential Measurements

Zeta potential is a useful tool for determining the interaction between flotation reagents and mineral surfaces in a pulp solution, since the surface charge of mineral particles is greatly affected by the pH of pulp and the addition of flotation reagents [37]. Figure 6a illustrates the zeta potential of cassiterite as a function of pH. In the absence of flotation reagents, the zeta potential of cassiterite decreased gradually as the value of pH increased, and the isoelectric point (IEP) of cassiterite was observed at approximately pH 2.5, which was in line with previously reported values [14,18]. The significant rise in the zeta potential of cassiterite after LN treatment signified Pb^{2+} cation adsorption, while the obvious decrease in the zeta potential of the cassiterite surface after SHA treatment, especially in the pH range of 6–8, signified SHA^- anion adsorption. In the presence of LN and SHA, the zeta potential of cassiterite was much lower than that with LN alone, indicating that LN addition can promote SHA adsorption on the cassiterite surface. After CMC treatment, within the studied pH range of 2–12, the zeta potential of cassiterite was basically the same as that without reagent treatment, indicating a relatively weaker interaction between CMC and cassiterite. After sequential addition of LN, CMC and SHA, the zeta potential of cassiterite was slightly lower than that in the presence of LN and SHA, suggesting that the interaction between CMC and the cassiterite surface has little effect on the adsorption of LN and SHA on the cassiterite surface.

Figure 6b shows the zeta potential of calcite as a function of pH. In the absence of flotation reagents, the zeta potential of calcite was negative at a pH range of 7–12. After LN or SHA treatment, no obvious change in the zeta potential of calcite was observed, indicating a low amount of adsorption of LN and SHA on the calcite surface. In the presence of LN and SHA, the zeta potential of calcite was much lower than that with LN alone, indicating that LN addition can promote SHA adsorption on the calcite surface. Due to the adsorption of negatively charged groups of CMC components dissolved in pulp, the zeta potential of calcite decreased dramatically with the addition of CMC, which was contrary to the result obtained with no flotation reagents treatment. After the sequential addition of LN, CMC and SHA, the zeta potential of calcite decreased sharply, indicating that the intensive interaction between CMC and the calcite surface has a negative effect on SHA adsorption.

In terms of the data shown in Figure 6a,b, it is interesting to note that in the presence of CMC at pH 7–8, the zeta potential of cassiterite slightly decreased by approximately 1 mV whereas for that of calcite, there was a greater decrease of around 15 mV. This result indicates that CMC can selectively depress calcite in the flotation of the cassiterite–calcite mixture. Also, at pH 7–8, the addition of SHA alone led to a greater decrease in cassiterite zeta potential compared with that of calcite, which indicates a much stronger interaction between SHA and the lead-activated cassiterite surface.

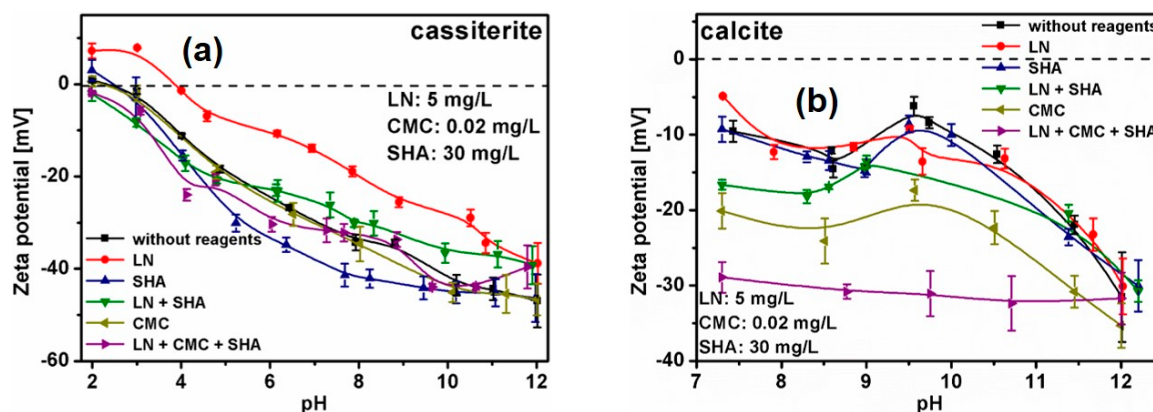


Figure 6. Zeta potential values of cassiterite (a) and calcite (b) as a function of pH in the absence and presence of different reagents.

3.4. Fourier Transform Infrared (FTIR) Spectroscopy Analysis

In order to further understand the interaction mechanism of the reagent scheme, FTIR spectroscopy, a widely-accepted method for determining adsorption types, was adopted in this study. The IR spectrum of CMC and SHA are illustrated in Figure 7. As shown in the IR spectrum of CMC, the broad adsorption band at 3435.10 cm^{-1} was due to the stretching frequency of the OH group; whereas for the band at 2923.80 cm^{-1} was caused by the C–H stretching vibration. The band caused by ring stretching of glucose appeared at 1627.89 cm^{-1} and the bands in the region $1350\text{--}1450\text{ cm}^{-1}$ were due to symmetrical deformations of CH_2 and COH groups. The weak bands at 713.54 cm^{-1} were related to ring stretching and ring deformation of $\alpha\text{-D-(1-4)}$ and $\alpha\text{-D-(1-6)}$ linkages. As shown in the IR spectrum of SHA, the highest frequency band at 3288.30 cm^{-1} was much sharper due to the N–H stretching vibration. For a free N–H group, this was a rather low frequency, indicating the existence of an intramolecular hydrogen bond. The strong broad band at 3177.10 cm^{-1} was caused by the stretching frequency of the OH group of the =N–OH moiety. The strong band at 1617.65 cm^{-1} was caused by the carbonyl stretching vibration in SHA. The weak bands at 1576.36 , 1523.02 , 1493.50 and 1454.24 cm^{-1} are related to benzene skeleton C–C vibration. These bands at 1354.82 and 1315.73 cm^{-1} were associated with the OH in-plane deformation vibration of the =N–OH moiety and phenolic group, respectively. The bands of medium intensity observed at 1246.88 , 1206.39 and 1166.98 cm^{-1} were assigned to the C–H in-plane bending. The bands at 1101.98 , 1053.41 and 1033.42 cm^{-1} were due to N–O stretching.

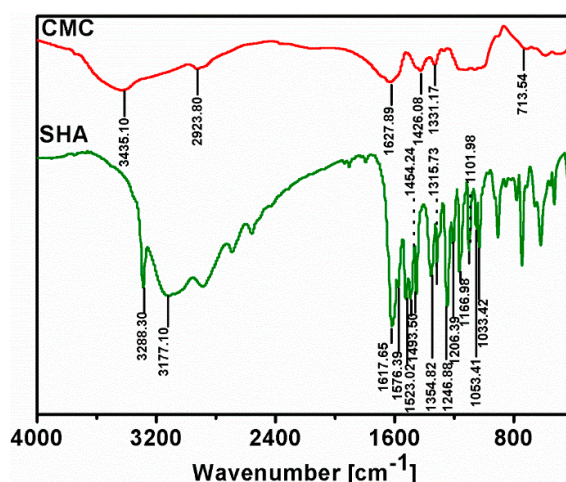


Figure 7. FTIR spectra of CMC and SHA.

Figure 8a depicts the IR spectrum of cassiterite with and without flotation reagent treatment. For untreated cassiterite, the characteristic adsorption bands were observed at 631.21 cm^{-1} (antisymmetric Sn–O stretching) and 532.27 cm^{-1} (symmetric Sn–O–Sn stretching). The broad bands at 3439.14 and 1629.00 cm^{-1} were caused by the adsorbed surface water (O–H stretching). After flotation reagent treatment, the IR spectra of cassiterite included carbonyl groups, benzene rings and hydroxyl groups as shown at peaks in the region from 1618 to 1030 cm^{-1} , which indicates a strong interaction between SHA and cassiterite in the presence of LN and CMC. Compared with the SHA spectrum, the disappearance of the OH group (of the =N–OH moiety) stretching adsorption band at 3177.10 cm^{-1} (as shown in Figure 7) was due to the formation of O–Metal (Pb or Sn) bonds.

Figure 8b depicts the IR spectrum of calcite both treated and untreated by flotation reagents. In terms of the untreated calcite, the adsorption band at 1424.46 cm^{-1} was caused by the stretching vibration of CO_3^{2-} and those at 875.56 and 709.26 cm^{-1} were caused by the deformation vibration of CO_3^{2-} . While after flotation reagents treatment, the new absorbance peak at 1627.65 cm^{-1} was a good sign of the interaction between CMC and calcite; the C–H vibration peak belonging to SHA was insignificant on the calcite surface, indicating a very weak adsorption of SHA onto calcite. FTIR results clearly showed that under the experimental conditions, SHA selectively adsorbs onto cassiterite rather than calcite, and CMC interaction with calcite blocks SHA adsorption on the calcite surface.

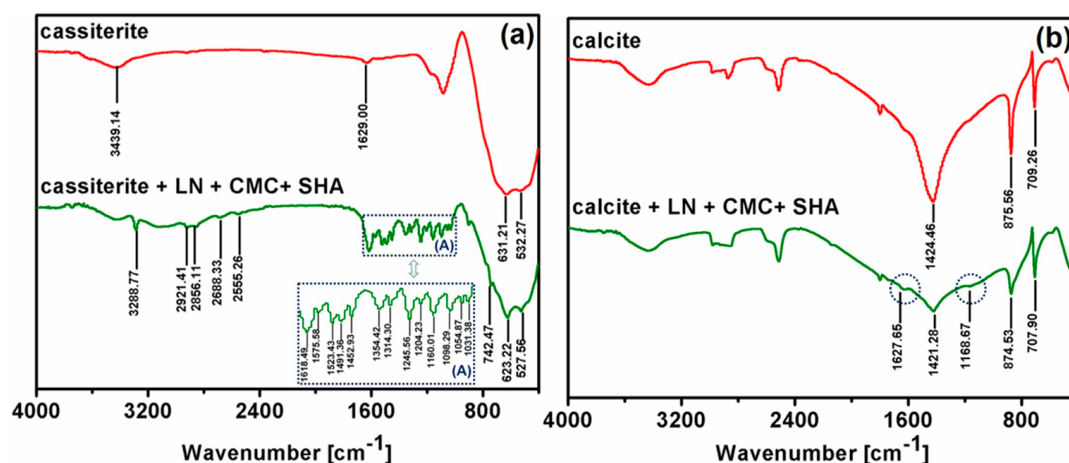


Figure 8. FTIR spectra of cassiterite (a) and calcite (b) untreated and treated by flotation reagents.

3.5. X-ray Photoelectron Spectroscopy (XPS) Analysis

The XPS technique is a good analytical tool for elemental analysis as the binding energy (BE) values of core levels depends to some extent on the molecular environment [28]. Hence, the interaction between flotation reagents and minerals was analysed by XPS. Figure 9 depicts the high-resolution XPS of Sn 3d for SHA-untreated and treated cassiterite samples. In the absence of SHA, the centres of Sn 3d_{3/2} and Sn 3d_{5/2} were at 495.06 and 486.64 eV. The binding energy difference between the two peaks was 8.4 eV, which indicates a normal oxidation valence state of Sn⁴⁺ in the SnO₂ crystals [38]. After SHA treatment, the shifts in the binding energy of the Sn 3d spectra were negligible. The result shows that Sn sites on the cassiterite surface exhibit very weak reactivity towards SHA adsorption.

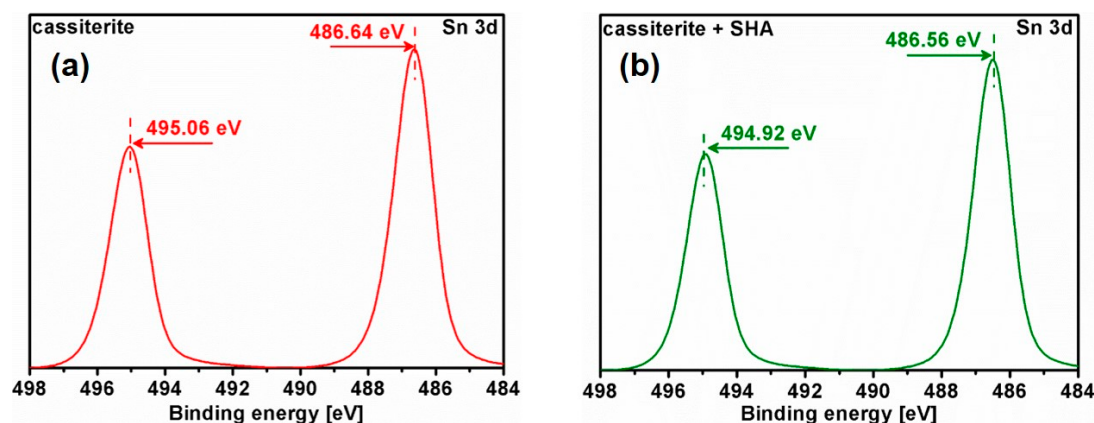


Figure 9. Sn 3d XPS spectra recorded from the surfaces of cassiterite in the absence (a) and presence (b) of SHA.

Figure 10 illustrates the O 1s XPS spectra recorded from cassiterite surfaces without and with the addition of Pb²⁺ and SHA. For pure cassiterite (Figure 10a), the state of O 1s could be deconvoluted into three peaks centred at 530.51 eV, 531.71 eV and 532.60 eV, respectively. The main component of O 1s at 530.51 eV could be attributed to bulk oxide (O₃) [39–41]. The minor peak at 531.71 eV was assigned to bridging oxygen (O_{bri}) [39–41]; whereas the peak at 532.60 eV, hydroxide surface groups (Sn–OH, O_{term}) was due to water adsorption [42,43]. For cassiterite treated by Pb²⁺ ions (Figure 10b), the positions of O_{bri} and O_{term} 1s were 0.23 and 0.34 eV, found at 531.94 and 532.94 eV, respectively, which were higher than those for pure cassiterite. The result indicates that O_{term} and O_{bri} atoms of cassiterite surface are the dominant active sites for Pb²⁺ ions' adsorption. The positive shift in the binding energy suggests that the electron density of O atoms decreases due to higher electron affinity of lead species. The component with the binding energy at 531.14 eV was assigned to Pb–(OH)_n, indicating the adsorption of Pb²⁺ ions on the cassiterite surface. As for cassiterite in the presence of LN and SHA (Figure 10c), the Pb–(OH)_n peak in the O 1s spectra registered a shift of 0.26 eV towards higher binding energy compared to that treated by LN alone, which can be attributed to chemical bonding between Pb cations and SHA. The component at 530.36 eV was related to the –C(=O)–NH–OH group of SHA.

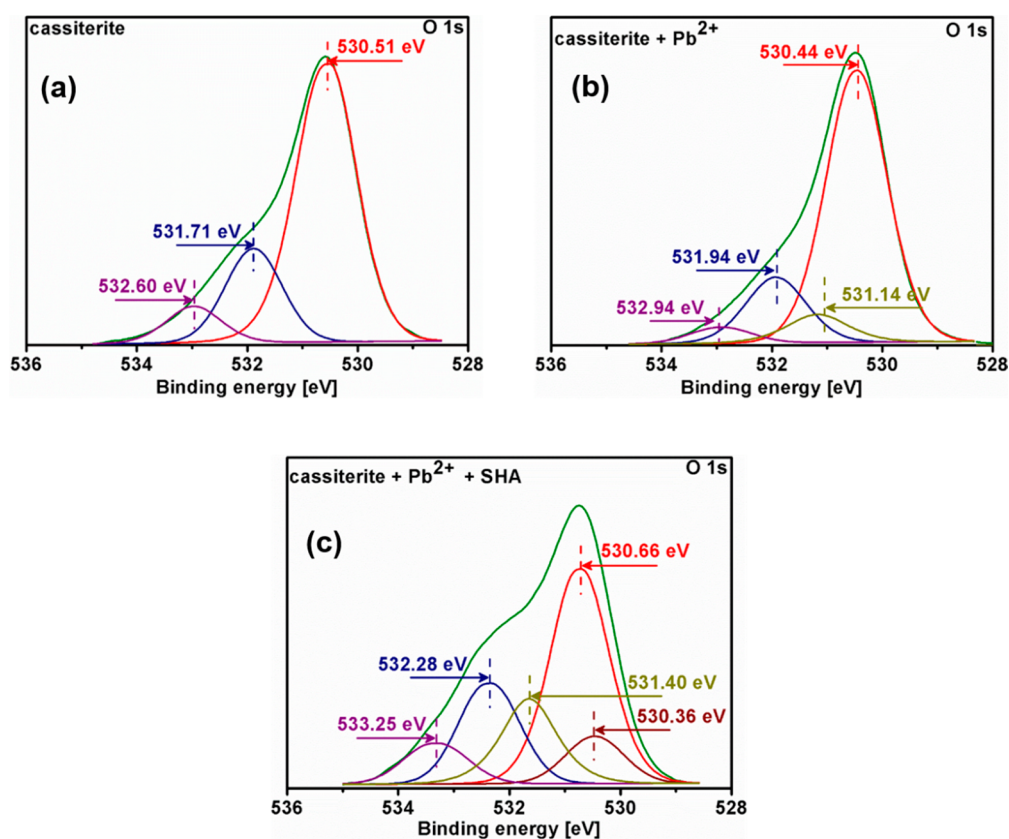


Figure 10. O 1s XPS spectra recorded from the surfaces of pure cassiterite (a) in the presence of Pb²⁺ (b) and Pb²⁺ and SHA (c).

Figure 11 shows the high-resolution spectra of the Pb 4f region. For cassiterite treated by Pb²⁺ ions, a characteristic spin-orbit splitting of Pb 4f_{7/2} peak and Pb 4f_{5/2} peak was observed, indicating the Pb²⁺ ion adsorption on the cassiterite surface. Spin-orbit splitting between Pb 4f_{7/2} and Pb 4f_{5/2} was 4.87 eV, which is characteristic of Pb oxides/hydroxides [44]. For cassiterite modified by LN and subsequently treated with SHA, the significant shifts in the binding energy occurred in Pb 4f_{7/2} and Pb 4f_{5/2} peaks compared with that in the absence of SHA, which can be attributed to the chemical bonding between Pb cations and SHA.

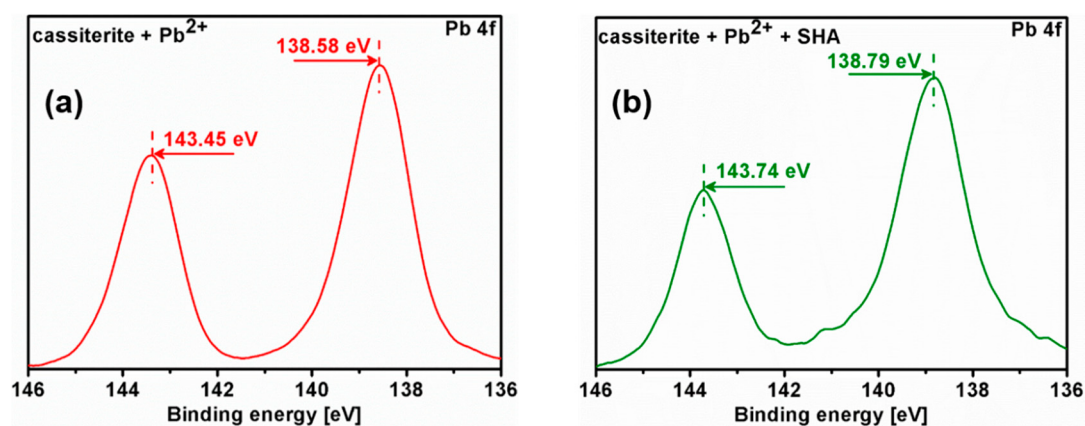


Figure 11. Pb 4f XPS spectra recorded from the surfaces of cassiterite treated by Pb²⁺ in the absence (a) and presence (b) of SHA.

Figure 12 depicts the Ca 2p XPS spectra of calcite in the absence and presence of CMC. For pure calcite, Ca 2p bands included 346.69 and 350.27 eV and were ascribed to Ca 2p_{3/2} and Ca 2p_{1/2}, respectively. For CMC-treated calcite, the bands shifted to 346.75 and 350.34 eV, indicating the CMC interaction with Ca²⁺ on the calcite surface. Thus, the active sites of calcite surface Ca²⁺ cations for SHA adsorption were occupied by CMC.

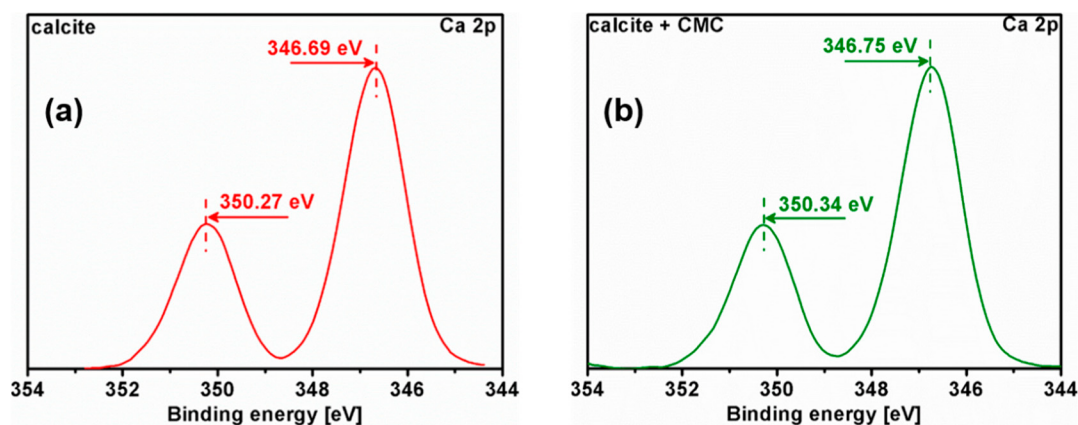


Figure 12. Ca 2p XPS spectra recorded from the surfaces of calcite in the absence (a) and presence (b) of CMC.

As shown in Figure 13, for pure calcite, the O 1s spectra are divided into three components. The highest binding energy component at 532.63 eV was clearly attributed to water adsorption [45]. The middle band at 531.74 eV was attributed to the oxygen belonging to the adventitious carbon contamination, carbonate or phosphate [46–49]. The main O 1s peak at 531.04 eV represented CO₃ [46]. For CMC-treated calcite, the main O 1s peak at 531.21 eV representing CO₃ had a shoulder peak at 1.52 eV higher binding energy, which represents the oxygen of CMC, but no other small peaks were observed, indicating that CMC adsorption can prevent calcite surface contamination.

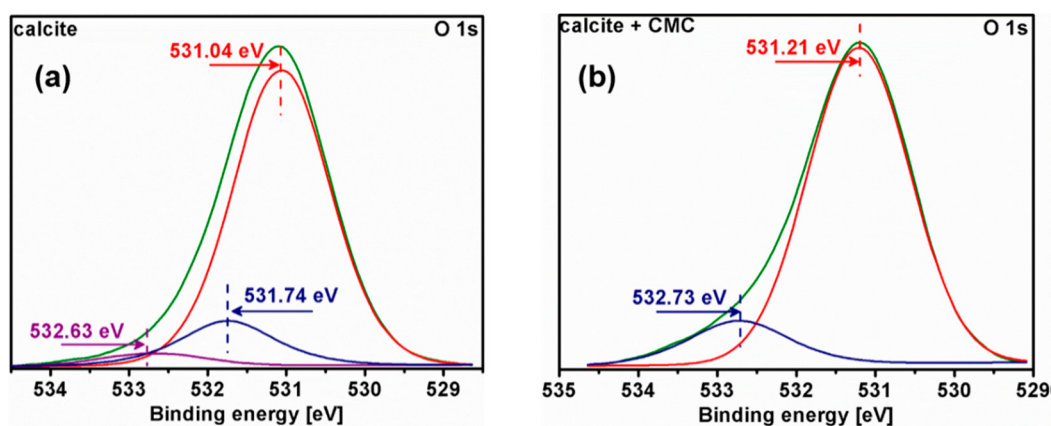


Figure 13. O 1s XPS spectra recorded from the surfaces of calcite in the absence (a) and presence (b) of CMC.

4. Conclusions

In the present study, salicylhydroxamic acid (SHA) collector, lead nitrate activator and carboxymethyl cellulose (CMC) depressant were employed to improve the separation selectivity of cassiterite from calcite. The mechanism of the selective separation of cassiterite from calcite was studied by zeta potential measurements, Fourier transform infrared (FTIR) spectroscopy and X-ray

photoelectron spectroscopy (XPS) analysis. According to the results of the investigation, the following conclusions can be drawn:

(a) The flotation experiment results indicated that SHA exhibits excellent selectivity towards cassiterite and that CMC shows a stronger depression on calcite than cassiterite. The combination of SHA and CMC can effectively realize the flotation separation of cassiterite from calcite.

(b) Zeta potential measurement results indicated that SHA has a strong adsorption on the cassiterite surface in the absence and presence of CMC and that the presence of CMC has an adverse impact on SHA adsorption on the calcite surface.

(c) FTIR spectroscopy results indicated that under experimental conditions, SHA selectively adsorbs onto the cassiterite surface by the formation of O-Metal (Pb or Sn) bonds rather than calcite.

(d) According to XPS results, O_{bri} and O_{term} atoms of cassiterite and lead species adsorbed on the cassiterite surface are the dominant reactive sites for the adsorption of Pb^{2+} and SHA, respectively.

Author Contributions: Z.G., M.T. designed the experiments; M.T., B.J. and R.F. performed the experiments and analyzed the data; M.T. and Z.G. wrote the paper; Z.G., R.L. and P.C. funded the research, and W.S. and Y.H. improved the paper.

Funding: This work was funded by the National Natural Science Foundation of China (51774328, 51404300), the Young Elite Scientists Sponsorship Program by CAST (2017QNRC001), the Innovation Driven Plan of Central South University (2017CX007), the Natural Science Foundation of Hunan Province of China (2018JJ2520), the National 111 Project (B14034), the Collaborative Innovation Centre of Hunan Province, the National Key Technologies R&D Program of China (2015BAB14B02) and the Innovation Program for Postgraduate Students of Central South University (2018zzts037).

Conflicts of Interest: The authors declare no conflict of interest.

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