

Received April 14, 2017; reviewed; accepted August 15, 2017

Flotation behavior and adsorption mechanism of sodium lauroamphoacetate to cassiterite

Yumeng Chen, Haozi Lv, Xiong Tong, Xian Xie

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

Corresponding author: xiongtong2000@yahoo.com (Xiong Tong)

Abstract: The flotation behavior and adsorption mechanism of cassiterite using sodium lauroamphoacetate (SLA) as a collector were investigated by adsorption tests, micro-flotation tests, zeta potential measurements, Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) analysis. Adsorption test results indicated that the adsorption of SLA on the cassiterite surface increased continually with the increase of SLA concentration. Micro-flotation test results demonstrated that SLA had a stronger collecting ability to cassiterite than salicylhydroxamic acid (SHA) and sodium oleate (NaOL) in the pH range of 2-12, and showed a higher selectivity in the separation of cassiterite-quartz than in cassiterite-clinocllore. The zeta potential measurement results indicated that the isoelectric point (IEP) of cassiterite minerals changed from pH 3.9 to 3.4, suggesting the adsorption of SLA on cassiterite surface. The FTIR spectra and XPS analysis further confirmed that SLA chemically adsorbed on cassiterite surface.

Keywords: sodium lauroamphoacetate, flotation behavior, adsorption mechanism, cassiterite

1. Introduction

Tin is an important metal with widespread applications, including soldering, plating, alloy production, chemistry and metallurgy. Cassiterite is the prime mineral from which to extract tin metal. Because the associated gangue minerals are generally lighter than cassiterite, gravity concentration is currently the main method for cassiterite beneficiation (Angadi et al., 2015). However, considering the brittle nature of cassiterite, it is not surprising that in such gravity concentration circuits up to 30% - 40% of the tin reports to tailings (Leistnera et al., 2016). Therefore, the gravity separation might not be an effective technique for the recovery of fine cassiterite. Froth flotation is an alternative method for separating fine cassiterite from gangue minerals, which mainly depends on the surfaces differences in physicochemical properties (Tian et al., 2017a; Feng et al., 2017; Meng et al., 2015; Zhou and Hu, 2013).

In the flotation separation process, flotation reagents are the critical techniques. Various reagents and their derivatives (known as collectors) have been employed, evaluated and developed to recover fine and ultrafine cassiterite particles from low-grade tin ores and gravity tailings. For instance, sodium oleate was the most representative of fatty acid salt, Xu and Qin (Xu and Qin, 2012) found that the adsorption of sodium oleate on the cassiterite surface was caused by the chemical exchanging of ions. However, sodium oleate suffered a low selectivity against gangue mineral. Polycarboxylic acid lacked selectivity and it was also sensitive to the variation of pH value. Baldauf et al. (1985) reported that the alkane dicarboxylic acid was an effective collector for cassiterite flotation, but the selectivity of the reagent was unsatisfied to separate cassiterite from topaz. Khangaonkar and Kamarudin (1994) studied the floatability of cassiterite with tetra-sodium sulpho-succinamate and found that cassiterite was suitable for flotation at acidic conditions. Phosphonic acid as an effective collector could avoid the environmental problems, such as the toxicity of arsonic acid. Li et al. (2015) demonstrated that a-hydroxy-octyl phosphinic acid had a superior collection ability and selectivity for cassiterite to those

of styrene phosphonic acid. Hydroxamate collectors exhibited superior selectivity in the froth flotation process. Qin et al. (2011) studied the flotation and surface interaction of cassiterite with salicylhydroxamic acid, and a complex multilayer adsorption model was proposed to illustrate the adsorption mechanism.

According to the previous studies, different kinds of collectors have different advantages and disadvantages because of the differences in the functional groups and structures. Sodium lauroamphoacetate (SLA) has three oxygen atoms as electron-donor, and the oxygen atoms in a chelating reagent structure tend to form stable metal chelate rings with most elements (Fuerstenau et al., 2000). This sight suggests us that SLA can be used as a collector for cassiterite flotation. Fig. 1 shows the molecular structure of SLA. Since it is primarily used as a very mild cleaning agent, such as shampoos and body washes for infants (Farn, 2006), environmental problems do not require too many considerations if SLA is used as a collector.

In the present work, the flotation behavior of cassiterite with SLA as a collector was studied by using micro-flotation tests. The adsorption mechanism of SLA on cassiterite surface was investigated by adsorption tests, zeta potential measurements, FTIR spectra and XPS analysis.

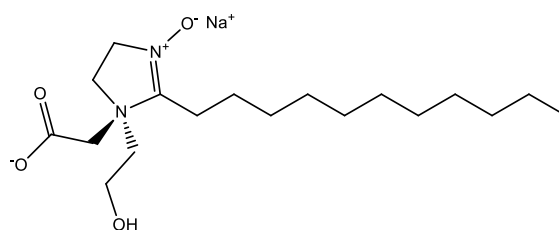


Fig. 1. Molecular structure of SLA

2. Material and methods

2.1 Minerals

Cassiterite, quartz and clinocllore samples were obtained from Dulong, Yunan province, Dahongshan, Yunan province and Haicheng, Liaoning province, respectively. The X-ray diffraction (XRD) results indicated a high purity of cassiterite, quartz and clinocllore (Fig.2). The mineral samples were crushed, ground and dry sieved to obtain the fraction of $-45+5\ \mu\text{m}$ which was used for micro-flotation and adsorption tests and a $-5\ \mu\text{m}$ fine fraction reserved for other measurements. Two kinds of artificial mixture mineral, cassiterite-quartz and cassiterite-clinocllore, were prepared with the mass ratio of 1:1. Distilled water was used in all the experiments, and hydrochloric acid (HCl) and sodium hydroxide (NaOH) were used to adjust the pH value. SLA, salicylhydroxamic acid (SHA) and sodium oleate (NaOL) were purchased from commercial suppliers as collectors and all chemicals used in this work were analytical reagents.

2.2 Adsorption tests

The concentration of SLA in aqueous solutions was determined at room temperature by using a UV-Vis spectrophotometer (UV-2700, Shimadzu, Japan). A 2 g cassiterite sample was dispersed into a 30 mL SLA solution with the desired concentration at pH 7.0. The pulp was agitated at 1000 rpm for 10 min by using a magnetic stirrer. Then, the pulp was separated at 3500 rpm for 20 min by using a centrifuge. The adsorption amount of SLA on the cassiterite surface was calculated by using Eq. (1)

$$G = \frac{(C_0 - C)V}{mS}, \quad (1)$$

where G is adsorption concentration of mineral (mg/cm^2), C_0 is the initial concentration of collector (mg/dm^3), C is the residual concentration of collector (mg/dm^3), V is the volume of flotation solution (cm^3), m is the mass of mineral (g), and S is the specific surfaces area of mineral (cm^2/g).

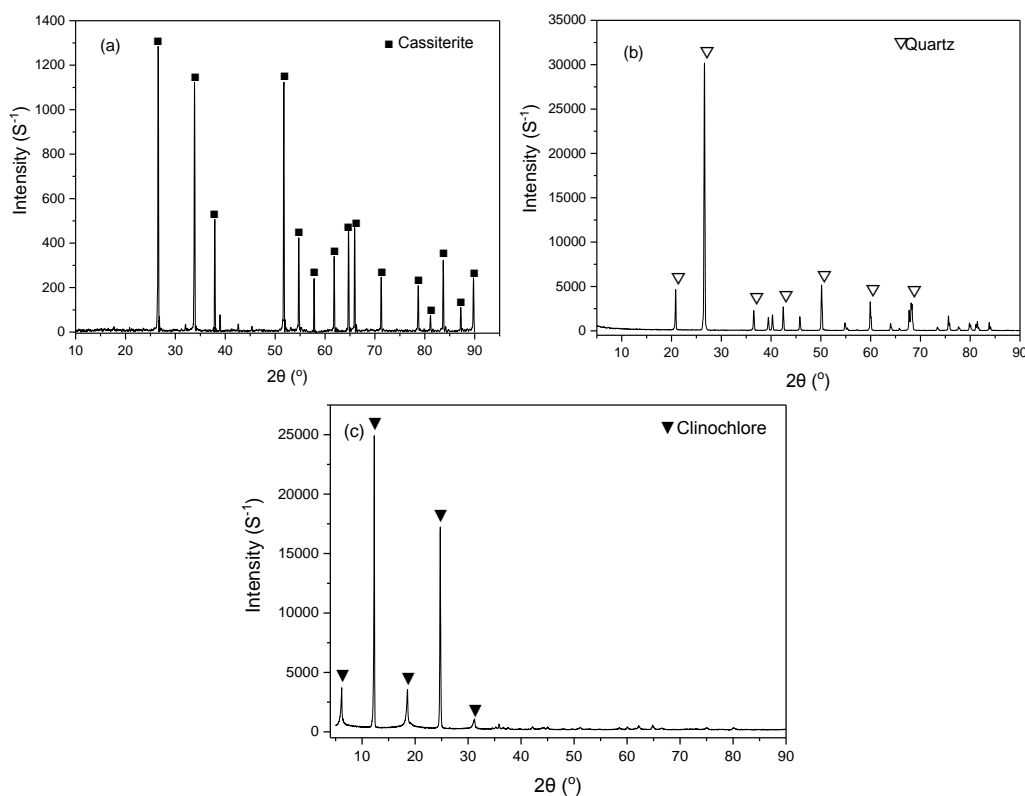


Fig. 2. XRD patterns of (a) cassiterite, (b) quartz and (c) clinocllore

2.3 Micro-flotation tests

Micro-flotation tests were conducted by using a XFG II flotation machine (Gao et al, 2016a, b). A 2 g sample was added to a flotation cell with 40 mL distilled water. The pH of pulp was adjusted by using HCl or NaOH solutions for 1 min, then the collector was introduced and the pulp was conditioned at 1800 rpm for 3 min, followed by flotation for 3 min. The floated and no-floated particles were collected, dried and weighed. After chemical analysis, the recovery and grade of cassiterite were obtained.

2.4 Zeta potential measurements

Zeta potential measurements were conducted at 298 K by using a DELSA micro electrophoresis instrument (DELSA-440SX, Brookhaven, USA). A suspension containing 0.2 wt% of the solid content in the 1×10^{-3} mol/dm³ KNO₃ background electrolyte solution was agitated at 800 rpm for 15 min with a magnetic stirrer. The pH was adjusted by using HCl or NaOH solutions. Measurements were performed in the absence and the presence of SLA (120 mg/dm³), respectively.

2.5 FTIR analysis

FTIR spectra were recorded on a TENSOR instrument (TENSOR27, Bruker, Germany) at room temperature in the range from 4000 to 500 cm⁻¹. A 2 g cassiterite sample was added to 30 mL distilled water with or without 120 mg/dm³ SLA. The pulp was agitated at 2000 rpm for 30 min, then washed twice with distilled water. Finally, the samples were filtered, dried and subjected to FTIR analysis.

2.6 XPS analysis

XPS spectra were recorded on a PHI5000 Versa Probe II (PHI5000, ULVAC-PHI, Japan) with an Al K_α X-ray source. A survey scan of the analyzed sample was conducted to detect elemental compositions, then high resolution scan with a certain element was performed. The MultiPak spectra software was used to calculate and analyze. The preparation methods of the test samples used in the XPS analysis were consistent with the FTIR analysis.

3. Results and discussion

3.1 Adsorption of SLA on cassiterite

The adsorption amount of SLA on cassiterite surface with different SLA concentration is presented in Fig. 3. It is obvious that the adsorption amount of SLA increases continually with the increasing SLA concentration. Even when the concentration of SLA increases to 240 mg/dm³, the adsorption equilibria on the cassiterite surface is not reached.

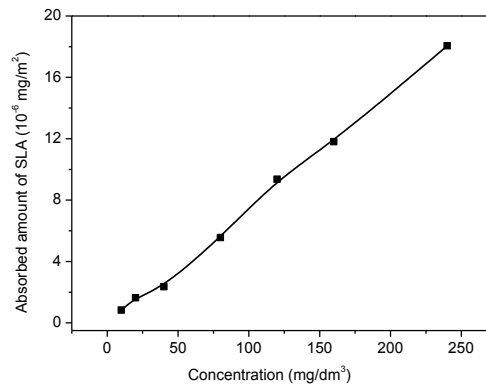


Fig. 3. Relationship between the adsorption amount of SLA and SLA concentration at pH 7.0

3.2 Micro-flotation tests

3.2.1 Flotation results with different SLA concentration

Fig. 4 shows the influence of SLA concentration on the recovery of cassiterite at pH 7.0. It shows that the recovery of cassiterite increases rapidly when the SLA concentration is less than 120 mg/dm³. Beyond this concentration, the recovery increases slowly and maintains above 90%.

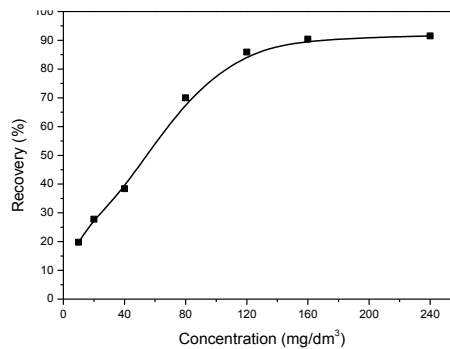


Fig. 4. Relationship between the recovery of cassiterite and SLA concentration at pH 7.0

3.2.2 Flotation results with different collectors

Recoveries of cassiterite, quartz and clinocllore with SLA, SHA and NaOL as collectors at different pH are presented in Fig. 5. For SLA, Fig. 5(a) indicates that the recovery of cassiterite is over 85% and the recoveries of quartz and clinocllore are less than 60%. At pH 7.0, SLA floats out 86% cassiterite, 41% quartz and 58% clinocllore, respectively. For SHA, Fig. 5(b) shows that the recovery of cassiterite is less than 60% under pH range 2-12. At pH 10.0, the maximum recovery of cassiterite is only 59%, and the recoveries of quartz and clinocllore are 31% and 45%, respectively. The results in Fig. 5(c) demonstrate that the recovery of quartz is less than 10% with NaOL as a collector under pH range 2-12. At pH 2.0, the recoveries of cassiterite and clinocllore are 4% and 30%, respectively. However, at pH 12.0, the recoveries of cassiterite and clinocllore are 85% and 58%, respectively. In acidic conditions, the recovery of clinocllore is higher than that of cassiterite, while the result is opposite in

alkaline conditions. Based on the results of single mineral micro-flotation, SLA exhibits an excellent collecting ability for cassiterite among the three studied collectors.

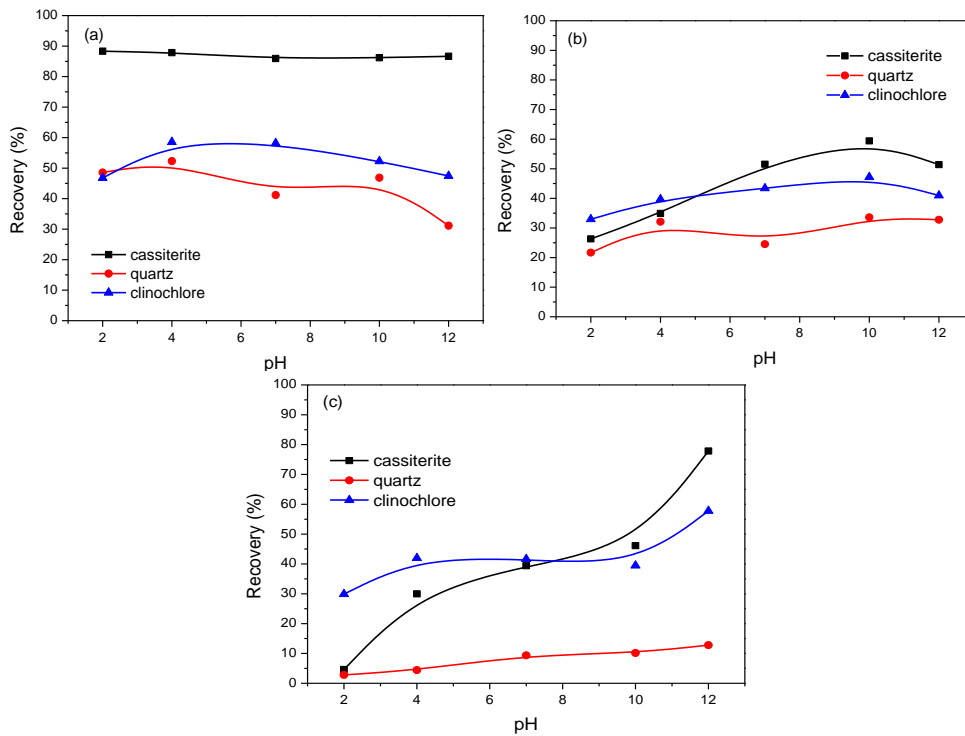


Fig. 5. Recoveries of cassiterite, quartz and clinochlore by using 120 mg/dm³ of (a) SLA, (b) SHA and (c) NaOL under pH range 2-12

3.2.3 Flotation results of artificial mixture mineral

The influence of SLA concentration and pH on the tin recovery and grade during cassiterite-quartz flotation separation is presented in Fig. 6. At pH 7.0, the results in Fig. 6(a) show that with the increase of SLA concentration, the tin recovery increases, while the tin grade decreases. The optimal combinations of tin recovery and grade are obtained with 30 mg/dm³ SLA, in which the tin recovery is 84% and its grade is 68%. Furthermore, the influence of pH is investigated when the SLA concentration is 30 mg/dm³. Fig. 6(b) illustrates that neutral is the suitable pH range for cassiterite flotation. The tin recovery and grade decrease both in acidic and alkaline conditions. Therefore, the optimal concentration of SLA is 30 mg/dm³ and the best separation phenomenon appears in neutral condition.

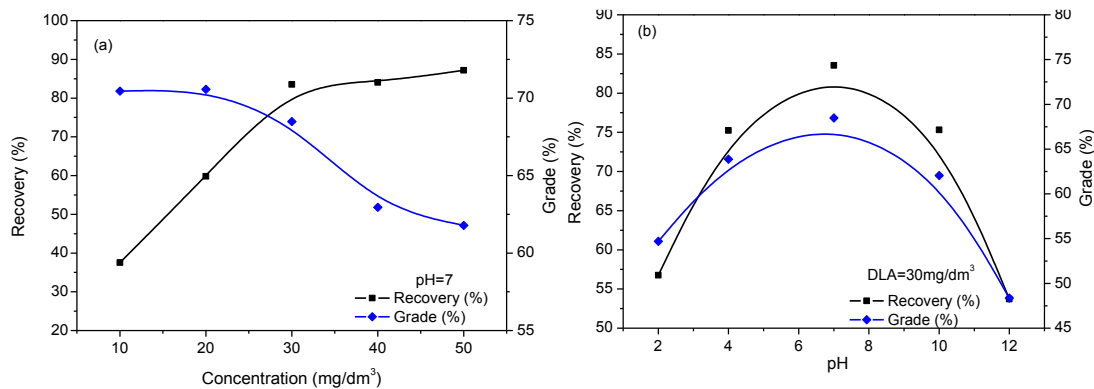


Fig. 6. The influence of (a) SLA concentration and (b) pH on the tin recovery and grade during cassiterite-quartz flotation separation

The influence of SLA concentration on the tin recovery and grade during cassiterite-clinocllore flotation separation is presented in Fig. 7(a). The tin recovery increases with the increasing SLA concentration, while the tin grade decreases slowly within 10~40 mg/dm³ SLA and begin to decrease rapidly beyond 40 mg/dm³ SLA. At the point with 40 mg/dm³ SLA, the tin recovery is 61% and its grade is 48%. Fig. 7(b) shows that the influence of pH on the separation of cassiterite-clinocllore with 40 mg/dm³ SLA. The tin recovery and grade in acid conditions are lower than the neutral conditions, and the results are the worst in alkaline conditions.

According to the results in Fig. 6 and Fig. 7, SLA can effectively separate cassiterite and quartz at a suitable pH, while SLA exhibits relatively poor selectivity in the separation of cassiterite and clinocllore.

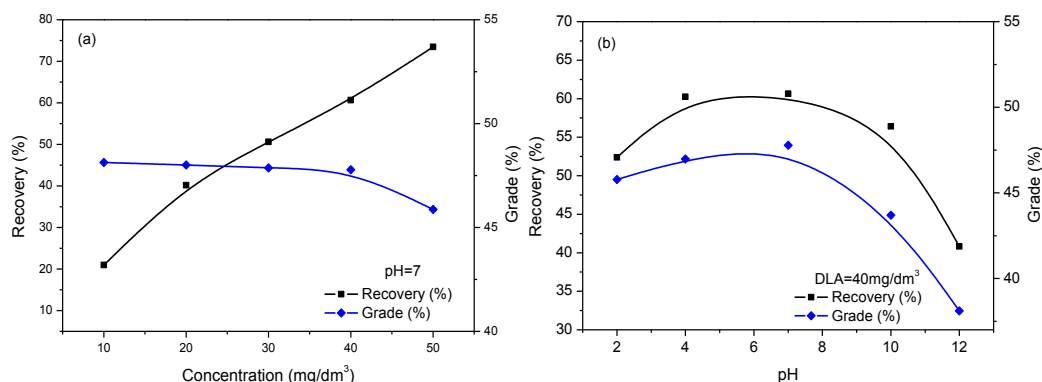


Fig. 7. The influence of (a) SLA concentration and (b) pH on the tin recovery and grade during cassiterite-clinocllore flotation separation

3.3 Zeta potential measurement

The relationship between the zeta potential of cassiterite and pH is shown in Fig. 8. The isoelectric point (IEP) of the untreated cassiterite appears approximately at pH 3.9, which is in accordance with the previous studies (Wang et al., 2013; Bogdanova et al., 2004). After SLA treatment, the IEP of cassiterite changes into pH 3.4, and the zeta potential decreases in the entire pH range. These results indicate that the zeta potential of cassiterite becomes more negative after SLA treatment, which suggests that SLA is adsorbed on cassiterite surface.

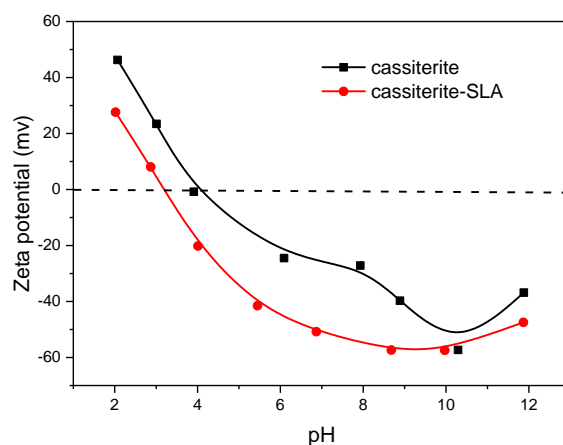


Fig. 8. Relationship between the zeta potential of cassiterite and pH

3.4 FTIR analysis

The FTIR spectra of cassiterite, cassiterite-SLA and SLA are presented in Fig. 9. The result of Fig. 9(a) illustrates that the peak at 632.58 cm⁻¹ for cassiterite might be belong to the stretching vibration band of Sn-O (Wu and Zhu, 2006). The FTIR spectra of SLA in Fig. 9(c) indicates that the peak at

1612.24 cm^{-1} is ascribed to the stretching vibration of C=O. The C-H vibration peaks of $-\text{CH}_2-$ and $-\text{CH}_3-$ groups appear at 2850.16 cm^{-1} and 2915.46 cm^{-1} . A peak at 1406.12 cm^{-1} is corresponding to the C-O stretching band of COO^- group. After SLA treatment (in Fig. 9(b)), the vibration bands of $-\text{CH}_2-$ and $-\text{CH}_3-$ groups appear on the cassiterite surface at 2853.00 cm^{-1} and 2921.14 cm^{-1} and the stretching vibration peak of C-O shifts 9.59 cm^{-1} to 1396.53 cm^{-1} (from 1406.12 cm^{-1}). It is observed that there is a significant change in peak positions of cassiterite and cassiterite-SLA. The results of FTIR spectra indicate that SLA is chemisorbed on cassiterite surface.

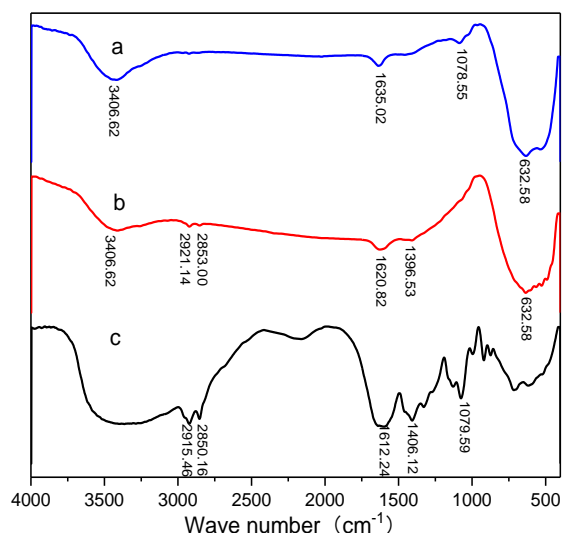


Fig. 9. FTIR spectra of (a) cassiterite, (b) cassiterite-SLA and (c) SLA

3.5 XPS analysis

Table 1 gives the elements identified by the XPS analysis on cassiterite surface. It demonstrates that after SLA treatment, the atomic concentrations of C, N and Sn increase and the atomic concentration of O decreases, which is an evident adsorption of SLA on cassiterite surface. The $\text{Sn}3d$ XPS spectra of cassiterite before and after SLA treatment are listed in Fig. 10. The untreated cassiterite is fitted by two pairs of spin-orbit split peaks, with a binding energy of 495.28 eV for $\text{Sn}3d_{3/2}$ level and 486.77 eV for $\text{Sn}3d_{5/2}$ level (in Fig. 10(a)) (Tian et al., 2017b). These peaks are ascribed to the Sn species from cassiterite surface (Feng et al., 2017). After SLA treatment, the $\text{Sn}3d_{3/2}$ peak and $\text{Sn}3d_{5/2}$ peak at 494.83 eV and 486.40 eV appear on cassiterite surface. These results indicate that an interaction occurs between the SLA and Sn sites on cassiterite surface. To further examine the interaction of SLA and cassiterite, the $\text{O}1s$ XPS spectra are analyzed as shown in Fig. 11. The results in Fig. 11(a) illustrate that the $\text{O}1s$ XPS spectra of original cassiterite are composed of two components, 531.34 eV for Sn-O and 530.63 eV for OH (Nowak et al., 2000). After SLA treatment, the $\text{O}1s$ XPS peaks appear at 531.54 eV and 530.46 eV (in Fig. 11(b)). It indicates that the adsorption of SLA on cassiterite surface changes the chemical circumstance of O atoms. The results in Fig. 12 indicate that the $\text{N}1s$ XPS peak of cassiterite treated by SLA appears at 399.61 eV, while the original cassiterite undetected the $\text{N}1s$ XPS peak. Consequently, the results of XPS analysis further confirm that the chemisorption of SLA exists on cassiterite surface.

Table 1. Elements identified by the XPS analysis on cassiterite surface

Elements (atomic %)	Cassiterite	Cassiterite+SLA	$^a\Delta$ *
C	42.4	43.33	0.93
O	43.23	41.21	-2.02
Sn	14.37	14.65	0.28
N	-	0.81	0.81

* $^a\Delta$ is defined as the value of after SLA treatment minus than that of before treatment.

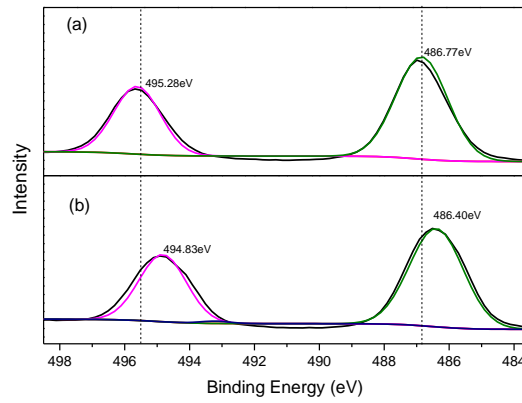


Fig. 10. Sn3d XPS spectra of (a) cassiterite and (b) cassiterite-SLA

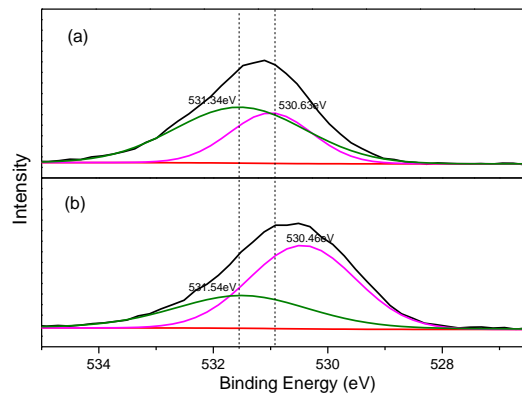


Fig. 11. O1s XPS spectra of (a) cassiterite and (b) cassiterite-SLA

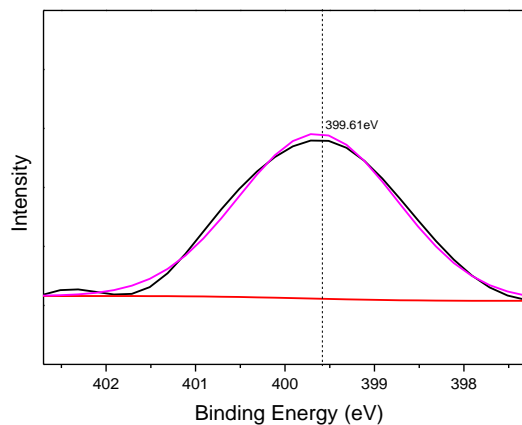


Fig. 12. N1s XPS spectra of cassiterite-SLA

4. Conclusions

In this paper, the flotation behavior and adsorption mechanism of SLA to cassiterite were investigated by adsorption tests, micro-flotation tests, zeta potential measurements, FTIR analysis and XPS analysis. Based on experimental results, the following conclusion could be drawn.

The micro-flotation results illustrated that SLA exhibited a stronger collecting ability than SHA and NaOL for cassiterite against quartz or clinocllore under pH range 2-12. SLA could effectively separate cassiterite-quartz at a suitable pH, while it exhibited relative poor selectivity in separation cassiterite-clinocllore.

The results of adsorption tests and zeta potential measurements deduced that SLA was adsorbed on cassiterite surface. The results of FTIR analysis indicated that there was a significant change in peak

positions of cassiterite and cassiterite-SLA. The results of XPS analysis demonstrated that the binding energies of Sn3d and O1s changed and N1s peak appeared on the cassiterite surface after SLA treatment. Overall, these results indicated that SLA was chemically adsorbed on cassiterite surface.

Acknowledgement

This work was supported by the Key Project of Yunnan Applied Basic Research under Grant no. 2014FA027.

References

- ANGADI, S.I., SREENIVAS, T., JEON, H.S., BAEK, S.H., MISHRA, B.K., 2015. *A review of cassiterite beneficiation fundamentals and plant practices*. Miner. Eng., 70, 178-200.
- BALDAUF, H., SCHOENHERR, J., SCHUBERT, H., 1985. *Alkane dicarboxylic acids and aminonaphthal sulfonic acids - a new reagent regime for cassiterite flotation*. Int. J. Miner. Process., 15, 117-133.
- BOGDANOVA, N.F., KLEBANOV, A.V., ERMAKOVA, L.E., SIDOROVA, M.P., ALEKSANDROV, D.A., 2004. *Adsorption of ions on the surfaces of tin dioxide and its electrokinetic characters in 1:1 electrolyte solutions*. Colloid J., 66, 409-417.
- FENG, Q.C., ZHAO, W.J., WEN, S.M., CAO, Q.B., 2017. *Activation mechanism of lead ions in cassiterite flotation with salicylhydroxamic acid as collector*. Sep. Purif. Technol., 178, 193-199.
- FUERSTENAU, D.W., HERRERA-URBINA, R., MCGLASHAN, D.W., 2000. *Studies on the applicability of chelating agents as universal collectors for copper minerals*. Int. J. Miner. Process., 58, 15-33.
- FARN, R.J., 2006. *Chemistry and technology of surfactants*. Oxford, Blackwell, 173 - 174.
- GAO, Y.S., GAO, Z.Y., SUN, W., HU, Y.H., 2016a. *Selective flotation of scheelite from calcite: A novel reagent scheme*. Int. J. Miner. Process., 154, 10-15.
- GAO, Z.Y., GAO, Y.S., ZHU, Y.Y., HU, Y.H., SUN, W., 2016b. *Selective flotation of calcite from fluorite: a novel reagent schedule*. Minerals, 6(4), 114.
- HANGAONKAR, P.R., KAMARUDIN, H., 1994. *Studies on the cassiterite-sulphosuccinamate flotation system*. Int. J. Miner. Process., 42, 99-110.
- LEISTNER, T., EMBRECHTSA, M., LEIßNER, T., CHEHREH CHELGANIC, S., OSBAHR, I., MÖCKEL, R., PEUKER, U.A., RUDOLPH, M., 2016. *A study of the reprocessing of fine and ultrafine cassiterite from gravity tailing residues by using various flotation techniques*. Miner. Eng., 96-97, 94-98.
- LI, F.X., ZHONG, H., ZHAO, G., WANG, S., LIU, G.Y., 2015. *Flotation performances and adsorption mechanism of α -hydroxyoctylphosphinic acid to cassiterite*. Appl. Surf. Sci., 353, 856-864.
- MENG, Q.Y., FENG, Q.M., SHI, Q., OU, L.M., 2015. *Studies on interaction mechanism of fine wolframite with octyl hydroxamic acid*. Miner. Eng., 79, 133-138.
- NOWAK, P., LAAJALEHTO, K., KARTIO, I., 2000. *A flotation related X-ray photoelectron spectroscopy study of the oxidation of galena surfaces*. Colloids Surf. A, 161, 447-460.
- QIN, W., XU, Y., LIU, H., REN, L., YANG, C., 2011. *Flotation and surface behavior of cassiterite with salicylhydroxamic acid*. Ind. Eng. Chem. Res., 50, 10778-10783.
- TIAN, M.J., GAO, Z.Y., HAN, H.S., SUN, W., HU, Y.H., 2017a. *Improved flotation separation of cassiterite from calcite using a mixture of lead (II) ion / benzohydroxamic acid as collector and carboxymethyl cellulose as depressant*. Colloids Surf. A, 113, 68-70.
- TIAN, M.J., HU, Y.H., SUN, W., LIU, R.Q., 2017b. *Study on the mechanism and application of a novel collector-complexes in cassiterite flotation*. Colloids Surf. A, 522, 635-641.
- WANG, P.P., QIN, W.Q., REN, L.Y., WEI, Q., LIU, R.Z., YANG, C.R., ZHONG, S.P., 2013. *Solution chemistry and utilization of alkyl hydroxamic acid in flotation of fine cassiterite*. Trans. Nonferrous Met. Soc. China., 23, 1789-1796.
- WU, X.Q., ZHU, J.G., 2006. *Selective flotation of cassiterite with benzohydroxamic acid*. Miner. Eng., 19, 1410-1417.
- XU, Y.B., QIN, W.Q., 2012. *Surface analysis of cassiterite with sodium oleate in aqueous solution*. Sep. Purif. Technol., 47, 502-506.
- ZHOU, Y., HU, W.Y., 2013. *Combined floatation-gravity-flotation flowsheet of a low grade wolframite slime*. Nonferrous Met. Sci. Eng., 5, 58-63.