Available online at www.sciencedirect.com
ScienceDirect
Trans. Nonferrous Met. Soc. China 34(2024) 643−654

Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

Enhanced separation of scheelite and calcite by metal-inorganic complex depressant

Guan-fei ZHAO[1,2,3], Bo FENG[1,2], Dong-mei ZHU[1,2], Xian-hui QIU[1,2],
Zhi-yong GAO[3], Hua-shan YAN[1,2], Rui-seng LAI[2], Ting-sheng QIU[1,2]

1. Jiangxi Provincial Key Laboratory of Mining Engineering, Jiangxi University of Science and Technology, Ganzhou 341000, China;
2. School of Resources and Environmental Engineering, Jiangxi University of Science and Technology, Ganzhou 341000, China;
3. School of Minerals Processing and Bioengineering, Central South University, Changsha 410083, China

Received 30 September 2022; accepted 5 June 2023

Abstract: The effect of metal-inorganic complex depressant composed of aluminum sulfate and sodium silicate (AlSS) on the flotation separation of scheelite and calcite was studied. Zeta potential and adsorption measurements confirmed that the negatively charged colloidal particles composed of $Al(OH)_4^-$ and $SiO_m(OH)_n^{4-2m-n}$ tended to be adsorbed on calcite surface, inhibiting the adsorption of sodium oleate (NaOL), while the adsorption of negatively charged colloidal particles on scheelite surface was relatively low, which resulted in the great adsorption capacity of NaOL on scheelite. The contact angle measurements showed that the hydrophobicity of scheelite was significantly better than that of calcite in the NaOL+AlSS solution. XPS measurement results indicated the adsorption of Al and Si on the calcite surface rather than on the scheelite surface. Compared to adding water glass (sodium silicate, SS) only, the depression effect on calcite was significantly enhanced by the combination of AlSS, while scheelite flotation was hardly affected. Scheelite concentrate with WO_3 grade of 68.34% and WO_3 recovery of 83.14% could be obtained from mixed scheelite and calcite ores by adding AlSS.

Key words: scheelite; calcite; separation enhancement; sodium oleate; metal-inorganic complex depressant

---

1 Introduction

Scheelite is rich in resources and has a low grade. It generally coexists with other calcareous gangue minerals [1]. The difficulty in the scheelite flotation is the separation of scheelite from calcium-bearing gangue minerals. For example, calcite and scheelite contain Ca^{2+} and active sites on the mineral surface, which have similar surface properties and chemical reactivity with the reagents, especially with the most frequently used fatty acid collectors [2−5]. MARINAKIS and KELSALL [6] believed that the dissolved ions from the scheelite surface have the same properties on the surface of calcite and fluorite, which are absorbed on the surface of scheelite in solution, which results in the low flotation efficiency of scheelite. Therefore, the selective inhibition of calcite is crucial in the beneficiation of scheelite.

The existing studies on scheelite flotation mainly focused on evaluating the performance and mechanism of new collectors, regulators, and inhibitors [7,8]. The high-efficiency collector [9−11] and inhibitor [12,13] can effectively separate the scheelite from calcite. However, the high-quality scheelite resources were gradually exhausted and tended to be fine, poor, and miscellaneous because

---

Corresponding author: Dong-mei ZHU, Tel: +86-15879790826, E-mail: 9120190063@jxust.edu.cn;
Ting-sheng QIU, Tel: +86-13803587811, E-mail: qiutingsheng@163.com

DOI: 10.1016/S1003-6326(23)66424-6

of their continuous exploitation. The development of a single high-performance reagent had a limited effect on improving the recovery and grade of scheelite, while the combination of reagents had some greater advantages [14−16]. AI et al [17] used sodium silicate as an inhibitor and GYR + salicylaldoxime as a combined collector to separate scheelite from calcite and fluorite. They deduced that the WO_3 grade and the WO_3 recovery were 62.34% and 73.78%, respectively. FENG et al [18] studied the effect of the sodium oleate and polyether combined collector and inhibitor sodium alginate on the flotation separation of scheelite from calcite. Their results showed that compared with the conventional collector sodium oleate, the combined collector sodium oleate and polyether can improve the flotation recovery of scheelite and reduce that of calcite.

Due to the increase of calcium-bearing gangue components in scheelite ore, the effective inhibition of calcium-bearing gangue minerals has gradually become the key to improving the grade of scheelite concentrate [19−22]. CHEN et al [23−25] used dextran sulfate sodium, sodium alginate and calcium lignosulfonate as depressants to separate scheelite from calcite and fluorite, and showed that a single depressant can selectively inhibit the flotation of calcite and fluorite. Camphor leaves were directly extracted as depressants using simple physical methods. It was deduced through a flotation experiment that the camphor leaf extract (CLE) has a strong depression effect on calcite and a minimal effect on scheelite [16]. WANG et al [26] used sulfonated naphthalene-formaldehyde condensate (SNF) as a depressant to separate scheelite from calcite. The results of their micro-flotation experiments showed that SNF has a stronger depressant performance on calcite than water glass. ZHOU et al [27] believed that the development of combination reagents and the study of the properties and mechanism of reaction are still the main research directions in fluorite flotation. The combined application of ferric ions (Fe^{3+}) and the small molecular organic chelating tartaric acid (TA) can efficiently perform the flotation separation of scheelite from calcite [28]. However, there exist few studies on the combined depressants of sodium silicate and Al^{3+} for the calcium-bearing gangue associated with scheelite flotation.

In this study, a metal-inorganic complex depressant, which is an efficient recipe of depressants composed of aluminum sulfate and water glass sodium silicate (AlSS), was adopted for the flotation separation of scheelite from calcite. The inhibition effect of AlSS on scheelite and calcite in the micro-flotation experiments and artificial experiments was studied. The underlying flotation separation mechanism was analyzed by zeta potential, adsorption, contact angle, and X-ray photoelectron spectroscopy (XPS) measurements. This study has a guiding significance for the scheelite flotation process and a reference significance for other mineral flotation separation processes.

2 Experimental

2.1 Materials and reagents

Pure minerals of scheelite and calcite used in the experiments were obtained from Henan Province, China. After a series of crushing (Jaw crusher), dry grinding (Ceramic ball mill), and screening (Standard sieve), minerals with particle sizes from 0.037 to 0.074 mm were used for flotation experiments. According to the X-ray diffraction patterns of scheelite and calcite shown in Fig. 1, there were not other characteristic peaks,

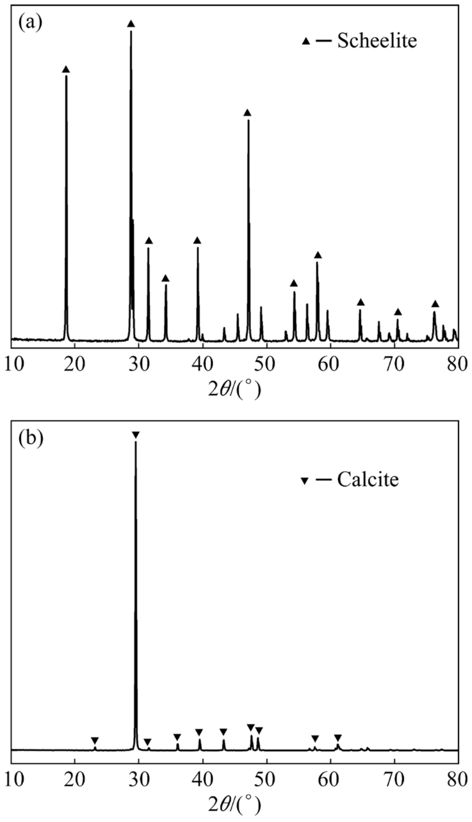

Fig. 1 XRD patterns of scheelite (a) and calcite (b)

which proved the high purity of the samples. As shown in Table 1, the content of WO_3 was 79.41% with a scheelite purity above 95%, and the content of $CaCO_3$ was above 98%.

Table 1 Chemical contents of scheelite and calcite samples

Mineral	Content/wt.%			
	CaO	WO_3	$CaCO_3$	SiO_2
Scheelite	16.68	79.41		3.91
Calcite			98.07	1.93

Sodium oleate (abbreviation NaOL), aluminum sulfate ($Al_2(SO_4)_3$) and water glass ($Na_2SiO_3 \cdot 5H_2O$) used in the experiments were of analytical grade. NaOH and HCl solutions were used to adjust the pH of the slurry. Deionized water was used in all the experimental procedures. The flotation test lasted from February to April, and $Na_2SiO_3 \cdot 5H_2O$ dissolved normally in the room temperature range of 4−27 °C after ultrasonic treatment. The metal-inorganic complex depressant of AlSS was prepared in advance. AlSS was prepared by mixing $Al_2(SO_4)_3$ and $Na_2SiO_3 \cdot 5H_2O$ in a mass ratio of 1:3 without special instructions. For example, if the concentration of AlSS is 40 mg/L, the concentration of $Al_2(SO_4)_3$ will be 10 mg/L, and the concentration of $Na_2SiO_3 \cdot 5H_2O$ will be 30 mg/L.

2.2 Zeta potential measurements

The zeta potential measurements were carried out in a Malvern Zetasizer Nano ZS90 instrument (Malvern, London, England) equipped with a rectangular electrophoresis cell. The samples used for zeta potential measurement were specially ground to be less than 0.02 mm. Before measurement, 30 mg of the single mineral powder was added to 40 mL of KCl aqueous solution (0.01 mol/L) and conditioned by magnetic stirring, during which reagents were added to the pulp. The concentrations of the reagents added in the zeta potential measurements were consistent with those in the flotation test. After standing for 20 min, the upper clear supernatant was used for zeta potential measurement. The measurement temperature was maintained at 25 °C, and the final result was the average of the three experiments. The average was the final result, and the error bar was the standard deviation.

2.3 Contact angle measurements

The contact angle measurements were implemented with a JY−82C contact angle meter. The samples used for contact angle measurement were specially treated. Prior to any comminution process, mineral sample blocks were picked and cut into rectangular parallelepipeds, which were then fixed with resin and finally polished with a polishing machine. Before each sample was tested for contact angle, the surface had been polished from coarse to fine until smooth. The mineral surface was polished one after another on the grinder by polishing paper with roughnesses of 350, 150, 75, 38, 18, 13, and 6.5 μm. In addition, polished surfaces needed to be repeatedly washed with deionized water to remove surface contaminants. After the surface was naturally air-dried, a drop of deionized water or flotation reagent solution was dropped on the mineral surface, and the contact angle was measured with a contact angle meter. Specifically, five contact angle tests were carried out on the same sample at different surface positions, and the maximum and minimum values are eliminated. Then, the other 3 groups of test data were calculated to obtain the average value.

2.4 Adsorption measurements

The adsorption amount of NaOL in the experiments was measured with an Elementar TOCII instrument (Elementar Co., Langenselbold, Germany), and the adsorption amount of Al^{3+} in the experiments was confirmed with inductively coupled plasma-optical emission spectrometry (ICP-OES, Thermo Scientific, Waltham, MA, USA). For each measurement, 2 g of pure mineral and 35 mL of deionized water were added to a Plexiglas cell (40 mL), and flotation reagents were added when the pulp was stirred. After the adsorption was completed, the pulp volume was fixed to 50 mL, solid–liquid separation was carried out by centrifugation, and finally, the supernatant was taken for measurement.

2.5 XPS measurements

X-ray photoelectron spectrometer (Thermo Fischer, ESCALAB Xi$^+$) was used for testing. The excitation source is an Al K_α ray ($h\nu$=1486.6 eV). The working voltage was 12.5 kV, and the filament current was 16 mA, according to samples of the case for signal accumulation. The test passing energy was 100 eV in the full spectrum and 20 eV in the narrow spectrum, with a step size of 0.05 eV and a stay time of 40−50 ms. All binding energies were calibrated using the characteristic C 1s carbon peak (C 1s, 284.80 eV). The samples used for XPS measurement were prepared in the same way as flotation experiments, except that the concentrate after the final filtration needed to be flushed with deionized water three times.

2.6 Flotation tests

Flotation tests consisted of single mineral experiments and artificial mixed mineral experiments. Flotation experiments were carried out in an XFG flotation machine at a spindle speed of 1920 r/min. For each single mineral flotation experiment, 2 g of pure mineral and 35 mL of deionized water were added to the flotation cell with a capacity of 40 mL. For artificially mixed mineral flotation experiments, 2 g of the mixed mineral consisted of 1 g scheelite and 1 g calcite. The flotation experiments were carried out according to the flowsheet shown in Fig. 2.

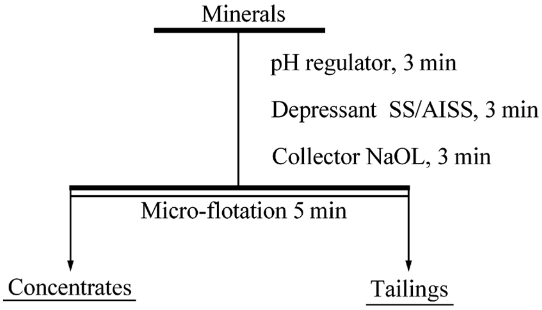

Fig. 2 Flowsheet of microflotation experiment

After artificial scraping, filtering, drying and weighing, the concentrates and tailings were collected for recovery and grade measurements. The grades of concentrate and tailings of artificial mixed ore were measured by chemical titration analysis. Each experiment was repeated three times. The average was the final result, and the error bar was the standard deviation.

3 Results and discussion

3.1 Zeta potential

The total potential difference between the mineral surface and solution can be defined as the surface potential, which is mainly determined by the concentration of localized ions in the solution. The dissolution of ions [29] and the adsorption of reagent molecules [13] on the surface of the mineral will result in changing the mineral surface electrical properties. Therefore, zeta potential measurements were performed to uncover the possible interaction mechanism between the flotation reagents and minerals.

After adding AlSS to scheelite and calcite solution, when the pH increased, the main forms of SS in the solution were $SiO_m(OH)_n^{4-2m-n}$, which included $Si(OH)_4$, $SiO(OH)_3^-$ and $SiO_2(OH)_2^{2-}$, while those of $Al_2(SO_4)_3$ were $Al_m(OH)_n^{3m-n}$, which included Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al(OH)_3$ and $Al(OH)_4^-$. Figures 3(a) and (b) show the species distribution diagrams of Al^{3+} and SS, respectively [7]. Because the AlSS was preconfigured, it was considered that the positively charged Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^+$, and $Al(OH)_3$ colloidal particles, as well as the negatively charged $Al(OH)_4^-$ and $SiO_m(OH)_n^{4-2m-n}$ colloidal particles will form negatively charged mixed colloidal particles and then adsorb on the mineral surface.

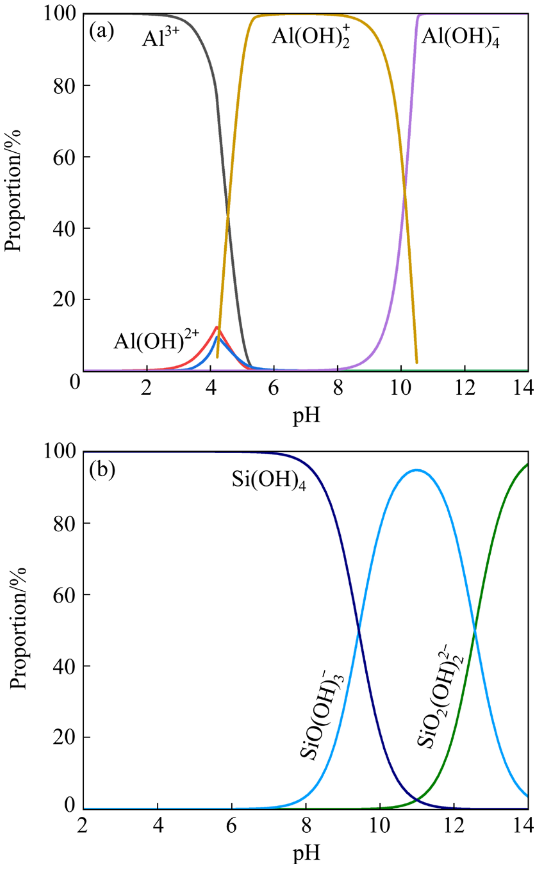

Fig. 3 Species distribution diagrams of Al^{3+} (a) and SS (b) as function of pH [7]

Figure 4 presents the influence of the pH on the zeta potential of scheelite and calcite in the SS, AlSS, NaOL, and AlSS+NaOL systems. It can be seen from Figs. 4(a) and (b) that, compared with the zeta potential of scheelite and calcite in deionized water, the addition of SS led to a negative shift in the studied pH range, which indicated that negatively charged SS colloidal particles were adsorbed on the scheelite and calcite surfaces. Within the pH range of the measurements, the addition of AlSS led to a negligible negative shift of scheelite (less than 2 mV), and the reduction in the surface potential of calcite was more obvious. This phenomenon may be because the negatively charged scheelite surface had difficulty in adsorbing negatively charged AlSS colloidal particles through electrostatic attraction, while the positively charged calcite surface can adsorb negatively charged AlSS colloidal particles through electrostatic attraction. The addition of NaOL led to an obvious negative shift of scheelite and calcite. However, in the presence of NaOL and AlSS, the zeta potential of scheelite significantly decreased, while that of calcite only decreased by 2−3 mV compared with that of AlSS. NaOL was an anionic collector. Hence, the change in the surface potential of scheelite and calcite in the AlSS+NaOL systems proved that a large amount of NaOL was adsorbed on the scheelite surface while only a small amount of NaOL was adsorbed on the calcite surface.

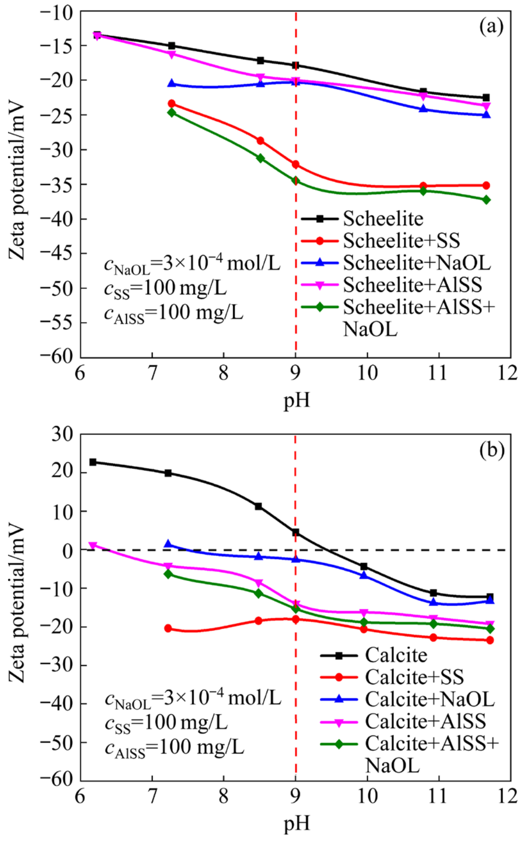

Fig. 4 Effect of pH on zeta potential of scheelite (a) and calcite (b) in SS, AlSS, NaOL and AlSS+NaOL systems

The above test results showed that when AlSS was used as an inhibitor, the optimal pH value of the scheelite and calcite flotation separation was 9.0. In addition, it can be seen from the red dotted line (pH=9.0) in Fig. 4 that the negative charge on the scheelite surface was −17.84 mV and the positive charge on the calcite surface was 4.49 mV after adding deionized water, while the negative charge on the scheelite surface was −34.47 mV and the negative charge on the calcite surface was −15.29 mV after adding AlSS and NaOL. The surfaces of scheelite and calcite were charged, and the electrostatic interaction energy (V_{E}) can be generated between the particles. V_{E} is expressed as

$$V_{\mathrm{E}}=\frac{\pi\varepsilon_{\mathrm{a}}R_1R_2}{(R_1+R_2)}\left(\psi_1^2+\psi_2^2\right)\cdot\left\{\frac{2\psi_1\psi_2}{\left(\psi_1^2+\psi_2^2\right)}\cdot\ln\left[\frac{1+\exp(-\kappa H)}{1-\exp(-\kappa H)}\right]+\ln\left[1-\exp(-2\kappa H)\right]\right\} \qquad (1)$$

where ψ_1 and ψ_2 are the surface charges of scheelite and calcite, respectively; ε_{a} is the dielectric constant of water; R_1 and R_2 are the radii of scheelite and calcite, respectively; κ^{-1} is the double electric layer thickness; H is the distance between scheelite and calcite.

It can be seen from Eq. (1) that when the surfaces of the scheelite and calcite particles had opposite charges, V_{E} was negative, which was stated as the mutual attraction energy. When there was a homogenous charge on the surface of the scheelite and calcite particles, V_{E} was positive, which was stated as mutual repulsion energy. Therefore, the mutual attraction energy between the scheelite and calcite particles translated into mutual repulsion energy under the reaction of the AlSS metal-inorganic complex depressant, and the value of the mutual attraction energy was less than that of the mutual repulsion energy. This result indicated that the effect of the heterogeneous coagulation between scheelite and calcite was weakened.

3.2 Adsorption capacity

The common flotation reagent adsorptions include the ion adsorption, ion exchange adsorption, molecular adsorption, and electrostatic adsorption. FU et al [30] showed that the adsorption of Pb-BHA on the surface of scheelite and calcite resulted in a positive shift of the zeta potential on the surface of the two minerals, and therefore the adsorption of Pb-BHA was considered as electrostatic adsorption.

The adsorption quantities of NaOL and Al^{3+} on the mineral surface were calculated as shown in Eqs. (2) and (3), respectively:

$$\Gamma_1=\frac{(c_{01}-c_1)V}{m} \tag{2}$$

$$\Gamma_2=\frac{(c_{02}-c_2)V}{m} \tag{3}$$

where Γ_1 and Γ_2 represent the concentrations of NaOL and Al^{3+} adsorbed on the sample surface, respectively; c_{01} and c_{02} are the initial NaOL and Al^{3+} dosages, respectively; c_1 and c_2 denote the residual NaOL and Al^{3+} dosages in the pulp, respectively; V and m are the volume of the solution and the mass of the minerals, respectively.

Figure 5 shows the amount of NaOL collector adsorbed on the scheelite and calcite surfaces as a function of the SS and AlSS depressant concentrations. It can be seen from Fig. 5 that without the addition of depressants ($c_{\text{SS/AlSS}}$=0 mg/L), the amounts of NaOL adsorbed on the scheelite and calcite surfaces were 1.045 and 1.085 mg/g, respectively. When the concentration of the SS depressant increased, the adsorption of NaOL on the scheelite surface continued to decrease until reaching 0.882 mg/g (c_{SS}=120 mg/L). However, the magnitude of the variation was insignificant, which indicates that the SS depressant has little effect on the scheelite flotation. In addition, the adsorption of NaOL on the calcite surface gradually decreased from 1.085 mg/g (c_{SS}=0 mg/L) to 0.518 mg/g (c_{SS}=120 mg/L). When NaOL was added with AlSS to scheelite and calcite, the adsorption of NaOL on the scheelite surface continued to decrease from 1.037 mg/g (c_{AlSS}=0 mg/L) to 0.847 mg/g (c_{AlSS}=100 mg/L), which indicates that the adsorption of NaOL on the scheelite surface still shows an inapparent change with the increase of the AlSS concentration. However, the amount of NaOL adsorbed on the calcite surface sharply decreased with the increase of the AlSS concentration, and the adsorption amount decreased from 1.074 mg/g (c_{AlSS}=0 mg/L) to 0.157 mg/g (c_{AlSS}=100 mg/L). The change in the adsorption amount of the NaOL collector on the scheelite and calcite surface also explained why the recovery of scheelite did not change much and the recovery of calcite significantly decreased when AlSS was used as a depressant, which verified the correctness of the flotation test.

There was competitive adsorption between the depressants and collectors on mineral surfaces [31]. Figure 6 presents the amount of Al^{3+} adsorbed on the scheelite and calcite surface as a function of the AlSS concentration. It can be seen from Fig. 6 that when the AlSS concentration increased, the amount of Al^{3+} adsorbed on the scheelite surface increased from 0 mg/g (c_{AlSS}=0 mg/L) to 0.119 mg/g (c_{AlSS}=100 mg/L), and the amount of Al^{3+} adsorbed on the calcite surface increased from 0 mg/g (c_{AlSS}=0 mg/L) to 0.392 mg/g (c_{AlSS}=100 mg/L). The results showed that the adsorption capacities of NaOL and AlSS on the scheelite and calcite surfaces were inversely proportional, indicating that

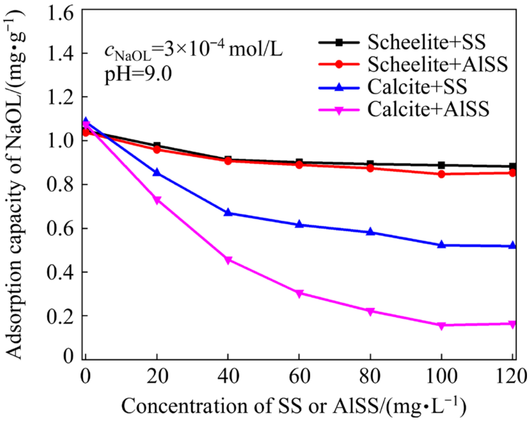

Fig. 5 Adsorption capacity of NaOL on surface of scheelite and calcite as function of SS and AlSS depressant concentrations

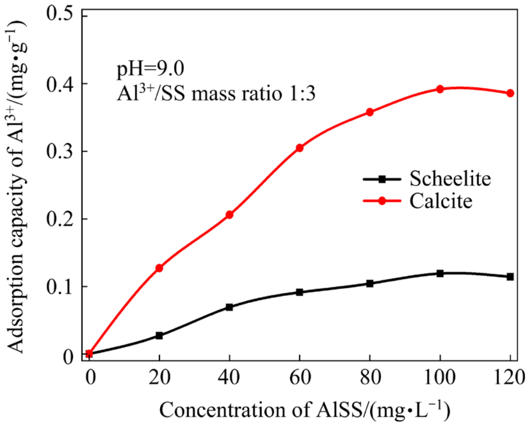

Fig. 6 Adsorption capacity of Al^{3+} on surface of scheelite and calcite as function of AlSS concentration

competitive adsorption existed between NaOL and AlSS on the scheelite and calcite surfaces.

3.3 Contact angle

Contact angle measurements were performed in most of the studies on the exploration of mineral wettability and floatability. The contact angle value was proportional to the hydrophobicity of the mineral surface, and when the contact angle value was larger, it was easier to separate by flotation [20]. It has been mentioned that the wettability and contact angle of the crystalline solid surfaces are mainly affected by the surface roughness and composition heterogeneity [32,33]. Therefore, to reduce or eliminate the influence of the surface roughness on the measurement results, the surface of commonly exposed samples in this study was successively polished with alumina polishing liquid with different particle sizes after fine grinding. In particular, to ensure the high measurement accuracy, five contact angle tests were conducted on the same sample at different surface positions, and the maximum and minimum values were eliminated. The other three groups of test data were then calculated to obtain the average value.

Table 2 shows the contact angles of scheelite and calcite in the deionized water, AlSS and AlSS + NaOL systems. It can be seen from Table 2 that the contact angles of scheelite and calcite were respectively 31.43° and 42.27° in the deionized water, which indicated that the hydrophobicity of calcite was stronger than that of scheelite. After adding 100 mg/L of AlSS, the contact angles of scheelite and calcite were reduced to 27.92° and 31.76°, respectively. This indicated that the adsorption of AlSS on the scheelite and calcite surfaces weakened their hydrophobicity. In the AlSS + NaOL system, the contact angles of scheelite and calcite were respectively 73.31° and 33.62°, which indicated that more NaOL was adsorbed on the scheelite surface and a good floatability of scheelite in this system was generated, while less NaOL was adsorbed on the calcite surface and led to a poor floatability of calcite. The contact angle results were also consistent with the flotation results, which verified the correctness of the flotation test.

Table 2 Contact angles of scheelite and calcite in different test systems (pH=9.0, *c*(NaOL)=0.3 mmol/L, and *c*(AlSS)=100 mg/L)

Test system	Contact angle/(°)	
	Scheelite	Calcite
Deionized water	31.43	42.27
AlSS	27.92	31.76
AlSS+NaOL	73.31	33.62

3.4 XPS results

The adsorption of flotation reagents on the surfaces of scheelite and calcite was detected by adsorption measurements. In addition, XPS analyses were conducted to confirm the interaction mechanism between the scheelite, calcite and flotation reagents. The XPS allows to analyze the relative contents of various components on the mineral surface and the chemical states of metal elements. Hence, XPS measurements were performed to analyze scheelite and calcite before and after AlSS treatment.

Figure 7 shows the survey scan XPS spectra of scheelite/calcite before and after AlSS treatment. It can be seen from Fig.7(a) that no new characteristic peak appeared on the surface of scheelite after being treated by the AlSS metal-inorganic complex depressant, which indicated that there was no adsorption of AlSS on the surface of scheelite. It can be seen from Fig. 7(b) that the Si 2p peak and Al 2p peak appeared in the spectrum of calcite after treatment with the AlSS metal-inorganic complex depressant, which demonstrated the adsorption of AlSS on the calcite surface.

This can also be confirmed by the change in the element content on the surface of calcite. It can be seen from Table 3 that the molar fractions of Si 2p and Al 2p on the calcite surface respectively reached 0.44% and 0.60% after treatment with AlSS. This also indicates the adsorption of AlSS on the calcite surface.

For a chemical reaction, the change in the binding energy of metal elements on the mineral surface will be higher than 0.2 eV [31]. Therefore, the change in the binding energy in the range of almost 0.2 eV may be caused by detection error. Figure 8 shows the precise scan of W 4f peaks and Ca 2p peaks on the scheelite and calcite surfaces before and after being treated by AlSS. It can be seen from Figs. 8(a) and (b) that the peak shifts for W 4f and Ca 2p are very small (less than 0.2 eV), and therefore it can be inferred that the chemical

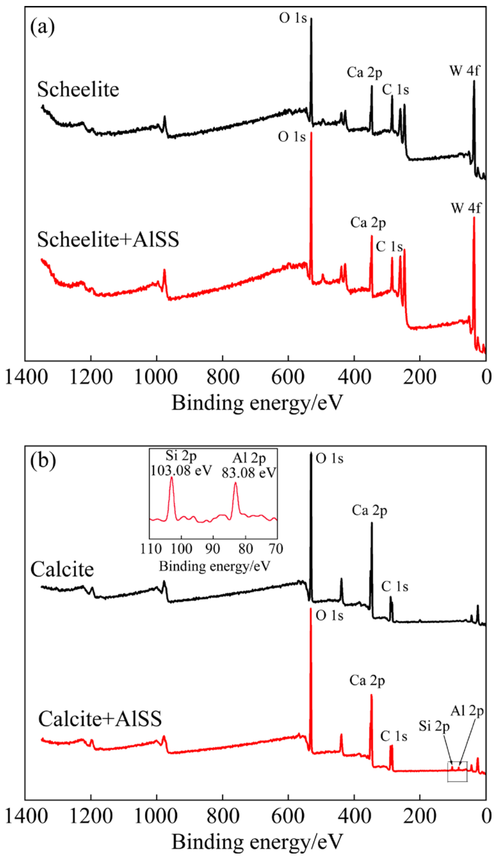

Fig. 7 Survey scan XPS spectra of scheelite (a) and calcite (b) before and after AlSS treatment

Table 3 Molar fractions and shifts of elements on calcite surface

Element	Molar fraction/%		Shift/%
	Calcite	Calcite + AlSS	
Ca 2p	17.97	17.18	−0.79
O 1s	49.42	47.03	−2.39
C 1s	32.61	34.75	2.14
Si 2p	0	0.44	0.44
Al 2p	0	0.60	0.60

environment of the scheelite surface was not changed by the addition of AlSS. It can be observed from Fig. 8(c) that after being treated with AlSS, the binding energies of Ca 2s and Ca 2p ranged from 350.98 to 350.58 eV and from 347.48 to 346.98 eV, respectively. Because the changes in the binding energies of Ca 2s and Ca 2p on the calcite surface after AlSS treatment were respectively 0.4 and 0.5 eV, it can be inferred that the adsorption of AlSS led to a change in the chemical environment on the calcite surface.

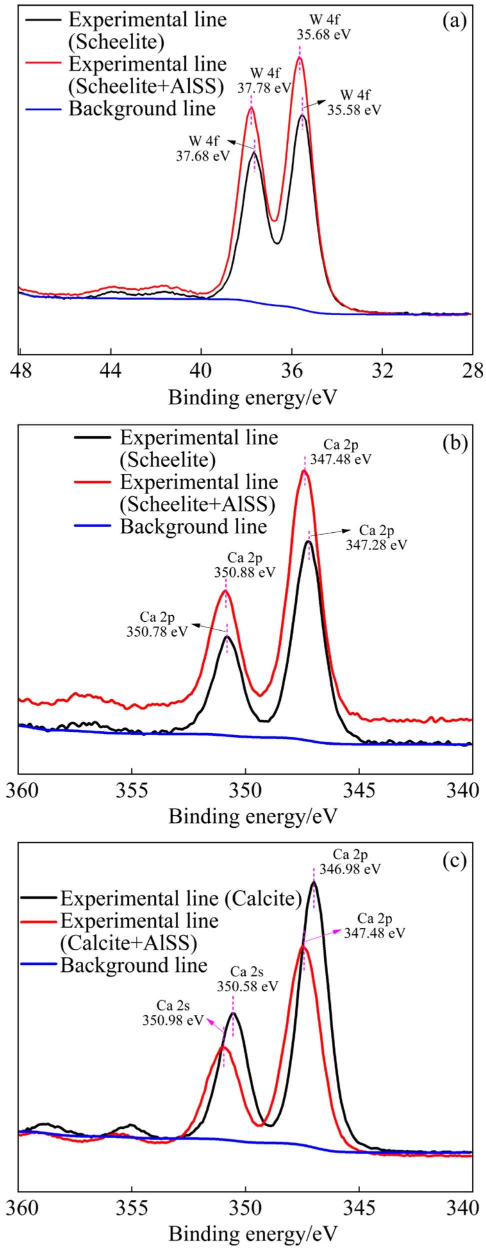

Fig. 8 W and Ca XPS spectra of scheelite (a, b) and calcite (c) before and after AlSS treatment

3.5 Flotation results

NaOL and SS are the most common flotation reagents for scheelite and calcite flotation separation [13]. $Al_2(SO_4)_3$ is also a common flotation reagent that is used as a regulator or flocculant. The flotation recoveries of scheelite and calcite in the presence of NaOL, SS and $Al_2(SO_4)_3$ are presented in Fig. 9.

The following conclusions can be drawn from Fig. 9: (1) When the NaOL collector was separately added, scheelite showed high flotation performance over the whole pH range, especially for a pH of 9.0. Calcite had good floatability and NaOL had poor

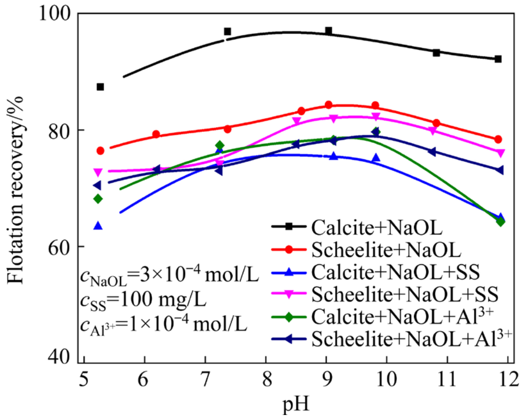

Fig. 9 Flotation recoveries of scheelite and calcite in the presence of NaOL, SS and $Al_2(SO_4)_3$

selectivity to calcite. (2) When NaOL was added to SS, SS had a stronger inhibition effect on calcite than on scheelite. Because the flotation recovery of calcite was still very high, it was clear that the flotation separation of scheelite and calcite was still very difficult by using the SS inhibitor alone. (3) When NaOL was added with $Al_2(SO_4)_3$, the added Al^{3+} reacted with the NaOL collector to form $Al(OL)_3$, which consumed part of the collector. Therefore, the flotation recoveries of scheelite and calcite were both reduced to a certain extent, and that of calcite was reduced more obviously. This result indicated that the flotation separation of scheelite from calcite was still not feasible in the presence of $Al_2(SO_4)_3$.

Compared with the single addition of inhibitors, the combined inhibitors can significantly enhance the selective inhibition of gangue minerals and improve the index of scheelite, which has wide application prospects [34]. Figure 10 shows the flotation recovery of scheelite and calcite in the presence of the AlSS combined inhibitor under different pH values and AlSS concentrations. Figure 10(a) shows that the flotation recovery of scheelite increased from the minimum value of 60.48% to the maximum value of 78.96% as the pH increased from 5.0 to 9.0, and then slowly decreased to 72.08% at pH 11.8. In the pH range of 5.0−11.0, the calcite flotation recovery slowly increased from 26.48% to 33.26%, and decreased to 29.14% as the pH continued to increase. Figure 10(b) shows that when the AlSS concentration increased from 0 to 120 mg/L at a pH of 9.0, the flotation recovery of scheelite slowly decreased from 84.32% to 77.76% and then slightly increased to 78.01%, while the flotation recovery of calcite sharply decreased from 97.02% to 32.33% and then slightly increased to 33.21% (c_{AlSS}= 120 mg/L). It was clear that the AlSS metal-inorganic complex depressant had good selectivity for the flotation recovery of scheelite and calcite.

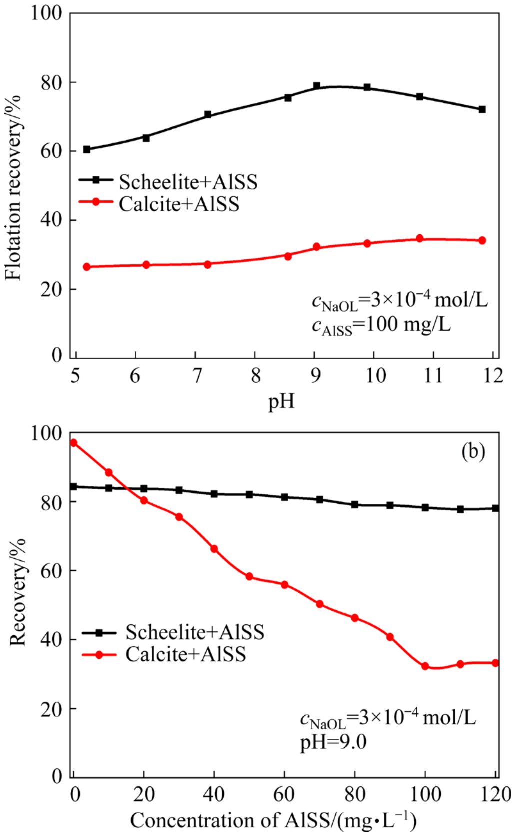

Fig. 10 Effect of pH (a) and concentration of AlSS (b) on flotation recoveries of scheelite and calcite

For the application of combined inhibitors, the mass ratio had a significant effect on the performance of the combined treatment [35]. Figure 11 shows the flotation recoveries of scheelite and calcite under different mass ratios of $Al_2(SO_4)_3$ to SS. It can be seen from Fig. 11 that the flotation recovery of scheelite slightly fluctuated, and the general trend was increasing with the increase of the mass ratio of $Al_2(SO_4)_3$ to SS, while the flotation recovery of calcite irregularly fluctuated. When the mass ratio of $Al_2(SO_4)_3$ to SS was equal to 1:3, the flotation recovery difference between scheelite and calcite was the largest (reaching 45.93%), and that of scheelite was 78.26%, which was very close to the maximum recovery of 78.31%. After comprehensive consideration, the mass ratio of Al^{3+} to SS was chosen to be 1:3 during the following study.

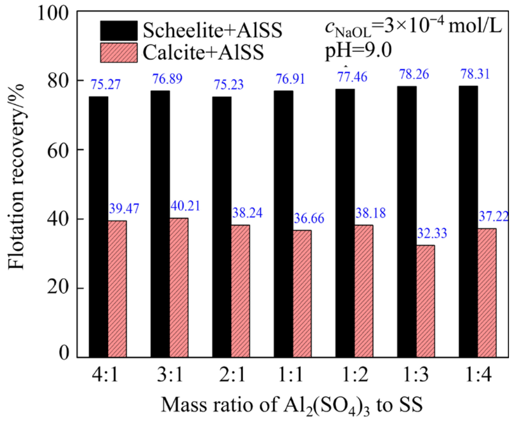

Fig. 11 Effect of mass ratio of $Al_2(SO_4)_3$ to SS on flotation recovery of scheelite and calcite

The results of the microflotation test showed that the AlSS metal-inorganic complex depressant had good selectivity for the flotation separation of scheelite and calcite. Therefore, an artificial mixed mineral flotation test was conducted to further study the performance of AlSS. It can be seen from Table 4 that when only the NaOL collector was added, the grade and recovery of WO_3 were 38.43% and 86.98%, respectively. When NaOL was added with SS, the flotation recovery of WO_3 remained 86.96%, while the grade of WO_3 increased by 9.88% and reached 48.31%. When NaOL was added with AlSS, the flotation recovery of WO_3 slightly decreased to 83.14%, while the grade of WO_3 sharply increased to 68.34%. Therefore, the AlSS metal-inorganic complex depressant also demonstrated sensational selectivity for the flotation separation of scheelite from calcite during artificial mixed minerals.

To more clearly observe the adsorption of SS, NaOL and AlSS on the scheelite and calcite surfaces, a schematic was drawn (Fig. 12). In the presence of SS and NaOL, a large amount of NaOL was adsorbed on both the scheelite surface and calcite surface. Moreover, more SS was adsorbed on the surface of calcite than on the surface of scheelite. In the presence of AlSS and NaOL, a large amount of NaOL was adsorbed on the scheelite surface. In addition, a small amount of NaOL and a large amount of AlSS were adsorbed on the calcite surface. This result indicated that scheelite had good floatability, and the floatability of calcite became very poor after adding AlSS. This may be because AlSS was adsorbed on the calcite surface by chemical reaction, which resulted in competitive adsorption with NaOL.

Table 4 Flotation results of mixed minerals at pH=9.0

Reagent	Product	Yield/%	WO_3 grade/%	WO_3 recovery/%
NaOL (0.3 mmol/L)	Concentrate	88.79	38.43	86.98
	Tailing	11.21	45.56	13.02
	Feed	100.00	39.23	100.00
NaOL (0.3 mmol/L)+ SS (100 mg/L)	Concentrate	70.68	48.31	86.96
	Tailing	29.32	17.48	13.04
	Feed	100.00	39.31	100.00
NaOL (0.3 mmol/L)+ AlSS (100 mg/L)	Concentrate	47.68	68.34	83.14
	Tailing	52.32	12.63	16.86
	Feed	100.00	39.19	100.00

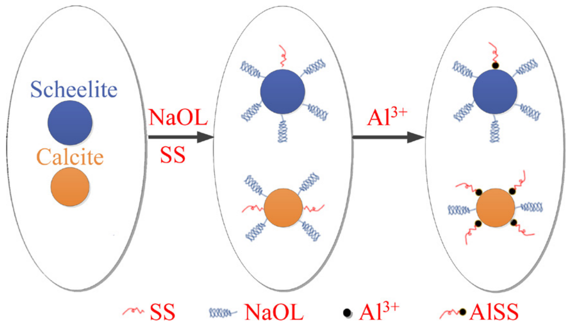

Fig. 12 Schematic illustration for adsorption of SS, NaOL and AlSS on scheelite and calcite surfaces

4 Conclusions

(1) Compared with scheelite, the depressant AlSS is more inclined to adsorb on the calcite surface, reducing the adsorption capacity of the collector NaOL on the calcite surface and its floatability. There exists competitive adsorption on calcite between colloidal particles of AlSS and NaOL.

(2) The colloidal particles composed of $Al_m(OH)_n^{3m-n}$ and $SiO_m(OH)_n^{4-2m-n}$ tended to adsorb on the calcite surface through chemical reaction, achieving the purpose of selective inhibition of calcite. $Al_m(OH)_n^{3m-n}$ and $SiO_m(OH)_n^{4-2m-n}$ may form a new silica−aluminum compound.

(3) The flotation separation of scheelite and calcite can be realized under the optimum conditions of pH 9.0, NaOL concentration of 0.3 mmol/L, and AlSS concentration of 100 mg/L; meanwhile, scheelite concentrate with WO_3 grade of 68.34% and WO_3 recovery of 83.14% was obtained from mixed scheelite and calcite ores.

CRediT authorship contribution statement

Guan-fei ZHAO: Testing, Resources, Data curation, Data analysis, Writing − Original draft; **Bo FENG:** Writing − Review & editing; **Dong-mei ZHU:** Methodology, Investigation, Validation, Formal analysis, Writing − Review & editing; **Xian-hui QIU:** Writing − Review & editing; **Zhi-yong GAO:** Writing − Review & editing; **Hua-shan YAN:** Editing; **Rui-seng LAI:** Testing, Editing; **Ting-sheng QIU:** Methodology, Writing − Review & editing, Supervision. All authors have read and agreed to the published version of the manuscript.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors gratefully acknowledge the National Key Research and Development Program of China (No. 2018YFC1903400), the Key Program for International S&T Cooperation Projects of China (No. 2021YFE0106800), the National Natural Science Foundation of China (Nos. 52164020, 52174248), and the Science and Technology Research Project of Education Department of Jiangxi Province, China (No. GJJ190442).

References

[1] KUPKA N, RUDOLPH M. Froth flotation of scheelite — A review [J]. International Journal of Mining Science and Technology, 2018, 28(3): 373−384.

[2] MA Z L, ZHANG L C, LI J T, ZHAO Z W. Process of removing phosphorus and molybdenum from complex scheelite concentrates with high phosphorus and molybdenum [J]. Nonferrous Metals Science and Engineering, 2020, 11(5): 25−31. (in Chinese)

[3] RAI B, SATHISH P, TANWAR J, PRADIP, MOON K S, FUERSTENAU D W. A molecular dynamics study of the interaction of oleate and dodecylammonium chloride surfactants with complex aluminosilicate minerals [J]. Journal of Colloid and Interface Science, 2011, 362(2): 510−516.

[4] GAO Z Y, BAI D, SUN W, CAO X F, HU Y H. Selective flotation of scheelite from calcite and fluorite using a collector mixture [J]. Minerals Engineering, 2015, 72: 23−26.

[5] GAO Y S, GAO Z Y, SUN W, YIN Z G, WANG J J, HU Y H. Adsorption of a novel reagent scheme on scheelite and calcite causing an effective flotation separation [J]. Journal of Colloid and Interface Science, 2018, 512: 39−46.

[6] MARINAKIS K I, KELSALL G H. The surface chemical properties of scheelite ($CaWO_4$). I: The scheelite/water interface and $CaWO_4$ solubility [J]. Colloids and Surfaces, 1987, 25(2/3/4): 369−385.

[7] ZHAO G F, ZHU D M. Enhanced flotation separation of cassiterite from calcite using metal-inorganic complex depressant [J]. Minerals, 2021, 11(8): 880−894.

[8] CHEN C, SUN W, ZHU H L, LIU R Q. A novel green depressant for flotation separation of scheelite from calcite [J]. Transactions of Nonferrous Metals Society of China, 2021, 31(8): 2493−2500.

[9] FOUCAUD Y, COLLET A, FILIPPOVA I V, BADAWI M. Synergistic effects between fatty acids and non-ionic reagents for the selective flotation of scheelite from a complex tungsten skarn ore [J]. Minerals Engineering, 2022, 182: 107566.

[10] LIU W B, PENG X Y, LIU W G, WANG X Y, ZHAO Q, WANG B Y. Effect mechanism of the iso-propanol substituent on amine collectors in the flotation of quartz and magnesite [J]. Powder Technology, 2020, 360: 1117−1125.

[11] ZHAO P X, LIU W B, LIU W G, TONG K L, SHEN Y B, ZHAO S K, ZHOU S J. Efficient separation of magnesite and quartz using eco-friendly dimethylaminopropyl lauramide experimental and mechanistic studies [J]. Minerals Engineering, 2022, 188: 107814.

[12] HUANG Z Y, KUANG J Z, ZHU L P, YUAN W Q, ZOU Z L. Effect of ultrasonication on the separation kinetics of scheelite and calcite [J]. Minerals Engineering, 2021, 163: 106762.

[13] GAO Z Y, DENG J, SUN W, WANG J J, LIU Y F, XU F P, WANG Q H. Selective flotation of scheelite from calcite using a novel reagent scheme [J]. Mineral Processing and Extractive Metallurgy Review, 2022, 43(2): 137−149.

[14] LIU C, NI C Q, YAO J X, CHANG Z W, WANG Z B, ZENG G S, LUO X B, YANG L M, REN Z, SHAO P H, DUAN L M, LIU T X, XIAO M. Hydroxypropyl amine surfactant: A novel flotation collector for efficient separation of scheelite from calcite [J]. Minerals Engineering, 2021, 167: 106898.

[15] HUO R H, XIE S, DENG P, ZENG Z Y, LIAO C F, WANG X. Preparation of Fe Mn W Sn alloy from alkali boiled black-and-white tungsten slag and red mud by synergistic carbothermic reduction and recovery [J]. Nonferrous Metals Science and Engineering, 2023, 14(3): 295−301. (in Chinese)

[16] PAN Z C, ZHANG YS,HU J J, JIAO F, QIN W Q. Camphor leaf extract as neoteric and environmentally friendly depressant in flotation separation of scheelite and calcite [J]. Transactions of Nonferrous Metals Society of China, 2023, 33: 275−284.

[17] AI G H, XU X Y, WU H B, QIU X H. Experimental research on beneficiation of a low-grade scheelite in Jiangxi [J]. Nonferrous Metals Engineering, 2017, 7(1): 44−48. (in Chinese)

[18] FENG B, ZHANG W P, GUO W, PENG J X, LUO G D, WANG H H. Role and mechanism of combined collector and sodium alginate in flotation separation of scheelite and calcite [J]. The Chinese Journal of Nonferrous Metals, 2019, 29(1): 203−210. (in Chinese)

[19] FENG Y S, XU S T, XU L G, YAN G L. Sustainable development of tungsten industry in Jiangxi Province from

the perspective of industrial cluster [J]. Nonferrous Metals Science and Engineering, 2021, 12(5): 103−109. (in Chinese)

[20] WANG X, QIN W Q, JIAO F, DONG L Y, GUO J G, ZHANG J, YANG C R. Effect and mechanism of combined depressant in flotation separation of scheelite and calcium-containing gangue minerals [J]. Transactions of Nonferrous Metals Society of China, 2023, 33: 2318−2338.

[21] WANG T T. Study on the performance and mechanism of flotation separation of scheelite and calcium bearing gangue mineral with organic depressants [D]. Zhenzhou: Zhengzhou University, 2020. (in Chinese)

[22] DONG L Y, JIAO F, QIN W Q, ZHU H L, JIA W H. New insights into the carboxymethyl cellulose adsorption on scheelite and calcite: Adsorption mechanism, AFM imaging and adsorption model [J]. Applied Surface Science, 2019, 463: 105−114.

[23] CHEN W, FENG Q M, ZHANG G F, YANG Q, ZHANG C, XU F P. The flotation separation of scheelite from calcite and fluorite using dextran sulfate sodium as depressant [J]. International Journal of Mineral Processing, 2017, 169: 53−59.

[24] CHEN W, FENG Q M, ZHANG G F, YANG Q, ZHANG C. The effect of sodium alginate on the flotation separation of scheelite from calcite and fluorite [J]. Minerals Engineering, 2017, 113: 1−7.

[25] CHEN W, FENG Q M, ZHANG G F, LIU D Z, LI, L F. Selective flotation of scheelite from calcite using calcium lignosulphonate as depressant [J]. Minerals Engineering, 2018, 119: 73−75.

[26] WANG Y H, PAN G C, CHU H R, LU D F, ZHENG X Y. Flotation separation of scheelite from calcite using sulfonated naphthalene–formaldehyde condensate as depressant [J]. Minerals, 2022, 12(5): 517−528.

[27] ZHOU L H, CHEN Z Y, FENG B, GUO W, LUO X P. Research status and prospect of fluorite flotation reagents [J]. Nonferrous Metals Science and Engineering, 2016, 7(4): 91−97. (in Chinese)

[28] DONG L Y, JIAO F, QIN W Q, WEI Q. Utilization of iron ions to improve the depressive efficiency of tartaric acid on the flotation separation of scheelite from calcite [J]. Minerals Engineering, 2021, 168: 106925.

[29] EL-MOFTY S E, PATRA P, EL-MIDANY A A, SOMASUNDARAN P. Dissolved Ca^{2+} ions adsorption and speciation at calcite−water interfaces: Dissolution and zeta potential studies [J]. Separation and Purification Technology, 2021, 257: 117924.

[30] FU J H, HAN H S, WEI Z, LIU R H, LI W H, XU T, JI D H. Selective separation of scheelite from calcite using tartaric acid and Pb-BHA complexes [J]. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2021, 622: 126657.

[31] WANG C T, LIU R Q, SUN W, JING N W, XIE F F, HE Q L, ZHAI D D. Selective depressive effect of pectin on sphalerite flotation and its mechanisms of adsorption onto galena and sphalerite surfaces [J]. Minerals Engineering, 2021, 170: 106989.

[32] HENG J Y Y, BISMARCK A, LEE A F, WILSON K, WILLIAMS D R. Anisotropic surface energetics and wettability of macroscopic form I paracetamol crystals [J]. Langmuir: The ACS Journal of Surfaces and Colloids, 2006, 22(6): 2760−2769.

[33] CHAU T T. A review of techniques for measurement of contact angles and their applicability on mineral surfaces [J]. Minerals Engineering, 2008, 22(3): 213−219.

[34] LI T G, QIU X Y, ZHOU X T. Research status of scheelite flotation reagents [J]. Materials Research and Application, 2018, 12(1): 8−12. (in Chinese)

[35] WEI Z, HU Y H, HAN H S, SUN W, WANG R L, SUN W J, WANG J J, GAO Z Y, WANG L, ZHANG C Y, SUN L, LIU R H. Selective separation of scheelite from calcite by self-assembly of H_2SiO_3 polymer using Al^{3+} in Pb-BHA flotation [J]. Minerals, 2019, 9(1): 43−58.

金属无机复合抑制剂强化分离白钨矿与方解石

赵冠飞 1,2,3，冯 博 1,2，朱冬梅 1,2，邱仙辉 1,2，高志勇 3，严华山 1,2，赖瑞森 2，邱廷省 1,2

1. 江西理工大学 江西省矿业工程重点实验室，赣州 341000；
2. 江西理工大学 资源与环境工程学院，赣州 341000；
3. 中南大学 资源加工与生物工程学院，长沙 410083

摘　要：研究由硫酸铝和水玻璃硅酸钠(AlSS)组成的金属无机复合抑制剂对白钨矿与方解石浮选分离的影响。Zeta 电位和吸附量测定结果表明，由 $Al(OH)_4^-$和 $SiO_m(OH)_n^{4-2m-n}$ 组成的负电荷胶体颗粒倾向于吸附在方解石表面，抑制油酸钠(NaOL)的吸附，而负电荷胶体颗粒在白钨矿表面的吸附量较低，导致 NaOL 在白钨矿表面的吸附量较大。接触角测量结果表明，白钨矿在 NaOL+AlSS 溶液中的疏水性明显优于方解石。XPS 测试结果表明，Al 和 Si 在方解石表面有吸附，而在白钨矿表面没有吸附。与只添加水玻璃 (硅酸钠，SS)相比，AlSS 对方解石的抑制作用明显增强，对白钨矿浮选几乎没有影响。在白钨矿与方解石混合矿中添加 AlSS，可获得 WO_3 品位为 68.34%、WO_3 回收率为 83.14%的白钨矿精矿。

关键词：白钨矿；方解石；分离强化；油酸钠；金属无机复合抑制剂

(Edited by Wei-ping CHEN)