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The effect of sodium carboxymethyl cellulose on the entrainment of zoisite in flotation

Zhengjun Zhang, Leming Ou, Saizhen Jin, Hao Zhou

School of Minerals Processing and Bioengineering, Central South University, Changsha 410083, China
Key Laboratory of Hunan Province for Clean and Efficient Utilization of Strategic Calcium-containing Mineral Resources, Central South University, Changsha 410083, China

Corresponding author: olm@csu.edu.cn (L. Ou)

Abstract: During flotation, fine gangue minerals can enter the concentrate through mechanical entrainment, which seriously affects the quality of concentrate. In this work, the effect of sodium carboxymethyl cellulose (CMC) on the flotation performance of zoisite, a silicate mineral, was studied. The role of CMC in reducing zoisite entrainment was investigated by dynamic foaming tests, surface tension measurements, rheology measurements, sedimentation tests, and optical microscopy experiments. The flotation results showed that zoisite mainly entered the concentrate by entrainment; the addition of low dosages of CMC decreased zoisite entrainment and efficiently separated cassiterite from zoisite; moreover, the concentrate grade and recovery of SnO_2 increased by 1.27 % and 5.63 %, respectively, by using CMC in closed-circuit flotation tests. Dynamic foaming studies on the two-phase and three-phase foam/froth revealed that the presence of CMC decreased the froth ability and froth stability, and greatly altered the three-phase froth structure. Basically, the bubbles in the foam were larger after adding CMC. For the two-phase foam, the change of foam property had little to do with surface activity and bulk viscosity. For the three-phase froth, the froth property was strongly affected by the interaction of CMC and zoisite. The results of the sedimentation test and microscopy experiment demonstrated that CMC can cause zoisite to flocculate and enlarge the particle size, which was the main reason for the decrease of froth stability and entrainment. This study indicates that the side effects of depressants should not be overlooked when discussing the role of depressants in flotation.

Keywords: entrainment, zoisite, froth stability, flotation, CMC flocculation

1. Introduction

In flotation, entrainment is essentially a dynamic transfer process by which unwanted minerals suspended in water enter the flotation froth, move upwards, and finally leave the flotation cell (Wang et al., 2015). Particle size and froth stability are the two most important factors affecting entrainment (Smith and Warren, 1989). Due to the low specific gravity, fine particles can easily overcome gravity and shear forces and pass upwards across the pulp/froth interface. In the froth phase, particles disperse in the Plateau borders formed by the thin water films and move with the liquid. As the liquid transfers, some particles are entrained and scraped to the concentrate, while other particles are reported back to the pulp through drainage (Neethling and Cilliers, 2002). Adding flocculant to enlarge mineral particle size can decrease entrainment, however, the use of flocculant not only reduces gangue recovery but also often lower recovery of valuable minerals. Therefore, how to reduce entrainment in flotation by modifying foam properties is one of the research directions.

Many factors can affect froth stability, e.g., frother type, frother concentration, and the nature and number of particles presented in the system. There are many researches on the effects of mineral particles, collectors, and frothers on froth stability (Aktas et al., 2008; Barbian et al., 2005; Barbian et al., 2003; Cilek and Karaca, 2015; Liu et al., 2020; Schwarz and Grano, 2005), however, few studies on the

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effects of depressants on froth have been conducted. Depending on the degree of substitution, CMC is usually used as a depressant of magnesium silicate minerals or pulp dispersant in flotation (Feng et al., 2012; Liu et al., 2006), but there is little discussion about the effect of CMC on foam properties. Viscosity and surface tension are often used to predict froth performance (Folmer and Kronberg, 2000; Li et al., 2016; Neethling and Cilliers, 2003). In two-phase foam system, surface tension and viscosity are the main factors influencing foam stability. In three-phase froth system, however, the situation is much more complicated, because the froth stability is not only related to rheology and surface tension, but also significantly affected by the state and behaviour of particles in the froth phase.

Flotation is the most important method to recover fine cassiterite. The flotation of cassiterite is often accompanied by a large number of silicate gangue, among which the hydrophilic fine minerals generally enter the concentrate through slurry-coating or entrainment. Zoisite ($Ca_2Al_3(SiO_4)$ (Si_2O_7) O (OH)) is a kind of nesosilicate mineral with a complex structure. There is little research on the flotation performance of zoisite.

In China, the Dulong mine plant (latitude 22.90° N and longitude 104.53° E) faces great challenges in treating its SnO_2 ores due to the high content of silicate minerals in the flotation concentrate. Before this study, we have found that in the flotation of cassiterite in the Dulong plant, when the content of zoisite in the feed was 2.59 %, a concentrate grade of 15.56 % zoisite was achieved; besides zoisite, the main gangue minerals in the concentrate were epidote, hornblende, chlorites, and garnet, with contents of 7.87 %, 9.75 %, 15.07 %, and 11.38 % respectively, and these silicate minerals were likely to enter the concentrate by entrainment due to their physicochemical properties; moreover, the Mineral Liberation Analysis (MLA) showed a high liberation (88.87 %) of cassiterite in the concentrate, so it's unlikely that the gangue minerals were recovered by the intergrowth with cassiterite. To explore the reasons for the low concentrate grade and the high enrichment ratio of zoisite in the flotation, the study was carried out.

The purpose of this paper was to study the role of CMC in zoisite flotation, and to separate cassiterite from zoisite by using CMC in the binary mixed minerals flotation. Besides, the closed-circuit flotation of a cassiterite ore from Dulong was also carried out. During the experiment, the side effects of CMC on flotation were discussed and analysed by several methods.

2. Materials and methods

2.1. Materials and reagents

A zoisite single mineral sample was obtained from Guangdong province of China. The results of X-ray fluorescence (XRF) analysis (Table. 1) and X-ray Diffraction (XRD) analysis (Fig. 1) confirm that its purity above 98 %. The cassiterite (100 % purity) and zoisite mineral samples were separately crushed by a ceramic ball to collect -0.037 mm particles to be used in the tests. The particle size distribution of the zoisite sample by Malvern Mastersizer 2000 is shown in Fig. 2. The D (4, 3) (volume mean particle size) of the zoisite sample was 0.021 mm.

A SnO_2 ore sample was taken from the Dulong plant in Yunnan province, China. The particle size distribution of this ore is shown in Fig. 3. The major valuable mineral in the sample was cassiterite, and the sample contained 0.60 % cassiterite and 2.59 % zoisite by XRD analysis. The main gangue minerals of the sample were hornblende, chlorites, pyrrhotite, and phlogopite, with contents of 8.67 %, 18.82 %, 12.79 %, and 8.47 % respectively.

Benzohydroxamic acid (BHA)(Tokyo Chemical Industry, above 98% purity) was used as the collector, which had a strong selectivity for cassiterite but a weak collecting ability (Sun et al., 2016). Lead nitrate (LN) (Aladdin Industrial Corporation, China, 99% purity) was used as the activator of cassiterite. Methyl isobutyl carbinol (MIBC) was used as the frother, and CMC (MW~300000, degree of

Table 1. Key elements composition of zoisite sample (wt%)

O	Si	Al	Ca	Fe	Mg	P
45.22	18.11	16.98	17.27	1.59	0.16	0.01
S	K	Ti	Mn	Cr	Na	Sr
0.02	0.09	0.07	0.03	0.18	0.26	0.02

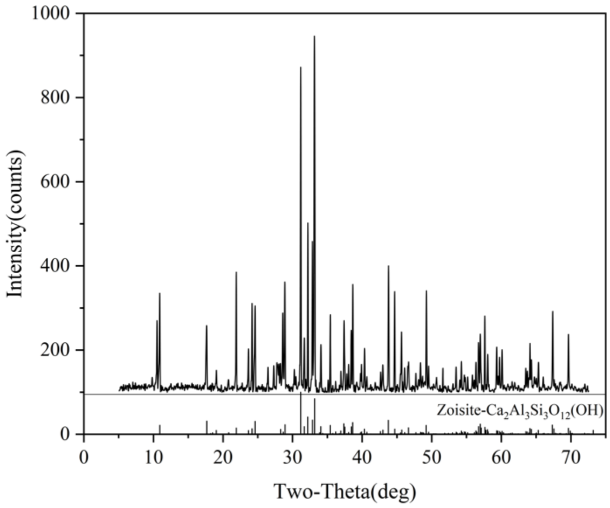

Fig. 1. XRD spectrums of zoisite sample

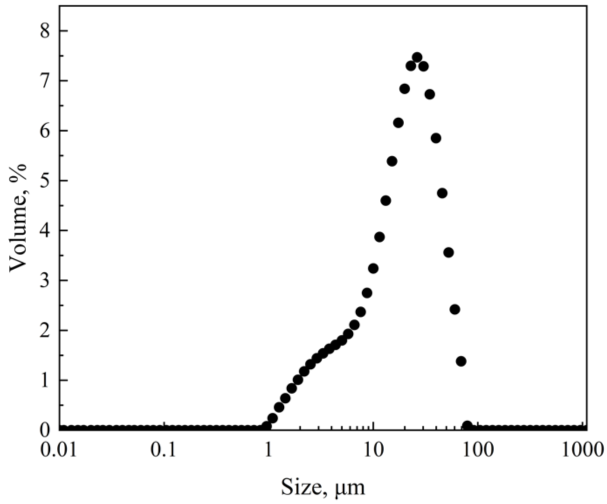

Fig. 2. The particle size distribution of zoisite sample

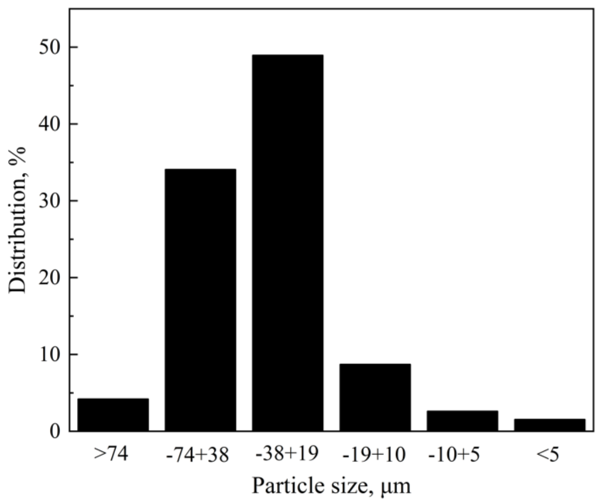

Fig. 3. The particle size distribution of cassiterite ore sample

substitution: 0.9, obtained from Changsha, China) was used to reduce the recovery of zoisite. HCl and NaOH solutions were used to adjust the pH of pulp. Distilled water was used throughout the experiment. For closed-circuit flotation, a new collector, JSY-19 (a mixture of hydroxamic acid and arsine acid in a ratio of 3:2) was used as the collector of cassiterite, and terpenic oil was used as the frother; other reagents were the same as micro-flotation tests. Both JSY-19 and terpenic oil were obtained from Dulong concentrator.

2.2. Flotation tests

Micro-flotation tests were carried out in an XFG flotation machine with a 40 mL cell at 1992rpm of agitation. The flotation pulp for single or binary mixed minerals (1g cassiterite and 1g zoisite) was prepared by adding 2 g of mineral samples to 40 mL of distilled water. After each of the desired reagents was added, the suspension was agitated for 3 min (MIBC for 1 min). The flotation pH was adjusted to 8~9 and the flotation time was 3 min. In the flotation process, the froth was scraped every 3 s to reduce errors. For single mineral flotation, the concentrates and tails were dried, weighed to calculate flotation recovery. For binary mixed minerals flotation, the concentrates and tails were dried, weighed, and assayed for SnO_2 grade for calculating cassiterite recovery.

To explore the relationship between water recovery and zoisite recovery, four concentrates were collected at 0.5, 1, 2 and 3 min in the flotation process; and the pulp level was maintained using a washing bottle. After the flotation, the wet weight of the concentrates was taken, and the concentrates and tails were dried and weighed for calculating the water recovery and zoisite recovery. The water recovery was calculated by the following equation:

$$Water\ recovery = \frac{(M_{water})_{con}}{40} \times 100\% \tag{1}$$

where the numerator was the mass of water in each concentrate.

Closed-circuit flotation tests were carried out in two XFG flotation machines (with a 1.5 L cell for rougher and scavengers and a 0.5 L cell for cleaners, respectively) at 1992 rpm of agitation. The cassiterite feed was slurry with a density of about 25 %, and the pulp pH was around 9. After 5 cycles, the concentrate collected and tailing were dried, weighed, and assayed for SnO_2 grade for calculating cassiterite recovery. The flowsheet is shown in Fig. 4.

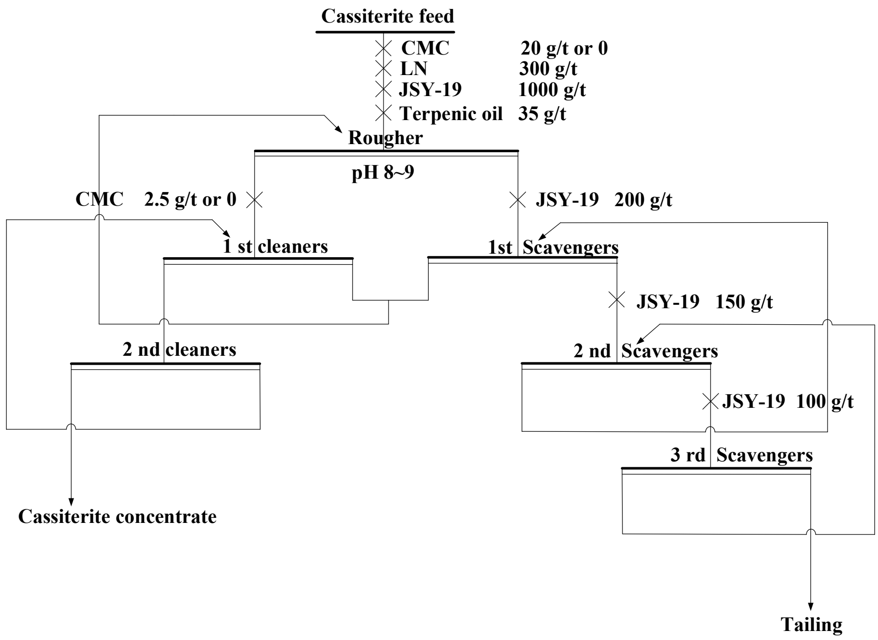

Fig. 4. Flowsheet of closed-circuit flotation tests

2.3. Dynamic foaming studies

The device for foamability tests was based on Lunkenheimer's report (Lunkenheimer and Malysa, 2003). As shown in Fig. 5, the assembled device includes a constant-flow pump, a flowmeter, and a glass column (4 cm in diameter and 50 cm in height) with scale. A venturi tube and a porous sand core in the bottom of the column can produce many air flows.

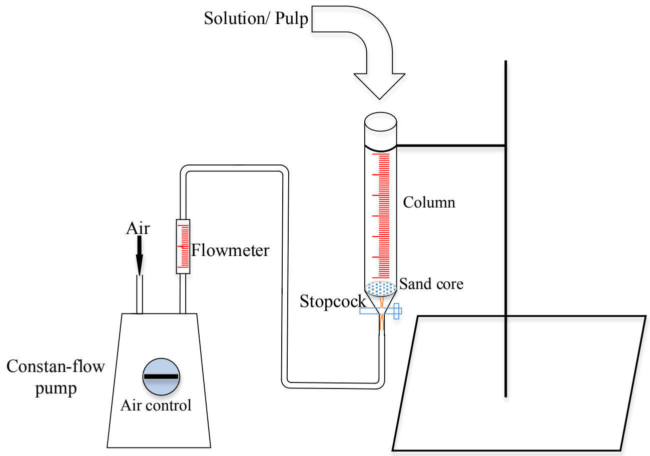

Fig. 5. Schematic diagram of foam testing system

Researchers have reported that dynamic method may more likely give a true indication of the froth stability in flotation (Farrokhpay, 2011). In this study, the maximum froth volume was used to represent the froth ability. Based on Bikerman's unit of foaminess (Bikerman, 2013), the froth stability was calculated by the following equation:

$$\Sigma = \frac{V_f}{Q} = \frac{S \cdot H_{max}}{Q} \quad (2)$$

where $\sum$ is the dynamic stability factor; V_f is the maximum froth volume (cm^3), Q is the air flow rate (cm^3/s), S is the cross-section area of the column (cm^2), and H_{max} is the maximum froth depth (cm).
The foam height/volume was measured in the two-phase and three-phase systems. All the frother concentrations (40, 100, 200, and 300 mg/L) were tested in combination with 500 mg/L or without CMC. 2 g of zoisite was used for each three-phase frothing test. Each test was repeated at least 3 times.
During the foaming test, the 100 mL configured solution/pulp was poured into the column firstly, and then the stopcock was opened; the airflow rate was increased from 0.5 to 3 L/min, with 0.5 L/min steps. The maximum height was recorded in each step when the foam height was stable. The foam volume was plotted vs. the air flow rate for each test.

2.4. Surface tension measurements

GBX3S surface tensiometer was used to measure the surface tension of polymer solution. MIBC solutions with different concentrations (0, 100, 200, 300 mg/L) were prepared and combined with 500 mg/L or without CMC. The 30 mL configured solution was added into the sample glass. Each condition was repeated 3 times, and the average value was taken as the final value.

2.5. Rheology measurements

Rheological properties were measured using Anton Paar MCR102 rheometer that was equipped with a 40 mL sample cup and two kinds of stirring impellers. The Rheology of CMC solution and pulp were measured using cylinder impeller and six-outer-blade impeller respectively. The polymer solutions were tested at concentrations of 0, 500, 1000, 2000 and 4000 mg/L respectively. The pulp density and pH value were the same as that of flotation tests. During measurements, the temperature was maintained at 25 C.

The measurement procedures involved the following steps: (1) pre-shearing of solution and suspension at 300 s^{-1} for 1 min and 3 mins respectively; (2) stabilization of solution and suspension for 5 s at 0 s^{-1}; and (3) measurement of shear stress and apparent viscosity with increasing shear rate of 0-600 s^{-1}.

2.6. Sedimentation tests

The flocculation behaviours of zoisite in suspension were investigated by settling tests. For each test, a 0.2 g zoisite was mixed with 100 mL distilled water in a beaker and stirred at 750 rpm for 3 minutes at pH 8 (a desired concentration of CMC was added). Afterwards, the suspension was transferred to a 100 mL settling cylinder, and settled for 3 min to siphon out the upper 25 mL suspension. The turbidity of the suspension was determined by a Scattering Turbidimeter. The degree of flocculation or dispersion was characterized by the turbidity, and a lower turbidity value generally represented better flocculation associated with particles in pulp.

2.7. Optical microscopy experiments

Optical microscopy experiments were conducted to visually examine the state of flocculation. The procedure for the suspension configuration was the same as for the sedimentation tests. After conditioning with or without CMC, a drop of the suspension was transferred to a slide and then examined under a Leika DM4800 microscope equipped with a video camera.

3. Results and discussion

3.1. Micro-flotation experiment

Fig. 6 shows the trend of zoisite recovery with the increase of MIBC concentration in the absence and presence of BHA and LN+BHA (BHA 60 mg/L and LN 30 mg/L were the optimal conditions for cassiterite flotation we had conducted). Zoisite recovery increased with the increasing MIBC concentration. The addition of BHA increased the zoisite recovery. This was not likely caused by the adsorption of BHA on zoisite promoting the hydrophobicity, since the contact angle of zoisite didn't change after BHA treatment (See Fig. S1 of the supporting information available with this article). Tian et al. (2018a) reported that BHA can improve froth stability within a certain range. Therefore, the increase in zoisite recovery may be attributed to BHA modifying the foam and enhancing entrainment. LN seems to enhance the adsorption of BHA on zoisite, just as the case of the flotation of cassiterite using LN+BHA (Tian et al., 2017).

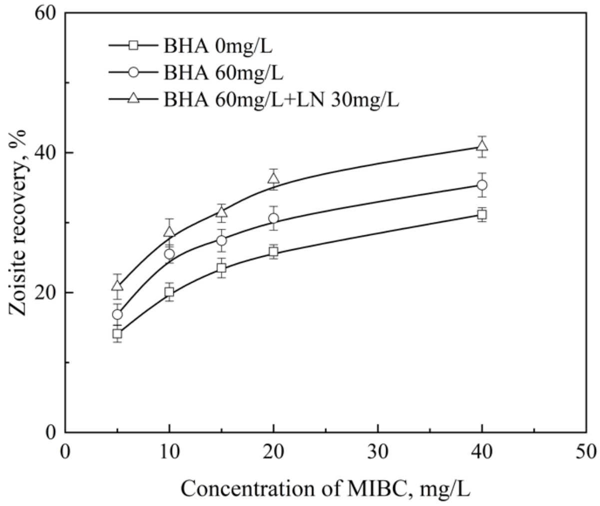

Fig. 6. Flotation recovery of zoisite as a function of MIBC concentration in the presence and absence of BHA and LN+BHA

To understand the way of zoisite entering the concentrate, the relationship of water recovery and zoisite recovery was studied. The recovery of zoisite as a function of water recovery under different CMC concentrations is shown in Fig. 7. According to the method proposed by Warren (1985), the points were fitted, and the intercept of the fitting line on the Y-axis was the recovery by true flotation. After adding 4 mg/L CMC, the zoisite recovery and the recovery by true flotation reduced from 30.49 % to 20.03%, 6.18 % to 4.68 %, respectively; the water recovery also reduced from 38.02 %to 34.22%. Clearly, zoisite mainly enters the concentrate by entrainment, and its recovery by entrainment decreases with the decreasing water recovery under different CMC concentrations.

The slope of the fitting line represents the degree of entrainment, which can reflect the severity of entrainment (Smith and Warren, 1989). The degree of entrainment decreased from 0.64 in the absence of CMC to 0.45 at 4 mg/L CMC, indicating that CMC can decrease zoisite entrainment.

To understand the effect of CMC on the flotation of cassiterite-zoisite mixture minerals, flotation tests were carried out under different CMC concentrations. The results are shown in Fig. 8. As shown in Fig. 8 (a) and Fig. 8 (b), both the mass recovery and the SnO_2 recovery reduced with the increase of CMC concentration, indicating that CMC restrained the flotation of cassiterite as well as zoisite. It is

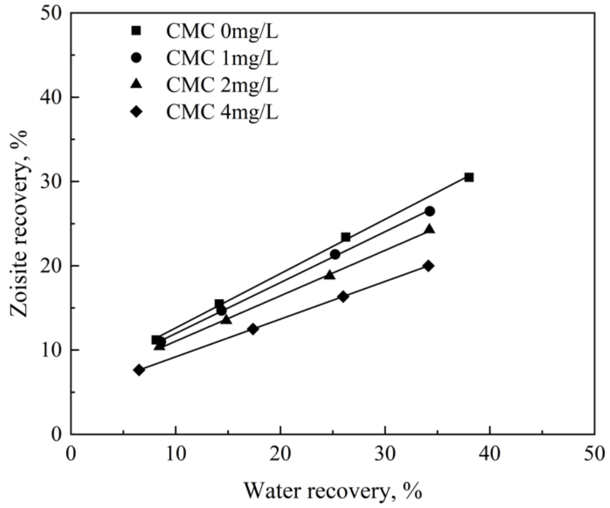

Fig. 7. Zoisite recovery as a function of water recovery at several CMC dosages (c(BHA)=60 mg/L, c(LN)=30mg/L, c(MIBC)=10 mg/L)

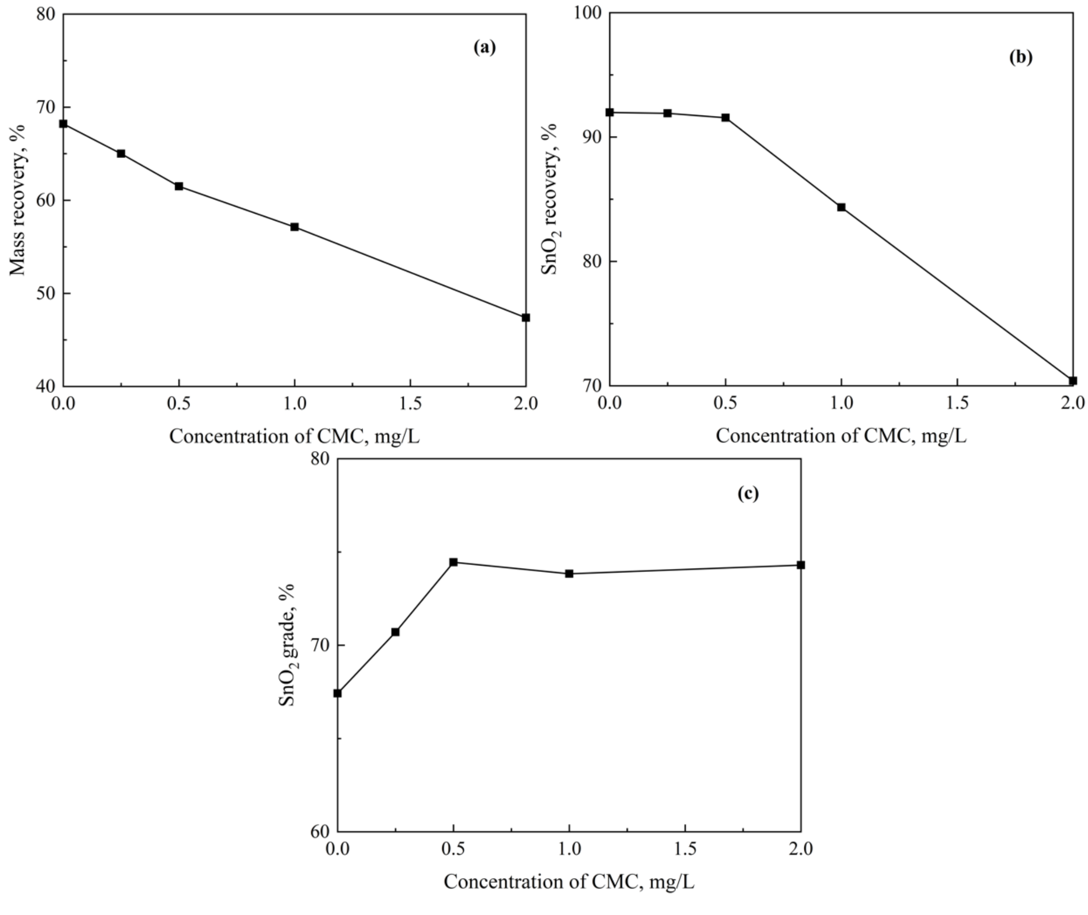

Fig. 8. (a) The mass recovery; (b) SnO_2 recovery; and (c) SnO_2 grade of flotation concentrates as a function of CMC concentration (c(BHA)=60 mg/L, c(LN)=30mg/L, c(MIBC)=10 mg/L)

known that CMC can highly inhibit the flotation of cassiterite even at low concentration(Tian et al., 2018b); however, it's interesting that CMC didn't inhibit cassiterite at low dosages, seen as the SnO_2 recovery remaining about 90% at the CMC concentration of 0.25 mg/L and 0.5 mg/L. It was shown in Fig. 8 (c), that at the CMC concentration of 0.5 mg/L, the SnO_2 grade was 7 % higher than that without CMC, indicating that adding a relatively low dosage of CMC can efficiently separate cassiterite from zoisite in flotation.

3.2. Closed-circuit flotation experiment

In this part, the collector and frother were different from those used in the micro-flotation experiment (Both JSY-19 and terpenic oil are currently used in the Dulong concentrator); however, CMC may decrease entrainment by interacting with zoisite.

Two sets of closed-circuit tests of the SnO_2 ore were conducted at a pulp pH of 8~9 to see the effect of CMC on the separation of cassiterite from gangue minerals. As can be seen from Table 2, after adding 20 g/t and 2.5 g/t CMC in the rougher and the first cleaner respectively, the SnO_2 grade and SnO_2 recovery increased by 1.27 % and 5.63 %, respectively, compared with that without CMC. It is known that CMC can decrease zoisite entrainment in the micro-floatation tests. Therefore, CMC may inhibit the flotation of zoisite and other silicate minerals, thus improving the concentrate quality.

Table 2. Effect of CMC on closed-circuit flotation of a commercial SnO_2 ore

Conditions	Products	Yield (%)	SnO_2 grade (%)	SnO_2 Recovery (%)
No CMC	concentrate	2.52	18.99	78.45
	Tailing	97.48	0.13	20.77
	Feed	100	0.61	100
Adding 20 g/t and 2.5 g/t CMC in the rougher and the first cleaner respectively	Concentrate	2.49	20.26	84.08
	Tailing	97.51	0.10	16.25
	Feed	100	0.60	100

Changes in the foam property were observed after adding CMC in the flotation process. Generally, bubble size in the froth phase appeared larger and less foam formed on top of the flotation cell, which was different from the small and dense bubbles in the absence of CMC. This usually represents a decrease in froth stability. It is known that froth stability can significantly affect entrainment; therefore, the reduced zoisite recovery and the improved separation effect of cassiterite from zoisite are probably due to the change of the foam properties by CMC. To explore the influence of CMC on foam properties, the dynamic foaming studies were conducted in the next section.

3.3. Foamability measurements

To understand the effect of CMC on the foaming ability of MIBC, two-phase foam volume of solutions containing the frother with or without CMC with the increasing airflow rate was measured (to avoid possible interference, BHA and LN were not used in this and subsequent sections). Results are shown in Fig. 9. As can be seen, it's obvious that CMC didn't foam and the foam volume increased with the increase of MIBC concentration. For MIBC solutions, the addition of 500 mg/L CMC somehow inhibited foaming when the air flow rate exceeded 1.5 L/min, especially at higher MIBC concentrations. The change of the foam volume suggested an interaction between CMC and MIBC.

Fig. 10 shows the effect of CMC on the dynamic froth stability with increasing airflow rate. As can be seen, when MIBC concentration was 40 mg/L and 100 mg/L, the addition of CMC decreased the froth stability in the whole range of air-flow rate; when MIBC concentration was 200 mg/L and 300 mg/L, CMC first enhanced and then decreased froth stability.

The role of CMC in the three-phase froth was also identified. As can be seen from Fig. 11, zoisite greatly enhanced the froth stability. It is known that mineral particles can have a great influence on frothing, especially in the case of small particle size (Hunter et al., 2008). In Hunter's paper, it has been mentioned that, in addition to the interaction mechanisms of stability (based on particles creating a

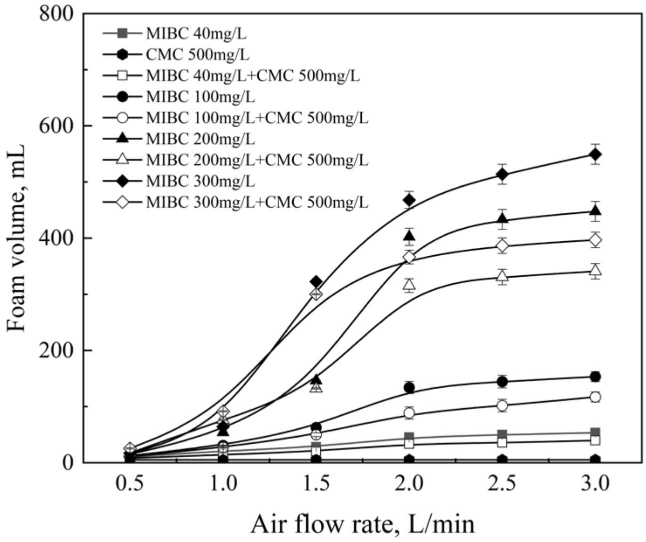

Fig. 9. Effect of concentration on the foaming of MIBC and MIBC-CMC blends

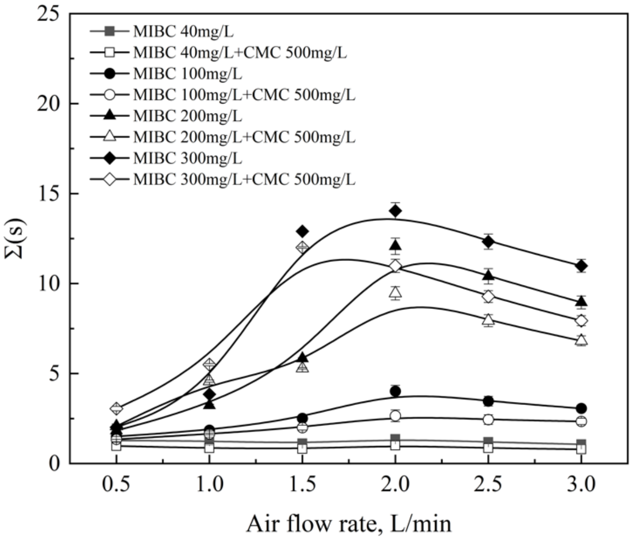

Fig. 10. Effect of CMC on the two-phase foam stability

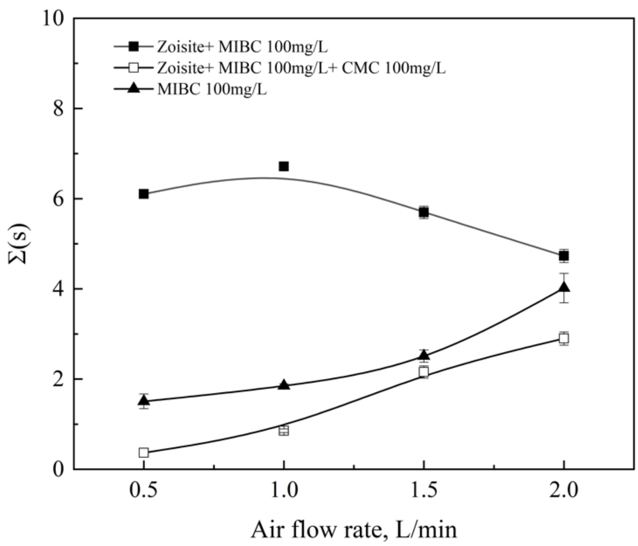

Fig. 11. Effect of CMC on the three-phase froth stability

steric barrier to coalescence), there is Non-absorbing inter-film stabilisation mechanism, by which non-absorbing particles may also stabilise foam through "stratification effect". In this experiment, it was observed that the foam flowed slower and more foam was produced, compared with that of the two-phase system. In the presence of CMC, as expected, the froth stability was significantly decreased.

3.4. Froth structure

During the three-phase foamability measurements, it was noticed that the structure of the foam formed in the absence and presence of CMC had a very distinct structure. The foam formed on the top of the column was photographed to investigate the froth structure (with air flow rate of 1 L/min). The two-phase foam structure was difficult to obtain, because the bubbles in the foam were too easy to burst, which also caused a similar foam structure before and after the addition of CMC.
The images of foam were presented in Fig. S2 (shown in the supporting information available with this article). The foam formed in the absence of CMC (Fig. S2a) was cloudy compared with that in the presence of CMC (Fig. S2b), suggesting more particles suspended in the foam; furthermore, in the presence of CMC, the foam appeared more fragile and drier, suggesting bubble coalescence and drainage were evident in the foam. To obtain the bubble size distribution, the images were first depicted manually and then processed by python-OpenCV. As seen in Fig. 12, the yellow part is composed of very small bubbles while the blue parts represent larger bubbles. After adding CMC, more large bubbles appeared in the foam (Fig. 12b).

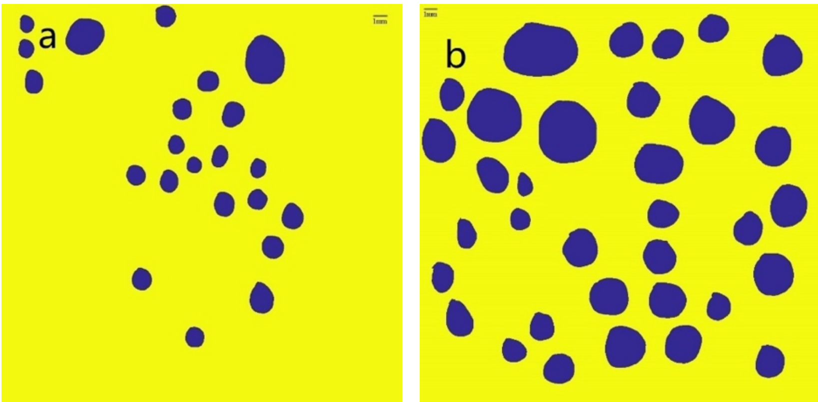

Fig. 12. Bubble size evaluation obtained from python- OpenCV: (a) in the absence of CMC; and (b) in the presence of CMC

Froth stability refers to the rate of bubble coalescence and bubble bursting (Wang et al., 2016), and the froth with relatively low coalescence implies high stability that promotes the recovery of gangue minerals by entrainment (Wang and Peng, 2013). Combined with the foamability test results, it was found that CMC modified the foam by decreasing the froth ability and froth stability, which was in good accordance with the observation in flotation tests.

3.5. Effect of CMC on surface tension

Measurements of surface tension at different MIBC concentrations in the presence and absence of CMC were conducted to see if the way of CMC changing foamability can be related to surface activity. It is important to note that researchers have reported that some polymers affect foam properties by the interaction with frothers (Schreithofer et al., 2011). As shown in Fig. 13, CMC can slightly affect the surface tension of MIBC solutions, which confirmed an interaction between CMC and MIBC. The presence of CMC increased the surface tension, which usually destabilized foam. However, the decrease in the two-phase foam stability was more likely attributed to the change in the foam viscosity caused by CMC itself or the complexation reaction with MIBC.

3.6. Effect of CMC on rheological property

Rheology is an important factor affecting entrainment (Farrokhpay, 2012; Zhang et al., 2015). In general,

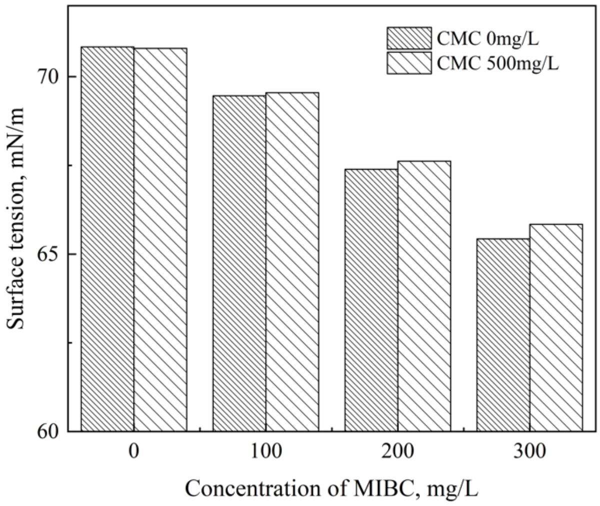

Fig. 13. Surface tension results as a function of MIBC concentration in the absence and presence of CMC

the slurry viscosity can determine the amount of solids entering the froth by affecting the state of solids suspension and the bubble break-up (Shabalala et al., 2011). Entrainment of fine particles is an important factor affecting the stability of three-phase froth. In some cases, it can enhance foam stability by slowing down foam drainage and bubble coalescence (Subrahmanyam and Forssberg, 1988). Thus, CMC may change the foam properties by influencing zoisite. In this section, the froth rheology was not measured; however, the slurry rheology can also indirectly affect foam properties by influencing entrainment.

The effect of CMC on the rheology of water and pulp was studied. The results are shown in Fig. 14. Fig. 14(a) shows the shear stress as a function of shear rate in different CMC concentrations. Polymer solutions behaved as a Newtonian fluid, and there was no detectable difference in the apparent viscosity/bulk viscosity (the slope of lines) even at high polymer concentration (the apparent viscosity of 4000 mg/L CMC solution increased by only 1.9 mPa·s compared with that of distilled water). Since CMC presents little effect on the bulk viscosity, the alteration of two-phase foam may be related to the surface viscosity, however, it is known that it's difficult to measure froth viscosity because of the shearing force rupturing bubble in the froth phase (Shi and Zheng, 2003).

Fig. 14(b) shows the apparent viscosity of pulp as a function of CMC concentration. 5 wt% zoisite suspension behaved as a non-Newtonian fluid without an obvious yield stress, of which the apparent viscosity increased with the increasing shear rate, so the corresponding viscosity at the average shear rate (100 s^{-1}) was taken as a comparison. Clearly, CMC had a relatively evident influence on the slurry viscosity, indicating that CMC can affect zoisite, which was in agreement with the results of foamability measurement. The increased viscosity can affect the float-up of particles in the pulp phase, which may decrease the entrainment of zoisite and change the froth properties.

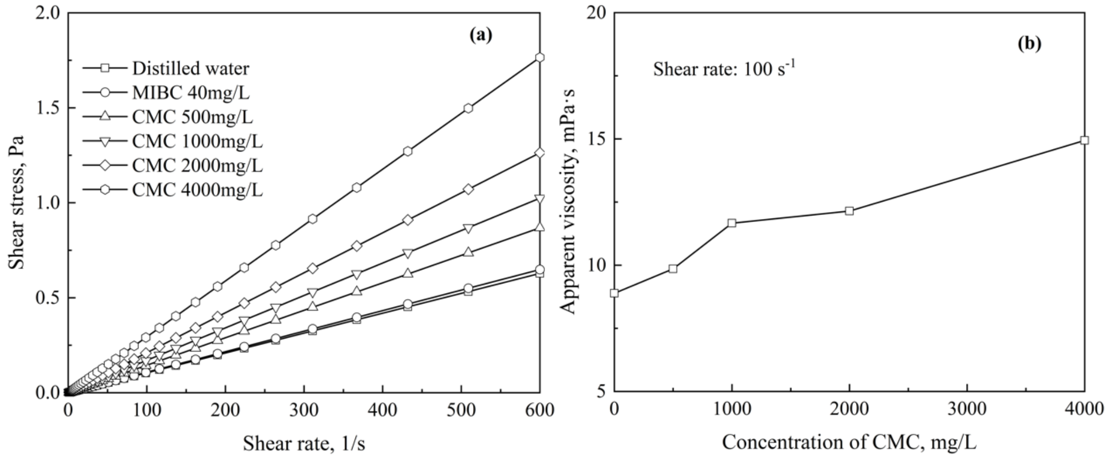

Fig. 14. Effect of CMC on rheological properties of: (a) water; and (b) pulp

Researches have shown that the presence of yield stress often indicates the formation of aggregates (Ndlovu et al., 2011). In this experiment, the slurry didn't show an obvious yield stress; however, the increase in slurry viscosity may also correlate with the flocculation of zoisite. The effect of CMC on zoisite flocculation will be discussed in the next section.

3.7. Effect of CMC on the particle size of zoisite

The particle size has a marked effect on entrainment. Generally, the entrainment of hydrophilic minerals decreases significantly as the particle size increase (Smith and Warren, 1989). Fig. 15 shows the effect of CMC on the suspension turbidity. After adding 25 mg/L CMC, the turbidity significantly decreased from 576 to 110. Further increasing the concentration, the turbidity began to increase. As a result, CMC can greatly flocculate zoisite under low concentration, and the flocculation effect decreases with the increasing concentration.

Researchers (Blaschke, 1976) found that CMC may act as a flocculant at lower concentrations, or as a dispersant at higher concentrations, in the selective flocculation of coal. Bakinov (Bakinov et al., 1964) pointed out that the carboxyl groups of CMC chemically interact with the cations on the mineral surface through electrostatic forces, and the adsorption of CMC causes the negative Zeta potential to increase, preventing further adsorption. Thus, the distinct change of the turbidity was probably due to the change of CMC adsorption strength on zoisite surface.

Fig. 16 shows the microscopic appearance of zoisite flocs treated with or without CMC. Zoisite particles not treated by CMC remained in a good dispersion state (Fig. 16a). After being treated by 25 mg/L CMC, the particles began to aggregate to form flocs (Fig. 16b). These flocs of different sizes are irregular in structure and have internal pores, indicating that the flocs are loose, which may be related to the chain structure of CMC.

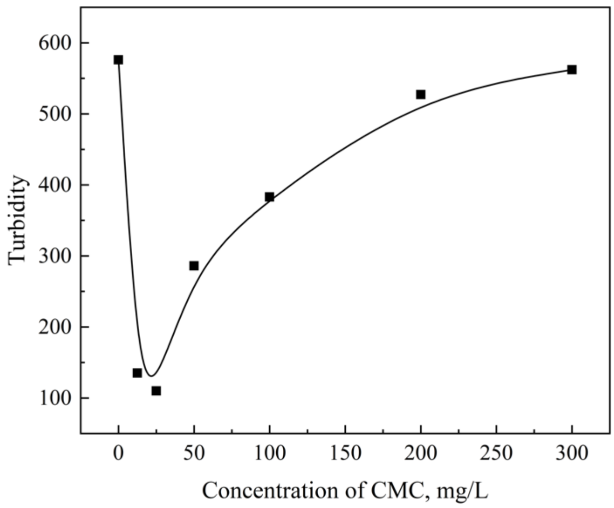

Fig. 15. Effect of CMC on the turbidity of zoisite suspension

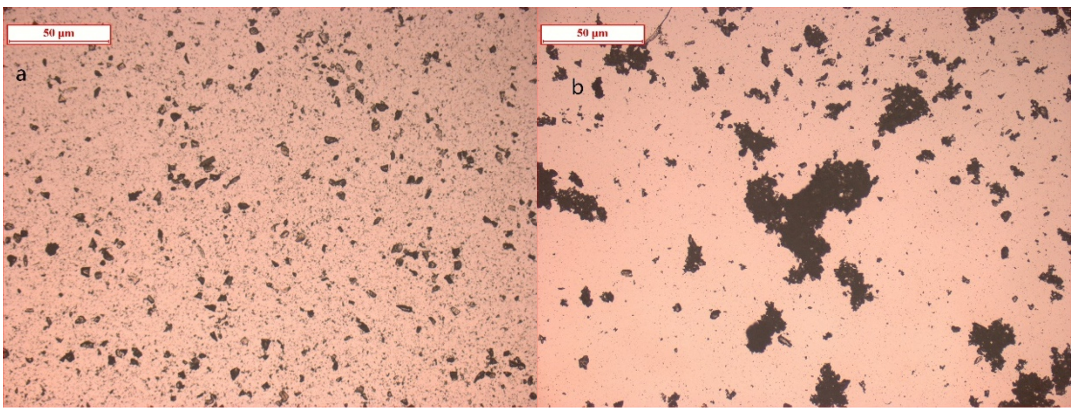

Fig. 16. Microscope images of zoisite flocs: (a) without CMC treatment; and (b) treated by 25 mg/L CMC

It was shown that CMC can cause zoisite to flocculate and enlarge the particle size, which should be the main reason for the reduction of zoisite recovery in flotation. In addition, with the decrease of entrainment amount of zoisite, its stabilizing effect on foam would be weakened, which was consistent with the results of dynamic foaming studies.

4. Conclusions

This study indicates that in flotation, CMC modifies the foam properties and enlarges the particle size of zoisite, and therefore decreases zoisite entrainment and improves the quality of concentrate. The flotation experiments of zoisite, cassiterite-zoisite mixed minerals, and the SnO_2 ore were conducted. The role of CMC in reducing the entrainment of zoisite and the relationship between foam properties and entrainment were discussed. The following primary conclusions were made from the experimental results:

(1) In flotation, zoisite mainly enters the concentrate through entrainment; Adding low dosages of CMC can decrease entrainment, and enhance the separation of cassiterite from zoisite.

(2) CMC can destabilize foam and thus decrease the entrainment of zoisite. It was shown that CMC affected the properties of two-phase and three-phase foam/froth. Generally, CMC decreased the froth ability and froth stability. After adding CMC, the foam volume decreased and more large bubbles appeared in the foam. For the two-phase foam, the change of foam properties had little relation with surface activity and bulk viscosity. For the three-phase froth, the presence of CMC strongly decreased the stabilizing effect of zoisite on froth stability.

(3) Through rheology measurements and sedimentation tests, it was found that CMC not only increased the slurry viscosity but also led to the flocculation of particles, which may be caused by the adsorption of CMC on zoisite surface. The microscopy results confirmed the CMC flocculating zoisite. Combined with the results of foamability measurement, it is concluded that the reason for the reduction of zoisite recovery by entrainment in flotation is that CMC enlarges the particle size and decreases the froth stability.

In future researches, the side effects of depressants in flotation need to be further investigate, and instruments for measuring flotation foam need to be developed.

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Supporting information

Contact angle measurements

The contact angle of zoisite was measured by JWG type contact angle tester. A cut block zoisite sample was prepared. During each test, the surface of the sample was sanded by abrasive paper, followed by ultrasonic treatment. The sample was then conditioned by desired reagents, dried naturally, and the contact angle was measured using droplet method.

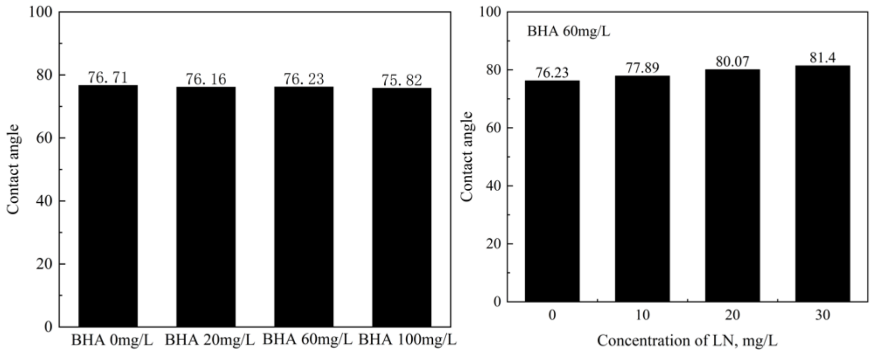

Fig. S1. The effect of BHA and BHA+LN on the wettability of zoisite

Froth structure

Fig. S2. Recorded images of the foam in the foam column: (a) in the absence of CMC; (b) in the presence of CMC.

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