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Flotation separation of scheelite from calcite using carboxyl methyl cellulose as depressant

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ABSTRACT

The effect of carboxyl methyl cellulose (CMC) on the flotation separation of scheelite from calcite using sodium oleate as collector was studied in this work. The results of flotation tests indicated that CMC could selectively depress the flotation of calcite. However, the addition of calcite strongly strengthened the depressing effect of CMC on scheelite flotation. The addition of sodium carbonate could eliminate the adverse impact of calcite on the performance of CMC in scheelite flotation, and a concentrate with both high grade of WO_3 and scheelite recovery could be achieved under CMC in the presence of sodium carbonate. Zeta potential results indicated that CMC adsorbed more strongly on calcite surface than that on scheelite surface, and the addition of CMC prevented the adsorption of the sodium oleate on the calcite surface.

1. Introduction

Scheelite ($CaWO_4$) is one of the most important tungsten-bearing minerals, and it is often associated with other calcium-bearing minerals such as calcite, fluorite and apatite. Scheelite concentrate is often recovered from scheelite ore using a direct froth flotation process (Hu et al., 2012; Shepeta et al., 2012; Yin and Wang, 2014).

The most widely used reagent in scheelite flotation is fatty acid or fatty acid derivatives (Yin et al., 2015). However, the flotation separation of scheelite from calcium-bearing minerals using fatty acid is difficult because of similar surface properties of calcium minerals and high reactivity with their conventional reagents (Houot, 1982; Shin and Choi, 1987). Therefore, collectors and depressants with good selectivity are important for scheelite flotation and have attracted much interest. Anionic collector mixtures (Gao et al., 2015), cationic collector mixtures (Arnold and Brownbill, 1978; HU et al., 2011) and a mixture of anionic/nonionic collectors (Filippov et al., 2012) have been used in the flotation separation of scheelite from calcite; these collectors have shown excellent selectivity. The most widely used depressant is water glass or modified water glass. However, the scheelite and calcite have the same active Ca atoms on their cleavage surfaces, and hence similar flotation response to conventional fatty acid, therefore, when carboxylic acid collectors are used, in order to strengthen the depressing effect of water glass on the flotation of calcite and fluorite, a large amount of water glass should be added into the pulp and some special treatments such as high-intensity agitating and heating should be taken (Hanna and Somasundaran, 1976). It should be noted that excessive water glass in the pulp also reduces the floatability of scheelite, therefore, more efficient depressants should be used in scheelite flotation.

It has been found that the dissolved mineral species could interfere the selective interactions between the reagents and minerals (Helle et al., 2011; Nunes et al., 2011; Chen et al., 2017), hence decreases the selectivity of depressants in the flotation. CMC is reported to strongly depress the calcite flotation but does not affect the scheelite recovery (Yu et al., 2013). To the best of our knowledge, however, the effect of calcite on CMC depressing effect on scheelite flotation has been rarely studied. The aim of this study is to separate the scheelite from calcite using CMC as the depressant. For such a purpose, the effect of calcite on the scheelite flotation in the presence of CMC and its elimination method were studied. These findings may be helpful in scheelite processing.

2. Materials and methods

2.1. Minerals and reagents

Scheelite and calcite used for all experiments were obtained from Yunnan Province, China. The chemical analyses of scheelite and calcite were shown in Table 1.

The samples were ground and then sieved to collect the −106 µm fraction for the microflotation tests. Hydrochloric acid (HCl) and

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Table 1
Chemical composition of scheelite and calcite.

Sample	CaO	WO_3	SiO_2	MgO
Scheelite	18.17	79.73	2.10	/
Calcite	55.37	/	/	0.53

sodium hydroxide (NaOH) were used as pH regulators. Sodium oleate, sodium carbonate and carboxyl methyl cellulose (CMC) were used as collector and regulators, respectively. The degree of substituent of CMC is 0.9 and the molecular weight is 700,000. All the reagents used in this study were of analytical grade. Deionized water was used for all tests.

2.2. Flotation tests

Flotation tests were carried out in a XFG flotation machine with a 40 mL plexiglass cell, at an impeller speed of 2000 rpm. The mineral suspension was prepared by adding 2.0 g of minerals to 40 mL of distilled water. The pH of the mineral suspensions was first adjusted by adding NaOH or HCl. Once the desired reagent was added, the suspension was agitated for 2 min and the pH measured before flotation. The flotation lasted for 4 min. For single mineral flotation tests, the flotation products were collected, dried and weighed, and the recovery was calculated. For mixed binary minerals, the flotation concentrates and tails were assayed for W and Ca.

2.3. FT-IR spectroscopy measurements

The FT-IR spectra were obtained by a Spectrum One FT-IR spectrometer. Approximately 1% (mass fraction) of the solid sample was mixed with spectroscopic grade KBr. The wave number of the spectra ranged from 400 to 4000 cm^{-1}. Each spectra of sample was recorded with 30 scans measured at 2 cm^{-1} resolution. Pure mineral particles were ground to -5μm so that the samples for FT-IR analysis were prepared. So did a suspension by adding 2.0 g of the pure mineral particles to 35 mL of deionized water in a 40 mL Plexiglas cell. The slurry was conditioned for 5 min in the presence of CMC and dried ahead of FT-IR analyses.

2.4. Zeta potential tests

Zeta potential measurements were performed using a Coulter Delsa440sx Zeta analyzer instrument. The suspensions (0.01% mass fraction) with small amount of minerals in a 1×10^{-3}M KCl background electrolyte solution were dispersed in a beaker magnetically stirred for 6 min at a desired pH. After 20 min of settling, the pH value of the suspension was measured and the supernatant was collected for zeta-potential measurements. The zeta-potential of each sample was measured three times, and the average value was reported and the standard deviation was calculated.

3. Results and discussion

3.1. Single mineral flotation experiments results

Single mineral flotation tests were conducted as a function of CMC dosage using 1.5×10^{-4} mol/L sodium oleate as collector. Fig. 1 shows that the calcite recovery decreases significantly with the increases in CMC concentration, and it is less than 10% when the concentration of CMC is above 8 mg/L. Interestingly, by increasing CMC concentration, the recovery of scheelite is roughly the same as in the presence of CMC, indicating that CMC has little effect on scheelite flotation. Therefore, CMC is a potential depressant on selective separation of scheelite from calcite using sodium oleate as collector.

The flotation recoveries of scheelite and calcite as a function of pH

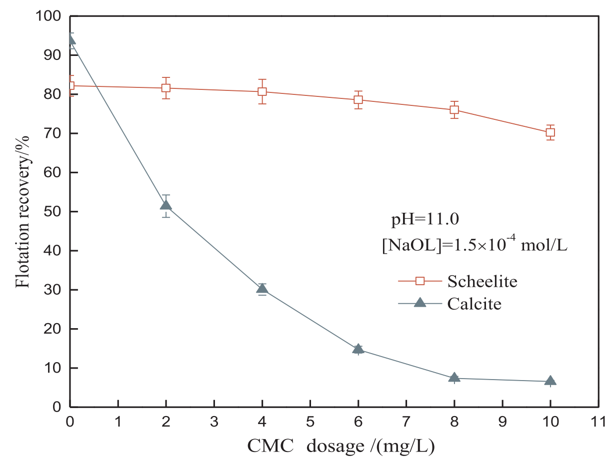

Fig. 1. Effect of CMC dosage on flotation recoveries of scheelite and calcite.

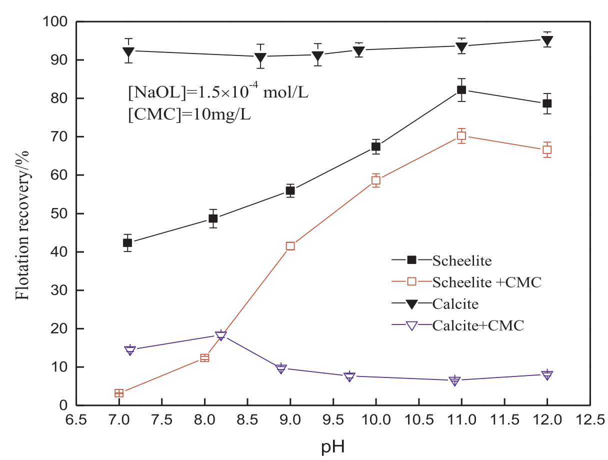

Fig. 2. Effect of pulp pH on flotation recoveries of scheelite and calcite.

in the absence and presence of CMC are presented in Fig. 2. Fig. 2 shows that the recovery of calcite decreases significantly across the entire pH range with the addition of 10 mg/L CMC. However, in the presence of the CMC, the recovery of scheelite changes slightly at pH 10–12 compares to without the addition of CMC, indicating that CMC has little influence on the scheelite flotation at pH 10–12. Therefore, the preferable pH for the separation of scheelite from calcite is 10–12.

3.2. Artificially mixed minerals micro-flotation results

The aforementioned single mineral flotation results indicate that CMC can act as an effective depressant of calcite in scheelite flotation. The flotation tests of mixed minerals were carried out to further investigate the selectivity performance of CMC because the surface properties of salt-type mineral are affected greatly by each other in solution. Flotation results of scheelite recovery and WO_3 grade at pH 11.0 in the presence of CMC and 1.5×10^{-4} mol/L NaOL for a 1:1 mixture of scheelite and calcite are shown in Fig. 3. As illustrated in Fig. 3, the recovery of scheelite drops from 89.14% to 18.92% and the grade of WO_3 increases from 39.01% to 70.14%, respectively. A concentrate with WO_3 grade of 64.33% and recovery of 60.41% is achieved in the presence of 6.0 mg/L CMC, suggesting that CMC remains its depressant effect in mixed mineral pulps. Meanwhile, considerable decrease in recovery of scheelite is observed, indicating that the scheelite is also partly depressed in the presence of calcite.

In order to eliminate the adverse effect of calcite on the CMC performance in scheelite flotation, the effect of Na_2CO_3 on the flotation results of mixed mineral flotation is investigated. Fig. 4 (a) shows the