

## ACTIVATION AND DEPRESSION OF CALCITE IN CALCIUM MINERALS FLOTATION<sup>①</sup>

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**ABSTRACT** In the flotation of scheelite ore containing fluorite and calcite, the treatment of calcite is important to obtain satisfactory scheelite and fluorite concentrate. It is better in scheelite rougher flotation to activate calcite with  $\text{Na}_2\text{CO}_3$  and to float it into scheelite rough concentrate, than to depress calcite into fluorite flotation operation like the conventional process. By activating calcite with  $\text{Na}_2\text{CO}_3$  in scheelite rougher flotation the fluorite flotation can be carried out more easily, and the fluorite concentrate with a grade of  $\text{CaF}_2$  97.42% and  $\text{CaCO}_3$  0.73%, compared with that of a grade of  $\text{CaF}_2$  95.78% and  $\text{CaCO}_3$  1.54% without  $\text{Na}_2\text{CO}_3$ , was gained. The calcite, which was activated and floated into scheelite rough concentrate, can be depressed and removed with Petrov's process or acid leaching, so it has no obvious negative effect on scheelite concentrate. The mechanism of activation is due to hom-ion effect of  $\text{Na}_2\text{CO}_3$  in calcite pulp.

**Key words** flotation calcite scheelite fluorite

### 1 INTRODUCTION

Scheelite ores always contain fluorite and calcite. When the head grade of fluorite is up to 15%  $\text{CaF}_2$ , the fluorite is of economic value. The conventional flotation technology processing for such ores is to float scheelite first by depressing calcite and fluorite<sup>[1]</sup>, and then to separate fluorite from calcite<sup>[2]</sup>. The drawback of this technology is obvious. As the same as scheelite and fluorite, calcite is also a kind of calcium minerals, its floatability is similar to that of scheelite and fluorite in commonly used flotation condition<sup>[3,4]</sup>.

It is difficult to separate scheelite or fluorite from calcite with oleic acid or sodium oleate as collector at room temperature. In flotation separation of fluorite from calcite it is necessary to closely control the depressant dosage<sup>[5]</sup>. Generally speaking, calcite can not be depressed

strongly if the depressant dosage is not enough, and when it is more than some limitation, both calcite and fluorite are all depressed. What is more, the price of fluorite concentrate is rather low, so the flotation technology should be as simple as possible. It seems impossible in this case to effectively separate fluorite from calcite<sup>[6]</sup>. Therefore, how to treat calcite in scheelite and fluorite flotation is worthy to be further studied.

Activating calcite and floating it into scheelite rough concentrate may be an effective method to prevent calcite from contaminating fluorite concentrate. The calcite contained in scheelite rough concentrate will not affect scheelite concentrate, because calcite can be effectively depressed in Petrov's process, and the minor quantities of calcite can be removed with acid leaching<sup>[7]</sup>. In addition, some new depressants can selectively depress calcite in scheelite cleaner

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flotation<sup>[8]</sup>.

## 2 EXPERIMENTAL MATERIALS AND METHODS

### 2.1 Samples

The samples of pure scheelite, fluorite and calcite were ground to  $<0.074$  mm in a porcelain laboratory mill, and their purities were 98.8 %, 98.2 % and 98.7 % respectively.

The scheelite ore was obtained from Shizhuyuan Mine, Hunan province. After it was crushed and the particles of 90 % were ground to  $<0.074$  mm, the magnetic minerals such as magnetite, wolframite and garnet were cleared away with magnetic separation, the sulphide minerals such as molybdenite, bismuthinite and pyrite were removed with flotation. The scheelite ore sample contains  $\text{WO}_3$  0.75 %,  $\text{CaCO}_3$  11.57 % and  $\text{CaF}_2$  30.80 %.

### 2.2 Flotation tests and reagents

The flotation tests of pure minerals and scheelite ore were carried out in a XFG and a FXD laboratory flotation cell, respectively. The reagents such as sodium oleate, NaOH and  $\text{Na}_2\text{CO}_3$  are of analytical grade, and sodium silicate with a formula as  $\text{Na}_2\text{O} \cdot 2.4\text{SiO}_2$  and frother pine camphor oil are industrial product.

### 2.3 Measurement of solubility

The calcite solubility was measured with a Z-8000 model flame atom absorption spectrophotometer made in Japan.

## 3 RESULTS

### 3.1 Flotation of pure minerals

The floatability of scheelite, fluorite and calcite is similar at a pH range of 8.0 to 10.0 with sodium oleate as collector and NaOH as pH regulator. However, when the pulp pH is up to 10.5, the floatability of fluorite decreases sharply. Meanwhile scheelite and calcite keep satisfactory floatability, as shown in Fig.1.

Fig.2 presents the influence of  $\text{Na}_2\text{CO}_3$  concentration on the floatability of scheelite, fluorite and calcite, with sodium oleate as collector,

NaOH as regulator and pulp pH around 11.0. It is shown that calcite can be activated to some extent by  $\text{Na}_2\text{CO}_3$ , and the floatability of scheelite and fluorite change little.

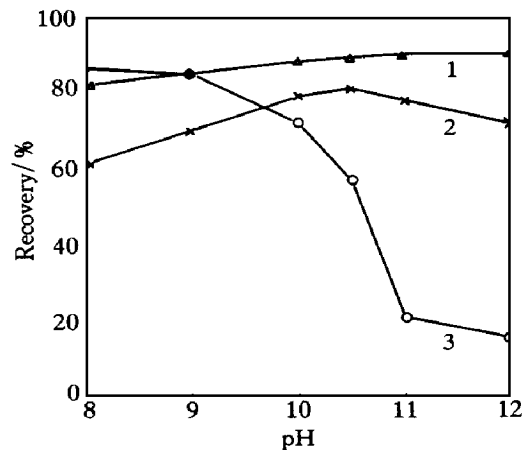


Fig.1 Effect of pH on the floatability of minerals

(sodium oleate  $100 \text{ mg} \cdot \text{L}^{-1}$ )

1 —Scheelite ; 2 —Calcite ; 3 —Fluorite

Fig.2 Effect of  $\text{Na}_2\text{CO}_3$  on the floatability of minerals

(pH=11.0 ; sodium oleate  $100 \text{ mg} \cdot \text{L}^{-1}$ )

1 —Scheelite ; 2 —Calcite ; 3 —Fluorite

### 3.2 Flotation of scheelite ore

Flotation test of pure minerals indicated that the pH value of scheelite rougher flotation should be around 11.0 in order to depress fluorite, and proper density of  $\text{Na}_2\text{CO}_3$  should be

used to activated calcite. Fig.3 is the basic flotation flowsheet.

Fig.3 Basic technology flowsheet

The scheelite rougher flotation, with sodium oleate as collector, NaOH as regulator and pH around 11.0, involved once rougher and scavenger. The scheelite cleaner operation involved Petrov's process and acid leaching. The fluorite flotation with sodium silicate as depressant and pH around 8.5, involved 1 rougher and 5 cleaners.

When the flotation conditions were kept unchanged except  $\text{Na}_2\text{CO}_3$  added into scheelite rougher, the influence of  $\text{Na}_2\text{CO}_3$  on scheelite rough concentrate, scheelite concentrate and fluorite concentrate was investigated. Table 1 presents the result of open-circuit test.

The result showed that, with  $\text{Na}_2\text{CO}_3$  800 g/t, calcite was activated and mainly floated into scheelite rough concentrate, fluorite concentrate

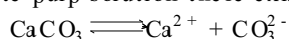
of higher grade was gained more easily.

The calcite contained in the scheelite rough concentrate had little negative effect on the quality of scheelite concentrate. Therefore it is rather reasonable to activate calcite than to depress it in scheelite rougher flotation.

It should be mentioned that, in above flotation tests, depressants such as sodium silicate were not added in the scheelite rougher flotation. Further tests showed the activation of  $\text{Na}_2\text{CO}_3$  to calcite disappeared gradually when sodium silicate was added at the same point as  $\text{Na}_2\text{CO}_3$  was, because in this case the depressing action of sodium silicate was more stronger than the activation of  $\text{Na}_2\text{CO}_3$ .

#### 4 DISCUSSION

The activation mechanism of  $\text{Na}_2\text{CO}_3$  to calcite may be explained with homo-ion effect. In calcite pulp solution there exists such a reaction:



$$K_{sp} = 4.5 \times 10^{-9} \text{ (at 298 K)}$$

The solubility of calcite is

$$[\text{Ca}^{2+}] = [\text{CO}_3^{2-}] = \sqrt{K_{sp}} = 6.7 \times 10^{-5}$$

Assuming the solubility is  $X$  when  $0.01 \text{ mol} \cdot \text{L}^{-1}$   $\text{Na}_2\text{CO}_3$  is added into the pulp, then

$$[\text{Ca}^{2+}] = X, [\text{CO}_3^{2-}] = 0.01 + X$$

$$[\text{Ca}^{2+}][\text{CO}_3^{2-}] = X(0.01 + X) = K_{sp}$$

$$X \approx 4.5 \times 10^{-7}$$

It is evident that the addition of  $0.01 \text{ mol} \cdot \text{L}^{-1}$   $\text{Na}_2\text{CO}_3$  makes the calcite solubility decrease a lot. With the decrease of solubility the adsorption of collector at calcite surface becomes firmer, which results in the increase of calcite floatability.

This deduction was further confirmed with experiments. Fig.4 is the floatability and solubility of calcite at different dosage of  $\text{Na}_2\text{CO}_3$ .

#### 5 CONCLUSIONS

In the flotation of scheelite ore containing fluorite and calcite, scheelite rougher flotation would better be carried out at higher pH value so that the fluorite can be depressed easily. Adding

Table 1 open-circuit test result

$\rho(\text{Na}_2\text{CO}_3)$ /( $\text{g} \cdot \text{t}^{-1}$ )	Product	Grade/ %			Recovery/ %	
		$\text{WO}_3$	$\text{CaCO}_3$	$\text{CaF}_2$	$\text{WO}_3$	$\text{CaF}_2$
0	1	6.25	48.50	14.00	84.65	-
	2	70.45	0.35	0.56	68.20	-
	3	-	1.54	95.78	-	65.50
800	1	4.78	65.00	12.56	83.88	-
	2	70.33	0.52	0.55	69.36	-
	3	-	0.73	97.42	-	68.80

\* 1 —scheelite rough concentrate; 2 —scheelite concentrate; 3 —fluorite concentrate;

some amount of  $\text{Na}_2\text{CO}_3$  to activate and float calcite into scheelite rough concentrate is better than the conventional flotation technology in which the calcite is depressed into fluorite flotation operation. In this case the fluorite concentrate with higher grade and satisfactory recovery can be gained more easily. There is no obvious

negative effect of the calcite contained in scheelite rough concentrate on scheelite concentrate, because the Petrov's process and acid leaching can effectively depress or remove calcite.

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**Fig.4** Effect of  $\text{Na}_2\text{CO}_3$  on calcite  
( pH = 11.0)

1 — Recovery; 2 — Solubility

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