## POTENTIAL-CONTROLLED FLOTATION OF SPHALERITE®

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#### ABSTRACT

The collector and collectorless flotation of sphalerite by potential control, called potential-controlled flotation (PCF), have been investigated in this paper. The results have shown that the oxidative environment of flotation pulp or higher pulp potential could improve and activate the PCF of sphalerite, which was depressed under reducing conditions or lower pulp potential. The mechanisms of PCF have been simply discussed.

Ker words: sphalerite potential-controlled flotation collectorless flotation

#### 1 INTRODUCTION

The major characteristic of potential-controlled flotation of sulphide mineral is that an electrochemical reaction at the mineral-solution interface is responsible for hydrophobization and flotation of the mineral, and is controlled and adjusted by potential-pH matching <sup>(1)</sup>. PCF has an advantage over convenional collector flotation (CCF) which is characterized by collector-pH and collector-depressant matching. CCF only considers the chemical actions of flotation reagents and does not consider the effects of pulp potential.

In the application of PCF of sulphide mineral, xanthate-type collectors may be present or absent, depending on flotation systems. PCF includes collector-induced and collector-less flotation. The CCF of sphalerite has been widely studied in the past <sup>[2]</sup>, but the report on the PCF of sphalerite has been published recently <sup>[3]</sup>. In this paper, the PCF of sphalerite was investigated, and the mecha-

nisms on PCF was simply discussed.

#### 2 EXPERIMENTAL

The pure sphalertie sample was ground in a ceramic mill. The –100+300 mesh size particles were used for flotation tests. The mineral surface was cleaned using an ultrasonic generator prior to flotation. The flotation tests were conducted in a common small cell with a volume of 30 mL under atmosphere. The pH buffer solutions were chosen as the flotation liquid phase in order to protect changes in pH. The additions of buffering agents were as small as possible and the effects of buffering agents on flotation may be neglected. The buffering agents and the pH range of buffer solutions are as follows.

Buffering agents
HNO <sub>3</sub>
HAc+NaAc
HAc+NH <sub>4</sub> OH
NaOH+NaHCO <sub>3</sub>
NaOH (0.01 mol / L)

The redox potential  $(E_{nt})$  of flotation pulp

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was controlled by  $(NH_4)_2S_2O_8$ ,  $Na_2S_2O_4$  and  $Na_2S$ .  $E_{ps}$  was measured using platinum-saturated calomel electrode pair, and is converted into standard hydrogen electrode scale (SHE).

Polyglycol ester was selected as frother and its dosage was  $10 \sim 15 \text{ mg} / \text{L}$ .

Our measurement showed that the electron conductivity of sphalerite under investigation is very poor.

# 3 RESULTS OF COLLECTOR-INDUCED FLOTATION

# 3. 1 Basic Flotation Behavior

Fig. 1 shows ethyl xanthate-induced flotation of sphalerite as a function of pH. It can be seen that in the acid solution, sphalerite can float well, but not in the alkaline. The flotation recovery at pH>9 is near zero. This figure also presents the result of pulp potential measurment. The  $E_{\rm pl}$  value rapidly decreases from 0. 683 V to 0. 242 V with increasing pH value from 2. 2 to 9. 3. The higher  $E_{\rm pc}$  corresponds to the higher flotation recovery. Thus, when  $E_{\rm pl}$  is considered as a varied factor, the collector-induced flotation of sphalerite needs higher  $E_{\rm pc}$ .

Ethyl xanthate (KE,N) is a reducing agent. Its addition can reduce pulp potential (see Fig. 2). Under lower  $E_{pv}$  the flotation recovery of sphalerite does not increase with KE,X concentrations (see Fig. 2). This shows that the hydrophobizing and collecting action by KE,X are associated with  $E_{pv}$ .

## 3. 2 Effects of Pulp Potential

When  $E_{\rm pt}$  is changed from 0. 275 V to 0.375 V through adding  $(NH_4)_2S_2O_8$  (see Fig. 3), the flotation recovery increases from 15%

to 90%, and remains unchanged with continuous increase in  $E_{\rm pt}$ . This shows that even in the alkaline solutions, increasing pulp potential can improve the hydrophobizing and collecting action of ethyl xanthate to sphalerite.

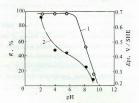


Fig. 1 Effects of pH on pulp potential (E<sub>pt</sub>) and collector-induced flotation of sphalerite (R) 1—R / pH, 2—E<sub>ret</sub> / pH, KE<sub>x</sub>X: 16 mg / L

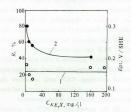


Fig. 2 Effects of concentration of KE,X  $E_{gr} / C_{KE,X}$  on pulp potential  $(E_{gr})$  and flotation recovery of sphalerite R at pH9. 2  $1-R/C_{KE,X}$   $2-E_{gr}/C_{KE,X}$ 

When Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> is added into flotation pulp, pulp potential and flotation recovery decrease, for example, 98% at 0. 365 V drops to 15% at 0. 07 V (see Fig. 4). This indicates that even in the acid solutions, lower pulp potentials can inhibit the hydrophobizing and

collecting action of ethyl xanthate to sphalerite.

Fig.5 presents the collector-induced flotation of sphalerite as a function of pulp potential at pH4.0 and 9.2. It is clear that whether in the acid solutions or in the alkaline solutions, the collector-induced flotation of sphalerite requires higher pulp potentials. The pulp potential is the most important factor determining flotation.

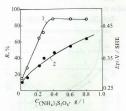


Fig. 3 Effects of concentration of  $(NH_d)_2S_2O_8$  on pulp potential and flotation recovery of sphalerite at pH9. 2 1-Recovery:  $2-E_{ab}$ . K.E.X.: 16mg / L

# 4 RESULTS OF COLLECTORLESS FL-OTATION WITHOUT Na<sub>2</sub>S

## 4. 1 Basic Flotation Behavior

Fig. 6 shows effects of pH on collectorless flotation of sphalerite in the absence of  $Na_2S$ . It can be found the collectorless flotation behavior is good in the acid solution but poor in the alkaline. Fig. 6 also presents the result of  $E_{\rm pt}$  measurement. The high  $E_{\rm pt}$  corresponds to the higher flotation recovery.

# 4. 2 Effects of Pulp Potential

Fig. 7 indicates that when  $E_{pt}$  is changed

from 0.30 V to 0.45 V through adding  $(NH_d)_2S_2O_8$ , the floatation recovery of sphalerite at pH 9. 2 increases from 31% to 96%, and remains unchanged with continuing to increase  $E_{\rm pt}$ . This reveals that the rising of  $E_{\rm pt}$  can improve the collectorless hydrophobization of sphalerite surface.

The flotation behavior at pH 6. 0 becomes poor due to the decrease in pulp potential by adding Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>, for example, 88% at 0. 32 V drops to 18% at 0. 30 V (see Fig. 8).

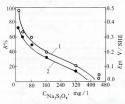


Fig. 4 Effects of concentration of Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> on pulp potential and flotation recovery of sphalerite at pH6. 0 1—Recovery;  $2-E_{ex}$ , KE,X; 16mg/L

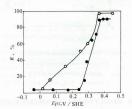


Fig. 5 Effects of pulp potential on collector-induced
flotation of sphalerite at pH 4. 0 and 9. 2

○─pH = 4. 0: ●─pH = 9. 2. KE<sub>1</sub>X: 16mg / L:
(NH<sub>d</sub>),S<sub>1</sub>O<sub>6</sub> as oxidant: Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> as reductant

Fig. 9 presents the collectorless flotation of sphalerite without Na<sub>2</sub>S as a function of pulp potential at pH 6. 0 and 9. 2. It can be seen that in wider ranges of pH, the flotation needs higher pulp potentials.

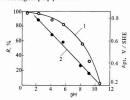


Fig. 6 Effects of pH on pulp potential and collectorless flotation of sphalerite without  $Na_2S$ 1—Recovery; 2—Ept, KE,X: 0 mg / L

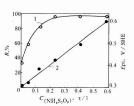


Fig. 7 Effects of concentration of  $(NH_d)_2S_2O_4$  on pulp potential and collectorless flotation of sphalerite without  $Na_2S$  at pH 9. 2 1-Recovery;  $2-E_{mi}$ ,  $KE_iX$ ; 0 mg / L

# 5 RESULT OF COLLECTORLESS FLOT-ATION WITH Na<sub>2</sub>S

Sodium sulphide is a stronger reductant. Its addition can reduce pulp potential and depress the collectorless flotation of sphalerite (see Fig.10). For example, adding 8 mg/L  $Na_2S$  can reduce  $E_{pt}$  from 0. 58 V to 0. 20 V and the flotation recovery from 82% to zero.

#### 6 DISCUSSION

## 6.1 Surface Oxidation of Sphalerite

It is possible that the oxidation of sphalerite surface takes place as follows<sup>[4]</sup> in the acid

$$ZnS \longrightarrow Zn^{2+} + S^0 + 2e$$
  
and in the alkaline  
 $ZnS + 2H_2O \longrightarrow Zn(OH)_2 + S^0 + 2H^+ + 2e$ 

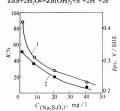


Fig. 8 Effects of concentration of  $Na_2S_2O_4$  on pulp potential and collectorless flotation of sphalerite without  $Na_2S$  at pH 6. 0

1—Recovery: 2—Ept, KE,X: 0 mg/L

The electron conductivity of pure spha-

The electron conductivity of pure sphalerite is very poor. It has a forbidden band energy of 3.6 eV that is much larger than that of galena (0.37 eV). A larger kinetic resistance, that is, a higher oxidation overpotential, exists in the oxidation process of sphalerite surface. Therefore, real oxidation potential = thermodynamical reverse potential + oxidation overpotential. This shows that the real oxidation potential is higher.

Under higher potentials, the sulfur anion (S<sup>2-</sup>) of sphalerite surface may lose electrons

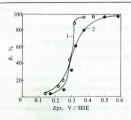


Fig. 9 Effects of pulp potential on collectorless

1-pH = 6.0: 2-pH = 9.2.

(NH.)-S.O. as oxidant: Na.S.O. as reductant

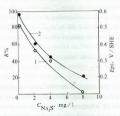


Fig. 10 Effects of concentration of Na<sub>2</sub>S on pulp potential and collectorless flotation of sphalerite with Na<sub>2</sub>S at pH 6. 0

1-Recovery; 2-Ept, KE,X: 0mg/L

and be converted into neutral sulfur  $(S^0)$ . The neutral sulfur is considered as a hydrophobic entity and is responsible for the collectorless

### flotation without Na S

# 6.2 Interaction Between HS<sup>-</sup> Ion and Sphalerite Surface

It is very difficult for the sphalerite surface to accept the electrons from HS<sup>-</sup> ion, because the electron conductivity of sphalerite is very poor and the addition of Na<sub>2</sub>S reduces the potential across the mineral-solution interface. HS<sup>-</sup> ion is not electrochemically oxidized into S<sup>0</sup> on the sphalerite surface. Therefore, unlike pyrite, adding Na<sub>2</sub>S does not improve the collectorless flotation of sphalerite.

### 7 CONCLUSIONS

- (1) The collector-induced and collectorless flotation of sphalerite by potential control require higher pulp potentials. Increasing pulp potential can obviously improve and activate flotation. Decreasing pulp potential can strongly depress flotation.
- (2) HS<sup>-</sup> ion is not electrochemically oxidized into neutral sulfur on sphalerite surface. Unlike pyrite, the adition of Na<sub>2</sub>S does not improve the collectorless flotation of sphalerite.

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