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ELECTROCHEMICAL KINETICS ON BULK CONCENTRATE SEPARATION OF PYRITE AND GALENA①

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ABSTRACT The electrochemical reduction kinetics of lead butyl-xanthate on galena surface and butyl-dixanthogen on pyrite surface has been investigated. The results showed that overpotentials of lead butyl-xanthate on galena surface and butyl-dixanthogen on pyrite surface were 308 mV and 151 mV respectively, and exchange current densities were 1.1×10^{-5} A/m^2 and 1.28×10^{-2} A/m^2 respectively. The kinetic difference between galena and pyrite extended the separation potential from 50 mV in thermodynamics to 207 mV in kinetics, thus the results offer theoretical basis for electrochemical separation of galena and pyrite. The kinetic results have been proved by bulk concentrate separation of galena and pyrite by controlling the pulp potential over pH 9.18 ~ 9.5.

Key words galena pyrite electrochemical floatation electrochemical reduction kinetics

1 INTRODUCTION

The separation of pulp electrochemical floatation of sulfide minerals depends on differences in characteristics of the three factors[1-3]: thermodynamics, kinetics and surface products. Thermodynamic results only indicate theoretical approaches of floatation and there exist some gap compared with actual flotation results. For example, some minerals (such as arsenopyrite and pyrite, galena and pyrite) can not be separated by electrochemical floatation ways according to thermodynamic analysis because the separation potential region even is narrow between those two minerals, but these minerals can be separated at given negative pulp potential[4,5]. The different results are mainly caused by the differences on electrochemical kinetics for a variety of mineral. On the basis of these differences on kinetics the potential region of floatation separation is extended, which is advantageous to mineral separation by means of electrochemical methods for actual process of separation. Therefore, the studies of electrochemical kinetics have theoretical value and actual application significance for electrochemical separation of sulfide floatation.

2 EXPERIMENTAL METHODS

The electrochemical reduction kinetics of the surface products of pyrite and galena was studied using galvanostatic polarization method and periodical V-A way. In order to clear away the effects of diffusion on electrode process rotation disk electrode system was used (ATA1), and HPD-1 bieletrode potentiostat was used for measuring electrochemical data.

$Na_2S_2O_4$ and $(NH_4)_2S_2O_8$ were used as potential regulator. At first, at the potential of 50 ~ 200 mV(SHE), pure mineral reacted 5 min with 5×10^{-4} mol/L butyl-xanthate, then the relationship between pulp potential and floatability was measured. Mineral size was > 53 ~ < 91 μm, mineral purity was galena 97.8%, pyrite 95.12% respectively.

Galena and pyrite were mixed by 1∶1 (in mass). The mixed minerals reacted 5 min with the butyl-xanthate of 5×10^{-4} mol/L, then pulp

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potential was adjusted, and floatation separation was carried out.

3 ELECTROCHEMICAL REDUCTION KINETICS OF COLLECTOR PRODUCTS

3.1 Electrochemical reduction kinetics of lead butyl-xanthate on galena surface

3.1.1 Formation of lead butyl-xanthate on galena surface

It was indicated from researcher[6] that the anode process of lead butyl-xanthate formation occurred according to equation

$$PbS + 2BX^- = Pb(BX)_2 + S^0 + 2e \qquad (1)$$

$$\varphi^{\ominus} = -178\ mV$$

Thermodynamics reversible potential of equation (1) is -19 mV when solution pH is 9.18 and xanthate concentration is 2×10^{-3} mol/L, so lead butyl-xanthate $Pb(BX)_2$ can be obtained on galena surface by the potentiostatic polarization at 100 mV.

3.1.2 Electrochemical reduction kinetics of lead butyl-xanthate

Electrochemical reduction reaction of lead butyl-xanthate may exist in two possible forms on the basis of thermodynamic theory:

$$Pb(BX)_2 + S^0 + 2e \rightarrow PbS + 2BX^- \qquad (2)$$

$$\varphi^{\ominus} = -178\ mV$$

$$Pb(BX)_2 + 2e \rightarrow Pb + 2BX^- \qquad (3)$$

$$\varphi^{\ominus} = -658\ mV$$

Fig.1 is the V-A curve of potential scanning to cathode potential after potentiostatic polarization of galena electrode at 100 mV, 10 s. When xanthate concentration is 2×10^{-3} mol/L, thermodynamics reversible potential of Eqns.(2) and (3) is -19 mV and -499 mV respectively. Potential value of equation (3) is approximate to peak current potential value (-560 mV) of galena cathode polarization. Electrochemical reduction process of lead butyl-xanthate on the galena surface is assumed to occur according to equation (3), then formation of lead butyl-xanthate should occur according to reverse reaction of equation (3) in the following anode polarization curve, however anode current did not occur while anode scanned at -650 ~ 100 mV. This fact indicated that electrochemical reduction of lead butyl-xanthate ($Pb(BX)_2$) occurred according to equation (2), but not equation (3).

Fig.1 V-A curve of galena electrode after polarizing 10 s at 100 mV potential

pH = 9.18; θ = 25 ℃; $c(KNO_3)$ = 0.5 mol/L;

v = 1 000 r/min

1 —$c(BX^-)$ = 0; 2 —$c(BX^-)$ = 2×10^{-3} mol/L

Thermodynamics reversible potential is -19 mV for equation (2) when xanthate concentrate is of 2×10^{-3} mol/L, which indicates lead butyl-xanthate $Pb(BX)_2$ should be reduced when the potential reaches -19 mV, but the results in Fig.1 indicated that electrochemical peak current of lead butyl-xanthate occurred at the potential of -560 mV, which has over 500 mV gap compared with theoretical value. So the electrochemical reduction kinetics of lead butyl-xanthate $Pb(BX)_2$ plays a crucial role for occurrence of equation (2).

Fig.2 describes the relationship curve between the potential (φ) and time (t) of galena electrode covered by lead buthylxanthate by galvanostatic polarization (i_k = 20 μA). Potential step started from -320 mV (namely, lead butyl-xanthate $Pb(BX)_2$ started to be reduced), and potential increased step by step with the increase of polarization time due to the reduction of lead butyl-xanthate on electrode surface. The electrode potential increased rapidly when all lead butyl-xanthate of electrode surface was reduced, whose transition time τ_0 was 11.2 s.

For the irreversible electrode process of electrochemical polarization and concentration polarization, the relationship between electrochemical current and overpotential can be represented by equation[7]

$$\eta = \frac{2.303\,RT}{\alpha nF}\lg\frac{J_k}{J_0} - \frac{2.303\,RT}{\alpha nF}\lg\left(1 - \sqrt{\frac{t}{\tau_0}}\right) \quad (4)$$

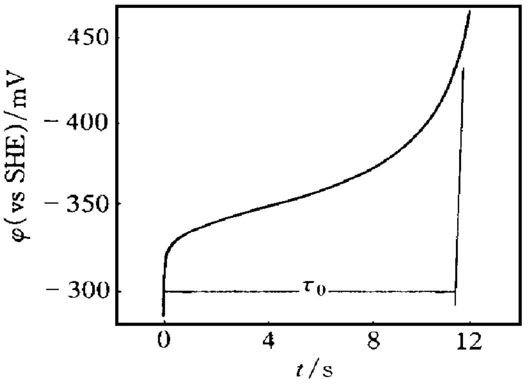

Fig.2 Relationship between potential φ and time t for the galena electrode covered with $Pb(BX)_2$

$pH = 9.18$; $\theta = 25$ ℃; $c(KNO_3) = 0.5$ mol/L; $v = 1\,000$ r/min

The relationship of overpotential η and $\lg(1 - \sqrt{t/\tau_0})$ (Fig.3) is obtained via transferring the data of Fig.2, and the slope and intercept of line are 0.062 and 0.308 respectively. Consequently, according to Eqn.(3) the kinetic equation of electrochemical reduction for lead butyl-xanthate on the galena electrode may be written as

$$\eta = 0.308 - 0.062\lg\left(1 - \sqrt{\frac{t}{\tau_0}}\right) \quad (5)$$

Comparing Eqn.(5) with Eqn.(4), the kinetic parameters of the electrochemical reduction of lead butyl-xanthate are obtained: transmission coefficient $\alpha = 0.476$, exchange current density $J_0 = 1.1 \times 10^{-5}$ A/m^2. The slope of equation (5), 0.062, which is near the theoretical value 0.059 and lower exchange current density indicate this reaction is irreversible.

It is indicated from above result that in electrochemical reduction of lead butyl-xanthate on the galena surface exists the overpotential of 308 mV in kinetics although thermodynamical reduction potential is -19 mV, so reduction potential of lead butyl-xanthate must be low to -327 mV in practice.

Fig.3 Relationship between overpotential η and $\lg(1 - \sqrt{t/\tau_0})$ for the galena electrode covered with $Pb(BX)_2$

$pH = 9.18$; $\theta = 25$ ℃; $c(KNO_3) = 0.5$ mol/L; $v = 1\,000$ r/min

3.2 Electrochemical reduction kinetics of dixanthogen on pyrite surface

3.2.1 Formation of butyl-dixanthogen on pyrite surface

The product of butyl-xanthate reacting with pyrite surface was butyl-dixanthogen[8]. The reaction of electrode can be written as

$$2BX^- = (BX)_2 + 2e \quad (6)$$

$$\varphi^{\ominus} = -128 \text{ mV}$$

While concentration of butyl-xanthate is 2×10^{-3} mol/L, the thermodynamically reversible potential of butyl-dixanthogen is 31 mV.

The pyrite electrode was pre-polarized 30 s at -400 mV for clearing away oxides of electrode surface in 2×10^{-3} mol/L xanthate solution, at pH 9.18, then potential was stepped to 200 mV, the relationship between the current of butyl-xanthate formation on pyrite surface and time was written as

$$J^{-1} = 3.13 \times 10^{-3} + 7.748 \times 10^{-3}t \quad (7)$$

When potentiostaic polarization time was 10 s, charge quantity (Q_a) passed the electrode was 412 μC by integrating Eqn.(7). As area of test pyrite electrode was 0.2 cm^2, the coarse degree of electrode may be taken as 5 and the radical group area of dixanthogen was 0.2 nm^2, layer of dixanthogen on pyrite electrode surface was calculated as 2.6.

3.2.2 Electrochemical reduction kinetics of dixanthogen

When pyrite electrode was polarized by galvanostatic method (polarization current was -30 μA) at $\varphi = 200$ mV, $t = 10$ s, the relationship between potential and time was obtained (Fig. 4). The butyl-dixanthogen started to be reduced at -115 mV, transition time was 10 s.

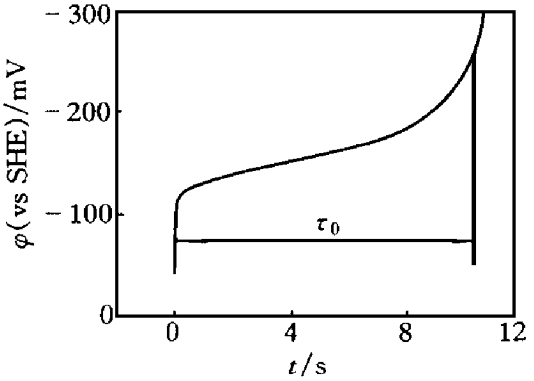

Fig.4 Relationship between potential φ and time t for the pyrite electrode covered with $(\mathrm{BX})_2$

pH = 9.18; $\theta = 25$ ℃; $c(\mathrm{KNO_3}) = 0.5$ mol/L; $v = 1\,000$ r/min

Provided the electrochemical reduction of butyl-xanthogen on pyrite surface is irreversible electrode process, then relationship between overpotential and $\lg(1 - \sqrt{t/\tau_0})$ (Fig.5) is obtained by transferring data of galvanostatic curve of Fig.4, and the slope and intercept of line are 0.073 and 0.151 respectively. Conseqently, according to Eqn.(3), the kinetic equation of electrochemical reduction for the dixanthogen on pyrite surface may be written as

$$\eta = \frac{2.303\,RT}{\alpha nF}\lg\frac{J_k}{J_0} - \frac{2.303\,RT}{\alpha nF}\cdot\lg(1 - \sqrt{t/\tau_0}) = 0.151 - 0.073\lg(1 - \sqrt{\frac{t}{\tau_0}}) \qquad (8)$$

where $\tau_0 = 10.5$ s.

The kinetic parameters of the electrochemical reduction of the butyl-dixanthogen on pyrite surface can be obtained from equation (8): transmission coefficient $\alpha = 0.404$, exchange current density $J_0 = 1.28 \times 10^{-2}\ \mathrm{A/m^2}$.

As known from the above discussion, the reduction of the butyl-dixanthogen on pyrite surface is irreversible, the overpotential of reduction is 151 mV, so the butyl-dixanthogen on pyrite surface may start to reduce only as the potential is below -120 mV.

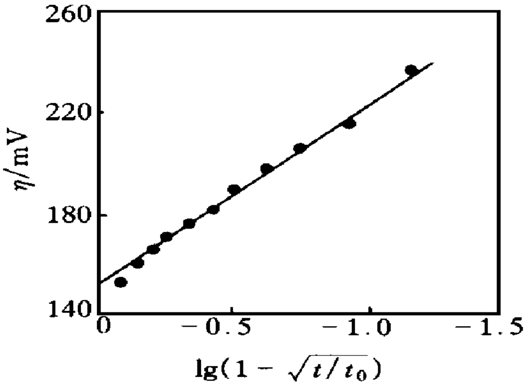

Fig.5 Relationship between overpotential η and $\lg(1 - \sqrt{t/\tau_0})$ for the pyrite electrode covered with $(\mathrm{BX})_2$

pH = 9.18; $\theta = 25$ ℃; $c(\mathrm{KNO_3}) = 0.5$ mol/L; $v = 1\,000$ r/min

The electrochemical reduction of the butyl-dixanthogen on pyrite surface has lower overpotential and higher exchange current density compared with reduction kinetic behavior of the lead butyl-xanthate on galena surface, so the butyl-dixanthogen on pyrite surface can be reduced and desorbed from pyrite surface quickly at lower negative potential. This difference of electrochemical behaviors between two minerals provide theoretical basis for carrying out bulk concentrate separation of galena and pyrite at the reductive pulp potential.

4 ELECTROCHEMICAL SEPARATION OF BULK CONCENTRATE OF PYRITE AND GALENA

Thermodynamic reduction potential of lead butyl-xanthate and butyl-dixanthogen is 18 mV and 68 mV respectively when xanthate concentration is 5×10^{-4} mol/L. It indicates that the reduction of lead butyl-xanthate on galena surface occurs when pulp potential is below 18 mV, and the floatability of galena starts decreasing; for pyrite mineral, its floatability becomes bad when pulp potential is below 68 mV. So the floatation separation for pyrite and galena can be carry out by controlling pulp potential at 18 ~ 68 mV. However, separation potential scope is so narrow (only 50 mV) that the electrochemical separation of galena and pyrite is difficult.

The results of the kinetics of two minerals are listed in Table 1. Because there are 308 mV and 151 mV overpotential respectively when the lead butyl-xanthate on galena surface and the butyl-dixanthogen on pyrite surface are reduced, so the electrochemical reductions of butyl-xanthate and butyl-dixanthogen occur at the potentials of - 290 mV and - 83 mV respectively in kinetics. The separation potential scope extend to 207 mV in kinetics, so it's convenient to separate galena and pyrite by controlling the pulp potential. In addition, it can be seen from exchange current density that the electrochemical reduction rate of the butyl-dixanthogen on pyrite surface is more faster than that of the buthyl-xanthate on the galena surface. The kinetic factors above provide advantagous condition for the separation of bulk concentrate of galena and pyrite.

Table 1 Analysis of thermodynamics and kinetics about electrochemical reduction of $Pb(BX)_2$ and $(BX)_2$

Mineral system and potential	Electrochemical reduction potential φ (vs SHE) / mV		Transmission current density $J/(A \cdot m^{-2})$
	Thermodynamics	Kinetics	
$2PbS \mid Pb(BX)_2$	18	- 290	1.1×10^{-5}
$FeS_2 \mid (BX)_2$	68	- 83	1.28×10^{-2}
Separation potential range / mV	18 ~ 68	- 290 ~ - 83	

4.1 Relationship between pulp potential and floatability

Fig. 6 describes the relationship between floatability of single mineral and pulp potential. It can be seen from Fig. 6 that galena kept good floatability at 200 ~ - 350 mV, and its floatability started decreasing when potential was below - 350 mV. For pyrite, its floatability decreased sharply when the pulp potential was below 0 mV, and the floatability was lost at the pulp potential of - 100 mV. The results of floatation fully verified the kinetic research results that the electrochemical reduction of the butyl-dixanthogen on pyrite surface had lower reduction potential and more speedy velocity of reduction compared with that of the lead butyl-xanthate on galena surface.

4.2 Electrochemical separation of artificial mixed concentrate (Fig. 6, Table 2) and sulfide ore (Table 3)

It is indicated from Fig. 6 that galena and pyrite bulk concentrate can be separated at - 100 ~ - 400 mV. The separation of artificial

Fig. 6 Relationship between potential and recovery for the floatation of galena and pyrite
pH = 9.18; butyl-xanthate 5×10^{-4} mol/L
1 —Galena; 2 —Pyrite

Table 2 Results of the electrochemical separation of artificial bulk concentrate of galena and pyrite

Product	Yield / %	Grade / %		Recovery / %		pH	φ_h (vs SHE) / mV
		Pb	Fe	Pb	Fe		
Concentrate	49.68	77.23	4.79	90.59	10.76		
Tailing	50.32	4.28	39.29	9.41	89.24	9.5	- 280
Summary	100	42.35	22.12	100	100		

Table 3 Results of the electrochemical separation of bulk concentrate of Pb-Zn-S ore of Dachang concentrator

Product	Yield/ %	Grade/ %			Recovery/ %			pH	φ_h(vs SHE) / mV
		Pb	Zn	S	Pb	Zn	S		
Concentrate	45.43	17.73	28.29	28.7	94.33	94.67	36.37	9.2	-200 ~ -250
Tailing	54.57	0.89	1.33	41.8	5.67	5.33	63.63		
Feed	100	8.54	13.58	35.85	100	100	100		

mix concentrate of galena and pyrite was carried out at the pulp potential of -280 ~ -300 mV, pH 9.5 adjusted by lime.

It is indicated from Table 2 that the galena and pyrite bulk concentrate can be separated by electrochemical floatation technique on the basis of the differences of the collector products on mineral surface.

The results of the electrochemical separation of Dachang Pb-Zn-S multimetal sulfide ore, listed in Table 3, indicates that, the pyrite can be depressed well at the pulp potential of -200 ~ -250 mV and pH 9.2 and the galena and sphalerite activated by copper ion keep good floatability.

5 CONCLUSIONS

(1) The thermodynamic behaviors of the electrochemical reduction of galena and pyrite are similar in the bulk concentrate floatation system, and separation potential scope is only 50 mV; however the kinetic behavior differences extend the separation potential range to 207 mV, in addition, the electrochemical reduction of the butyl-dixanthogen on pyrite possesses higher exchange current density than that of the lead buthyl-xanthate on galena surface. These kinetic differences between two minerals provides the advantages for separating galena and pyrite.

(2) Electrochemical reduction kinetics indicates that the reductions of butyl-dixanthogen on the pyrite and lead butyl-xanthate on the galena possess 308 mV and 151 mV overpotential respectively, and the exchange current density of electrochemical reduction is 1.1×10^{-5} A/ m^2 and 1.28×10^{-2} A/ m^2 respectively. So the butyl-dixanthogen on the pyrite surface is more easily to be reduced than the lead butyl-xanthate on the galena surface. The kinetic researches have been verified by single mineral floatation.

(3) Floatation separation of artificial mix concentrate can be carried out by controlling the pulp potential at -280 ~ -300 mV. The electrochemical separation results of ore verified the results above.

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