Leaching mechanism of sulfide ores in slurry electrolysis[①]

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Abstract: Anodic polarization curves of sulfide mineral particle oxidation on graphite anode in slurry electrolysis have been examined to make certain of the leaching mechanism of sulfide ores in slurry electrolysis and to build up the relationship between the anodic current density, solid content in slurry and stirring speed. The results show that the leaching mechanism of sulfide minerals depends on the operating conditions. The anodic oxidation of mineral particles is the main reaction when no iron and copper ions exists in the slurry and at a low current density. In existence of iron or copper ions in slurry, the main anodic reaction is the oxidation of ferrous and cuprous ions at a low current density. At high current density, Cl^- ion oxidation on anode occurs and Cl_2 and $HClO$ are produced. Sulfide leaching depends mainly on oxidation by $HClO$. Based on the consideration of the double layer structure and particle motion, the relationship between the anodic current density (i), solid content in slurry (c_s) and stirring speed (N_R) is determined as $i = Qc_sN_R^2$, where $Q = 4\pi^2 r^2 nFk\lambda$, and r is the distance between stirring axis and anode surface, n is the particle number contacting with unit anodic area ($1 \, cm^2$) in unit time, k the rate constant, λ the proportional constant. Particle size does not affect the current density. The equation shows good agreement with the experimental results.

Key words: leaching mechanism; sulfide mineral; slurry electrolysis   **Document code: A**

1　INTRODUCTION

Since Kruesi P R invented slurry electrolysis in 1971, various views about leaching mechanism of sulfide minerals have appeared. The earliest one is that the main reason for chalcopyrite leaching is oxidation of mineral particles contacting with anode[1]. QIU[2, 3] indicated that chalcopyrite leaching in slurry electrolysis includes chemical oxidation and anodic oxidation. Zhang[4] measured polarization curves of galena concentrate in 300 g/ L NaCl solution on graphite anode in absence and existence of $FeCl_2$ in slurry, the results showed that the current density is very low at anode potential below 1. 0 V(vs SCE) in absence of $FeCl_2$. Under the same condition, the current density is much higher in existence of $FeCl_2$. In this paper, anodic oxidation of mineral particles and leaching mechanism have been investigated. The relationship between the anodic current density (i), solid content in slurry (c_s) and stirring speed(N_R) has been determined.

2　EXPERIMENTAL

2. 1　Samples

Gold concentrate from Yuanyang, Yunnan Province was used as samples in the experiments. Its chemical composition are given in Table 1. Lead in the concentrate is mainly come from galena, iron is mainly come from pyrite and copper is mainly come from chalcopyrite.

2. 2　Electrochemical measurements

The anodic polarization curves of slurry have been generated with PH-2 type electrochemical integrated measuring apparatus. The electrochemical measurements were made using a typical three-electrode system, consisting of the graphite working electrode (with exposed surface area of $1 \, cm^2$), platinum counter electrode and saturated calomel reference electrode. The reference electrode was separated from the slurry resulting from the salt bridge to avoid any contamination by the slurry. The anodic current and potential were registered on an X-Y recorder. The cell was maintained in a thermostatted water bath to keep the temperature being constant (± 1 ℃). Agitation of solution was conducted with regenerated rotating disc electrode of ATA-1A type at constant speed.

2. 3　Experimental conditions

The experimental temperatures were 25 ℃ and 60 ℃, respectively. The slurry consisted of both gold concentrate and solution. NaCl and HCl concentrations of the solution in all experiments were 200 g/ L and 0. 1 mol/ L, respectively. The $FeCl_2$ and CuCl concentration of solution were 0 or 0. 01 g/ L. All reagents used in the experiments were analytical grade. The content of gold concentrate in slurry is expressed by c_s(g/ L).
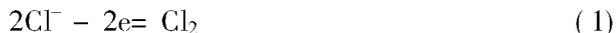
3　RESULTS

Anodic polarization curves with different slurry

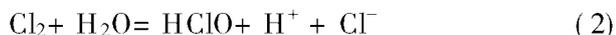**Table 1**	Chemical composition of Yuanyang gold concentrate

Element	Pb	Cu	Fe	Zn	Sb	S	CaO	MgO	SiO$_2$	Ag	Au
Content/%	13.01	4.04	28.78	0.18	0.24	35.13	1.28	0.86	10.83	490 g/t	64.35 g/t

composition are shown in Fig. 1(a) and Fig. 1(b).

Curve 1 is polarization curve of Cl$^-$ anodic oxidation, that is

$$2Cl^- - 2e = Cl_2 \qquad (1)$$

and then

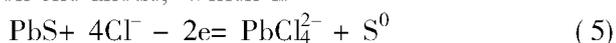$$Cl_2 + H_2O = HClO + H^+ + Cl^- \qquad (2)$$

This process takes place enormously only if anodic potential is larger than 1.0 V(vsSCE).

Curve 3 and curve 5 are the polarization curves of Fe(II) and Cu(I) anodic oxidation:

$$Fe^{2+} - e = Fe^{3+} \qquad (3)$$

$$Cu^+ - e = Cu^{2+} \qquad (4)$$

Curve 2 is the polarization curve of mineral particles on the anode, which is

$$PbS + 4Cl^- - 2e = PbCl_4^{2-} + S^0 \qquad (5)$$

Curve 4 and curve 6 in Fig. 1 are the simultaneous anodic oxidation of mineral particles and Fe(II) or Cu(I). When the potential is much higher, oxidation of Cl$^-$ and formation of Cl$_2$ occur. Various polarization curves tend to be the same. Under this conditions oxygen is possible to be formed simultaneously. This was proved by Arsan[5,6].

4 RESULTS AND DISCUSSION

4.1 Leaching mechanism of PbS

There are three ways for PbS to be leached as mentioned by the authors[7]. They are anodic oxidation, chemical oxidation and chemical dissolution. The main mechanism can be determined only through kinetic research.

When the slurry contains only mineral particles and NaCl and neither Fe or Cu, the current density is low (such as curve 2 in Fig. 1(a), $i < 15$ A/m^2 and curve 2 in Fig. 1(b), $i < 28$ A/m^2), the main leaching way is the oxidation of mineral particles on the anode.

When the slurry contains mineral particles and Fe(II) or Cu(I) and the current density is low (such as curve 4 in Fig. 1(a), $i < 90$ A/m^2; curve 4 in Fig. 1(b), $i < 170$ A/m^2; curve 6 in Fig. 1(a), $i < 70$ A/m^2; curve 6 in Fig. 1(b), $i < 135$ A/m^2), the direct oxidation of mineral particles on the anode takes only a small amount of electron transportation, the predominant anode reaction is the oxidation of Fe(II) or Cu(I).

In the range of low current density, the existence of Fe(II) or Cu(I) in the slurry can reduce the anodic potential (so does the cell voltage), or under the same cell voltage, increase the current density. This not only accelerates leaching, but also reduces the energy consumption of slurry electrolysis.

When the slurry contains Fe or Cu and the current density is high, for example, $t = 25$ ℃, in Fig. 1(a), curve 4, $i > 90$ A/m$_2$ and curve 6, $i > 70$ A/m^2 respectively; $t = 60$ ℃, in Fig. 1(b), curve 4, $i > 170$ A/m^2 and curve 6, $i > 140$ A/m^2, oxidation of Cl$^-$ and production of chlorine occurs. At this time, the predominant leaching process is the sulfide oxidation by HClO.

4.2 Effect of double layer on oxidation rate of mineral particles

According to BDM model for double layer on the electrode surface proposed by Bockris in 1963, the double layer consists of the compact part and the
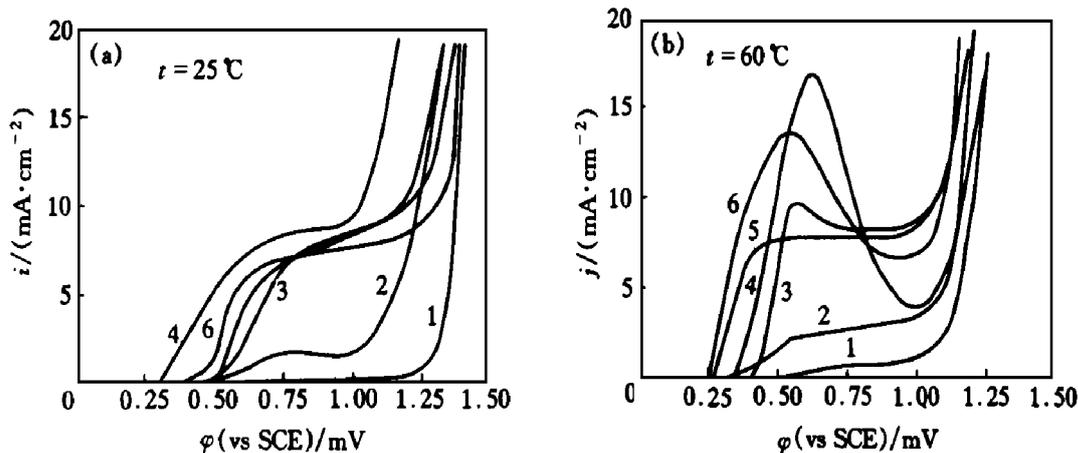

Fig. 1	Polarization curves under various slurry compositions(pH = 1, $n = 700$ r/min, $v = 1$ mV/s)
1 —NaCl 200 g/L;   2 —NaCl 200 g/L+ gold concentrate ($c_s = 100$ g/L);   3 —NaCl 200 g/L+ 0.01 mol/L FeCl$_2$;
4 —NaCl 200 g/L+ 0.01 mol/L FeCl$_2$+ gold concentrate ($c_s = 100$ g/L);   5 —NaCl 200 g/L+ 0.01 mol/L CuCl;
6 —NaCl 200 g/L+ 0.01 mol/L CuCl+ gold concentrate ($c_s = 100$ g/L)

diffuse part. The compact part consists of inner compact layer ——the so-called inner Helmoholtz plane (IHP) and outer compact part ——the so-called outer Helmholtz plane(OHP). The IHP is a layer consisting of orderly arranged water molecules.

The mineral particles can be oxidized on anode only when they contact with the anode surface. In order to contact with the anode surface, the solid particles must pass through liquid boundary layer and drainage water molecules in IHP. If the direction of slurry flow with velocity big enough is not parallel with that of anodic surface, especially vertical to the anodic surface, the slurry flow can rash the solid surface. The particle diameters are much bigger than the thickness of boundary layer and double layer, so particles can be bumped on to the anodic surface by the stirring or through the kinetic energy of the particles. As soon as the particles come into contact with the anode, the particles are oxidized:

$$MeS- 2e= Me^{2+} + S^0$$
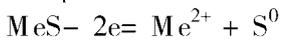
This process takes place not only on the contacting point, but also on the whole surface of particles, because the particles become one part of the anode at the contacting moment.

The anodic oxidation rate of particles depends on the particle number contacting on the anode surface in unit time. If the slurry contains only NaCl and mineral particles, the anodic potential is not big enough to produce chloride gas. Under the same over potential, the anodic reaction rate (v) and the current density (i) are as follows:

$$\left.\begin{array}{l} v = kN \\ i = nFv = nFkN \end{array}\right\} \quad (6)$$

where k is rate constant, n is particle number contacting with unit anodic area (1 cm^2) in unit time. N is proportional to N' (particle number in unit volume of the slurry) and kinetic energy of particles, so

$$N = \lambda N' m_i V^2 \quad (7)$$

where λ is proportional constant; m_i is the mass of one particle, g; V is the linear velocity of liquid flowing near the electrode surface, cm/s.

$$N' = \frac{c_s}{m_i} \quad (8)$$

$$V = 2\pi r N_R \quad (9)$$

where c_s is solid content in slurry, g/mL; r is the distance between stirring axis and anodic surface, cm; N_R is stirring speed, r/min.

Substitution of equations (7), (8), (9) in (6) leads to

$$i = 4\pi^2 r^2 nFk \lambda c_s N_R^2$$

Let $Q = 4\pi^2 r^2 nFk \lambda$

We can obtain

$$i = Q c_s N_R^2 \quad (10)$$

Equation(10) shows that under the same over potential, current density (i) has the linear relationship with solid content of slurry(c_s), and the square of stirring speed (N_R^2). Particle size does not affect the current density (i). This conclusion is proved by the experimental results shown in Figs. 2(a) and (b).

4. 3   Contribution of anodic oxidation of mineral particles to leaching

One extreme situation is that the direction of slurry flowing is vertical or nearly vertical to the anode surface, and the flowing rate is big enough for the slurry to directly touch the anode surface. At this time, all the mineral particles in the slurry can bump the anode surface. It has not been seen that mineral particles pile up on the anode surface. So it can be thought that mineral particles continuously bump and leave away, which forms a layer of mineral particles on anode surface. The number of such particles is approximately constant. Assume a slurry flowing column with the cross section area of 1 cm^2, the first batch of particles bumping on to the anode surface is
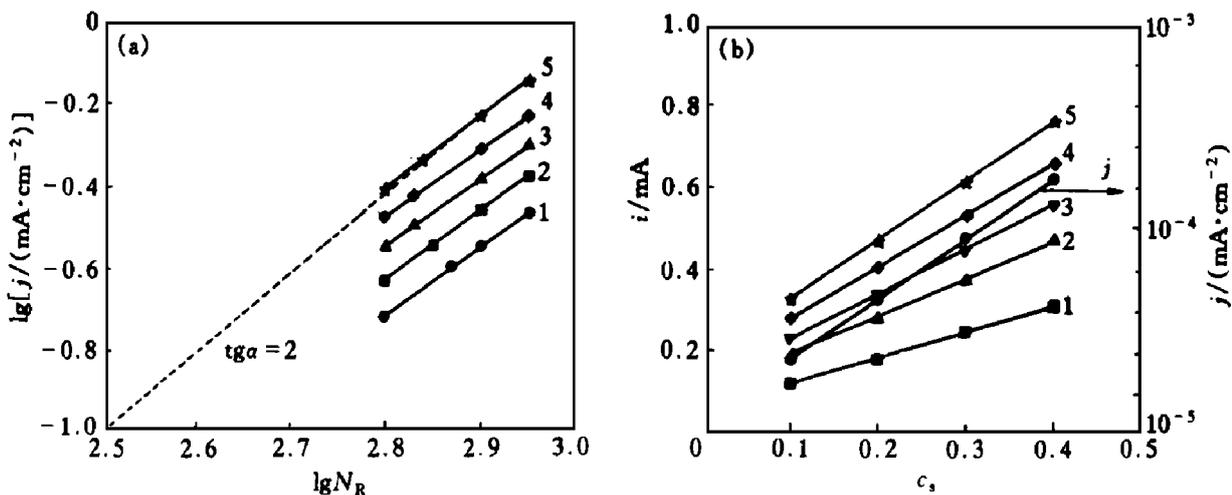

Fig. 2 lg$i$ vs lgN_R and i vs c_s curves
1 —Overpotential 100 mV; 2 —Overpotential 120 mV; 3 —Overpotential 140 mV;
4 —Overpotential 160 mV; 5 —Overpotential 180 mV

particles of the front part of column with the thickness of particle diameter, the number is N^0. At any moment, the particle number attached to the 1 cm^2 area of anode surface should be equal to or closely equal to N^0.

$$N^0 = \frac{c_s d}{(4/3)\pi d^3 \rho} = \frac{3c_s}{4\pi d^2 \rho} \qquad (11)$$

The whole surface area of these mineral particles is S^0

$$S^0 = \frac{3c_s}{4\pi d^2 \rho} \cdot 4\pi d^2 = \frac{3}{\rho}c_s \qquad (12)$$

where d is particle diameter, cm; ρ is particle density, g/cm^3. S^0 has no relationship with d. Take c_s = 0. 1 g/mL, ρ(Yuanyang golden concentrate) = 4. 16 g/cm^3, ρ(galena) = 7. 50 g/cm^3, there are S^0 = 0. 072 cm^2 (for Yuanyang gold concentrate minerals and S^0 = 0. 04 cm^2 for galena). This means that only on 0. 04~ 0. 072 cm^2 area of 1 cm^2, anode surface oxidation of particles takes place. On the other parts of anode surface, oxidation of Fe(II) or Cu(I) occurs. The direct oxidation of mineral particles takes up 0. 04 n~ 0. 072 n (n is the lost electron number of oxidation of one sulfide molecule). This explains well the reason that the contribution of anodic oxidation for mineral particles to leaching is small, about 14% for Yuanyang gold concentrate.

5 CONCLUSIONS

1) Sulfide leaching mechanism in slurry electrolysis process depends on the operating conditions.

2) Under the same over potential, the oxidation rate expressed by current density (i), solid content in slurry(c_s) and the square of stirring speed(N_R^2) have the relationship $i = Qc_s N_R^2$. Particle size does not affect the current density.

3) The existence of Fe(II) or Cu(I) in slurry can not only accelerate sulfide leaching, but also reduce energy consumption.

4) Under the conditions of ρ_{NaCl}= 200 g/L, c_{Cu} = 0. 01 mol/L, c_{Fe} = 0. 01 mol/L, pH = 1, L/S(liquid/solid)= 10: 1 and t = 60 ℃, the suitable current density i for slurry electrolysis of Yuanyang gold concentrate is not bigger than 140 A/m^2. Under this condition, chloride is not produced. The contribution of direct anodic oxidation of mineral particles to sulfide leaching is small. The leaching mainly depends on non-electrode process(chemical oxidation or chemical dissolution).

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