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Mechanism of influence of ferric ion on electrogenerative leaching of sulfide minerals with $FeCl_3$

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Abstract: A dual cell system was used to study the influence of ferric ion on the electrogenerative leaching of sulfide minerals. Reaction mechanisms for the ferric chloride electrogenerative leaching of a series of sulfide minerals were proposed based on the data collected from the dual cell experiments. The influences of ferric ion on the electrogenerative leaching of sulfide minerals are similar. Ferric ion plays an important role on limiting the electrogenerative leaching rate at a relatively low concentration of $FeCl_3$ (about less than 0.15 mol/L). The mathematical models based on the Butler-Volmer relation were delineated, and kinetic equations with respect to ferric ions for each sulfide mineral were obtained. The kinetic equations show that when the concentration of ferric ion is relatively low, the electrogenerative leaching rates are predicted to be proportional to 6/7, 4/5, 2/3 and 2/3 order of ferric ion for nickel concentrate, chalcopyrite concentrate, sphalerite and galena respectively. As the concentration of ferric ion increase, the correlative dependence between electrogenerative leaching rate and concentration of ferric ion becomes weak. The above conclusions are in agreement with the experimental results.

Key words: ferric ion; sulfide minerals; electrogenerative leaching; leaching rate; mechanism

1 Introduction

Electrogenerative leaching process is a newly-developed technique in hydrometallurgy. Although its principle has developed since the late 1960s[1], this technique has been overlooked in metallurgy until ZHANG et al[2] introduced it to the leaching of synthetic Ni_3S_2 with $FeCl_3$. In order to utilize the chemical energy in leaching process reasonably and simplify the purification process, WANG et al[3−8] completed experimental studies of electrogenerative leaching a series of sulfide minerals through a dual cell system technique with $FeCl_3$ and acidic MnO_2 as oxidant respectively. It was indicated that a slight increase of $[FeCl_3]$ resulted in a sharp increase of the output current and power at a relatively low $[FeCl_3]$ (<0.15 mol/L). Over this value, the output current and power become independent of $[FeCl_3]$. The similar influence of $[FeCl_3]$ was found in some traditional leaching experiments [9−15]. In order to elucidate the role of $[FeCl_3]$ in electrogenerative leaching process, a reaction mechanism was proposed in this study.

2 Experimental

A dual cell system technique was used to study the influence of $[Fe^{3+}]$. Nickel concentrate (Ni_3S_2, Ni 55.2%, mass fraction), chalcopyrite concentrate ($CuFeS_2$, Cu 22.3%), sphalerite (Zn 61.39%), galena (Pb 60.1%), were taken as the anodic materials respectively.

An ion-selective membrane connected the separated anolyte and catholyte compartments so that the effect of solution variables on each half cell can be independently evaluated. Solutions used in the experiments were prepared with analytical-grade chemicals and distilled water. Two mini-stirrers were used for agitating and water bath thermostat was used for heating. Each of half-cell potentials(φ) was measured versus the saturated calomel electrode(SCE), and the output voltages(V) of the leaching cell were measured with a digital voltmeter. The current(I) was measured with a low resistance

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Corresponding author: WANG Shao-fen; Tel: +86-731-5128112; E-mail: wangsf711117@163.com milliammeter.

3 Results

3.1 Influence of [Fe^{3+}] on electrogenerative leaching rate

The anolyte of the electrogenerative leaching system was NaCl (3.0 mol/L), and the catholyte was HCl (2.0 mol/L) plus a certain concentration of $FeCl_3$. Under mild stirring (rate: 1 100 r/min), all the output currents along with the increase of the $FeCl_3$ concentration were measured at 298.8 K for the electrogenerative leaching process of the four sulfide minerals systems. For the galena system, the relation of the logarithm of the maximum output current ($\lg I_{max}$) versus the logarithm of the ferric ion concentration ($\lg[Fe^{3+}]$) is plotted in Fig.1.

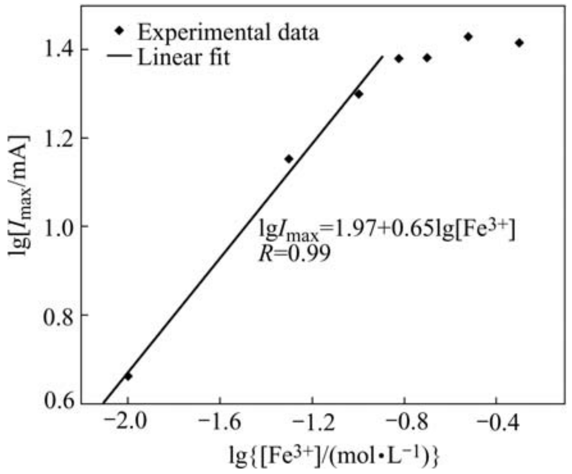

Fig.1 $\lg I_{max}$—$\lg[Fe^{3+}]$ relation in electrogenerative leaching galena with $FeCl_3$ system

From Fig.1, the influence of the [Fe^{3+}] on the electrogenerative leaching rate is illustrated, that is the increase of [Fe^{3+}] can raise the electrogenerative leaching rate at a relatively low [Fe^{3+}] concentration (<0.15 mol/L). Above that concentration, the output current and power become relatively independent of concentration. All the other three sulfide minerals systems show the same phenomenon. From the data collected from the four systems, the mathematical equations are used to express the linear relation of $\lg I_{max}$ and $\lg[Fe^{3+}]$, which are listed in Table 1.

In conclusion, the electrogenerative leaching rate of sulfide minerals is directly proportional to $[Fe^{3+}]^B$ at relatively lower concentration and deviate from this order at higher [Fe^{3+}].

3.2 Influence mechanisms

In order to describe mechanism of the influence of ferric ion concentration on the electrogenerative leaching rate, an electrochemical model was introduced. In this model, it is assumed that the electrogenerative leaching occured through a redox couple between sulfide minerals and ferric ion. The rate controlling step is the electrochemical charge transfer process on the electrode surface, so an electrochemical charge transfer mechanism was used in this analysis.

Table 1 Relation between I_{max} and $\lg[Fe^{3+}]$ (0.01−0.1 mol/L)

System	$\lg I_{max}=A+B\lg[Fe^{3+}]$	Correlative exponential
Nickel concentrate	$\lg I_{max}=1.85+0.71\lg[Fe^{3+}]$	0.71
Chalcopyrite concentrate	$\lg I_{max}=1.36+0.72\lg[Fe^{3+}]$	0.72
Sphalerite	$\lg I_{max}=1.12+0.58\lg[Fe^{3+}]$	0.58
Galena	$\lg I_{max}=1.97+0.65\lg[Fe^{3+}]$	0.65

1) Fe^{3+} was adsorbed on Pt electrode:

$$Pt+Fe^{3+}(aq)=[Pt\cdot Fe^{3+}]_{ads} \tag{1}$$

According to Langmuir isothermal adsorption equation, the following relation is obtained:

$$\theta=\frac{K_1[Fe^{3+}]}{1+K_1[Fe^{3+}]} \tag{2}$$

where θ represents the fraction of total available surface sites occupied by Fe^{3+}, K_1 represents the equilibrium constant of Eqn.(1).

2) As the external resistance is varied from an infinitely high value (open circuit) down to a very low value, sulfide minerals are oxidized as shown in Eqns.(3)−(6) and Fe^{3+} is reduced in cathode as shown in reaction(7):

$$Ni_3S_2(s)=3Ni^{2+}(aq)+2S^0(s)+6e \tag{3}$$

$$CuFeS_2(s)=Cu^{2+}(aq)+Fe^{2+}(aq)+2S^0(s)+4e \tag{4}$$

$$ZnS(s)=Zn^{2+}(aq)+S^0(s)+2e \tag{5}$$

$$PbS(s)=Pb^{2+}(aq)+S^0(s)+2e \tag{6}$$

$$[Pt\cdot Fe^{3+}]_{ads}+e=[Pt\cdot Fe^{2+}]_{ads} \tag{7}$$

θ

For the cathodic reaction (7), the Butler-Volmer equation is

$$i_7=nFA_cK_7\theta\exp[\frac{-\alpha nF\varepsilon}{RT}]-nFA_cK_7^{'}[Fe^{2+}]_{ads}\exp[\frac{\beta nF\varepsilon}{RT}] \tag{8}$$

where n is the number of electron in reaction (7) and n=1; α and β represent transfer coefficients and the values are 0.5, respectively. $\alpha+\beta=1$, commonly; ε is the polarization potential; A_c is the surface area of Pt electrode; K_7 and $K_7^{'}$ represent equilibrium constants of reaction (7) and reverse reaction of reaction (7). Eqn.(8) can be simplified as Eqn.(9) owning to that there is no external Fe^{2+} existed in solution and the reverse reaction of reaction (7) can be ignored:

$$i_7 = FA_c K_7 \theta \exp[\frac{-F\varepsilon}{2RT}] \tag{9}$$

For Eqns.(3)-(6), the Butler-Volmer equations are as follows:

$$i_3 = 6FA_a K_3 \exp[\frac{3F\varepsilon}{RT}] - 6FA_a K_3'[\mathrm{Ni}^{2+}]^3 \exp[\frac{-3F\varepsilon}{RT}] \tag{10}$$

$$i_4 = 4FA_a K_4 \exp[\frac{2F\varepsilon}{RT}] - 4FA_a K_4'[\mathrm{Cu}^{2+}][\mathrm{Fe}^{2+}] \exp[\frac{-2F\varepsilon}{RT}] \tag{11}$$

$$i_5 = 2FA_a K_5 \exp[\frac{F\varepsilon}{RT}] - 2FA_a K_5'[\mathrm{Zn}^{2+}] \exp[\frac{-F\varepsilon}{RT}] \tag{12}$$

$$i_6 = 2FA_a K_6 \exp[\frac{F\varepsilon}{RT}] - 2FA_a K_6'[\mathrm{Pb}^{2+}] \exp[\frac{-F\varepsilon}{RT}] \tag{13}$$

where A_a is the surface area of mineral electrodes; K_3-K_6 and $K_3' - K_6'$ represent the equilibrium constants of reactions (3)−(6) and reverse reactions of (3)−(6). Owning to that there are no external sulfide mineral mental ions exist in solution and the reverse reactions of (3)−(6) can be ignored. The Butler-Volmer Eqns.(10)−(13) can be simplified as

$$i_3 = 6FA_a K_3 \exp[\frac{3F\varepsilon}{RT}] \tag{14}$$

$$i_4 = 4FA_a K_4 \exp[\frac{2F\varepsilon}{RT}] \tag{15}$$

$$i_5 = 2FA_a K_5 \exp[\frac{F\varepsilon}{RT}] \tag{16}$$

$$i_6 = 2FA_a K_6 \exp[\frac{F\varepsilon}{RT}] \tag{17}$$

Considering $i_7=i_3$, $i_7=i_4$, $i_7=i_5$, $i_7=i_6$ when the electrogenerative leaching is ongoing, Eqn.(9) is combined with Eqns.(14)−(17) respectively, the following equations are obtained:

$$\frac{i_3}{i_7} = \frac{6A_a K_3}{K_7 A_c \theta} \exp[\frac{7F\varepsilon}{2RT}] = 1 \tag{18}$$

$$\frac{i_4}{i_7} = \frac{4A_a K_4}{K_7 A_c \theta} \exp[\frac{5F\varepsilon}{2RT}] = 1 \tag{19}$$

$$\frac{i_5}{i_7} = \frac{2A_a K_5}{K_7 A_c \theta} \exp[\frac{3F\varepsilon}{2RT}] = 1 \tag{20}$$

$$\frac{i_6}{i_7} = \frac{2A_a K_6}{K_7 A_c \theta} \exp[\frac{3F\varepsilon}{2RT}] = 1 \tag{21}$$

$\exp[F\varepsilon/RT]$ for each system can be expressed as follows, respectively:

$$\exp[\frac{F\varepsilon}{RT}] = (\frac{K_7 A_c \theta}{6A_a K_3})^{\frac{2}{7}} \tag{22}$$

$$\exp[\frac{F\varepsilon}{RT}] = (\frac{K_7 A_c \theta}{4A_a K_4})^{\frac{2}{5}} \tag{23}$$

$$\exp[\frac{F\varepsilon}{RT}] = (\frac{K_7 A_c \theta}{2A_a K_5})^{\frac{2}{3}} \tag{24}$$

$$\exp[\frac{F\varepsilon}{RT}] = (\frac{K_7 A_c \theta}{2A_a K_6})^{\frac{2}{3}} \tag{25}$$

The overall electrogenerative leaching rates, expressed as the rates disappearance of sulfide minerals, are related to the anodic current through the following equations which are essentially the statement of Faraday' Law:

$$-\frac{\mathrm{d}n_{\mathrm{Ni_3S_2}}}{\mathrm{d}t} = \frac{i_{\mathrm{Ni}}}{n_{\mathrm{Ni}} FA_a} = \frac{i_3}{6FA_a} \tag{26}$$

$$-\frac{\mathrm{d}n_{\mathrm{CuFeS_2}}}{\mathrm{d}t} = \frac{i_{\mathrm{Cu}}}{n_{\mathrm{Cu}} FA_a} = \frac{i_4}{4FA_a} \tag{27}$$

$$-\frac{\mathrm{d}n_{\mathrm{ZnS}}}{\mathrm{d}t} = \frac{i_{\mathrm{Zn}}}{n_{\mathrm{Zn}} FA_a} = \frac{i_5}{2FA_a} \tag{28}$$

$$-\frac{\mathrm{d}n_{\mathrm{PbS}}}{\mathrm{d}t} = \frac{i_{\mathrm{Pb}}}{n_{\mathrm{Pb}} FA_a} = \frac{i_6}{2FA_a} \tag{29}$$

Combining Eqns.(14)−(17) yields

$$-\frac{\mathrm{d}n_{\mathrm{Ni_3S_2}}}{\mathrm{d}t} = K_3^{\frac{1}{7}} (\frac{k_7 A_c \theta}{6A_a})^{\frac{6}{7}} = K_3^{\frac{1}{7}} (\frac{K_7 A_c}{6A_a})^{\frac{6}{7}} (\frac{K_1[\mathrm{Fe}^{3+}]}{1+K_1[\mathrm{Fe}^{3+}]})^{\frac{6}{7}} \tag{30}$$

$$-\frac{\mathrm{d}n_{\mathrm{CuFeS_2}}}{\mathrm{d}t} = K_4^{\frac{1}{5}} (\frac{k_7 A_c \theta}{4A_a})^{\frac{4}{5}} = K_4^{\frac{1}{5}} (\frac{K_7 A_c}{4A_a})^{\frac{4}{5}} (\frac{K_1[\mathrm{Fe}^{3+}]}{1+K_1[\mathrm{Fe}^{3+}]})^{\frac{4}{5}} \tag{31}$$

$$-\frac{\mathrm{d}n_{\mathrm{ZnS}}}{\mathrm{d}t} = K_5^{\frac{1}{3}} (\frac{k_7 A_c \theta}{2A_a})^{\frac{2}{3}} = K_5^{\frac{1}{3}} (\frac{K_7 A_c}{2A_a})^{\frac{2}{3}} (\frac{K_1[\mathrm{Fe}^{3+}]}{1+K_1[\mathrm{Fe}^{3+}]})^{\frac{2}{3}} \tag{32}$$

$$-\frac{\mathrm{d}n_{\mathrm{PbS}}}{\mathrm{d}t} = K_6^{\frac{1}{3}} (\frac{k_7 A_c \theta}{2A_a})^{\frac{2}{3}} = K_6^{\frac{1}{3}} (\frac{K_7 A_c}{2A_a})^{\frac{2}{3}} (\frac{K_1[\mathrm{Fe}^{3+}]}{1+K_1[\mathrm{Fe}^{3+}]})^{\frac{2}{3}} \tag{33}$$

When concentration of Fe^{3+} is relatively lower, $1+K_1[Fe^{3+}]\approx 1$ in Eqns.(30)-(33) and the electrogenerative leaching rate of nickel concentrate, chalcopyrite concentrate, sphalerite and galena predict 6/7, 4/5, 2/3 and 2/3 order dependence on Fe^{3+}, respectively. $K_1[Fe^{3+}]$ in Eqns.(30)−(33) can not be ignored as concentration of Fe^{3+} increases, which results in the correlative dependence between electrogenerative leaching rate and $[Fe^{3+}]$ become weak. The results are in agreement with the experiment study: the rate of electrogenerative leaching of nickel concentrate, chalcopyrite concentrate, sphalerite and galena is directly proportional to $[Fe^{3+}]^{0.71}$, $[Fe^{3+}]^{0.72}$, $[Fe^{3+}]^{0.58}$, $[Fe^{3+}]^{0.65}$ at relatively lower concentration and deviate from this order at higher $[Fe^{3+}]$.

4 Conclusions

The influence of $[Fe^{3+}]$ on the electrogenerative leaching system was investigated through a dual cell system technique. Fe^{3+} was involved in the electrogenerative leaching process of sulfide minerals directly. The output power increases as $[Fe^{3+}]$ increases. There has weaker influence on the electrogenerative leaching rate when the $[Fe^{3+}]$ reaches a certain value.

The mechanism of cathodic reaction was deduced under reasonable hypothesis and kinetic equations with respect to $[Fe^{3+}]$ for each sulfide mineral were obtained as follows:

$$-\frac{\mathrm{d}n_{\mathrm{Ni_3S_2}}}{\mathrm{d}t}=K_3^{\frac{1}{7}}(\frac{k_7A_\mathrm{c}\theta}{6A_\mathrm{a}})^{\frac{6}{7}}=K_3^{\frac{1}{7}}(\frac{K_7A_\mathrm{c}}{6A_\mathrm{a}})^{\frac{6}{7}}(\frac{K_1[\mathrm{Fe}^{3+}]}{1+K_1[\mathrm{Fe}^{3+}]})^{\frac{6}{7}}$$

$$-\frac{\mathrm{d}n_{\mathrm{CuFeS_2}}}{\mathrm{d}t}=K_4^{\frac{1}{5}}(\frac{k_7A_\mathrm{c}\theta}{4A_\mathrm{a}})^{\frac{4}{5}}=K_4^{\frac{1}{5}}(\frac{K_7A_\mathrm{c}}{4A_\mathrm{a}})^{\frac{4}{5}}(\frac{K_1[\mathrm{Fe}^{3+}]}{1+K_1[\mathrm{Fe}^{3+}]})^{\frac{4}{5}}$$

$$-\frac{\mathrm{d}n_{\mathrm{ZnS}}}{\mathrm{d}t}=K_5^{\frac{1}{3}}(\frac{k_7A_\mathrm{c}\theta}{2A_\mathrm{a}})^{\frac{2}{3}}=K_5^{\frac{1}{3}}(\frac{K_7A_\mathrm{c}}{2A_\mathrm{a}})^{\frac{2}{3}}(\frac{K_1[\mathrm{Fe}^{3+}]}{1+K_1[\mathrm{Fe}^{3+}]})^{\frac{2}{3}}$$

$$-\frac{\mathrm{d}n_{\mathrm{PbS}}}{\mathrm{d}t}=K_6^{\frac{1}{3}}(\frac{k_7A_\mathrm{c}\theta}{2A_\mathrm{a}})^{\frac{2}{3}}=K_6^{\frac{1}{3}}(\frac{K_7A_\mathrm{c}}{2A_\mathrm{a}})^{\frac{2}{3}}(\frac{K_1[\mathrm{Fe}^{3+}]}{1+K_1[\mathrm{Fe}^{3+}]})^{\frac{2}{3}}$$

The above conclusions are in agreement with the experimental results: the rate of electrogenerative leaching of nickel concentrate, chalcopyrite concentrate, sphalerite and galena is directly proportional to $[Fe^{3+}]^{0.71}$, $[Fe^{3+}]^{0.72}$, $[Fe^{3+}]^{0.58}$, $[Fe^{3+}]^{0.65}$ at relatively lower concentration and deviate from this order at higher $[Fe^{3+}]$.

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