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APPLICATION OF THERMO-ELECTROCHEMISTRY TO SIMULTANEOUS LEACHING OF SPHALERITE AND MnO_2*

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In order to enhance the electrogenerative leaching rate of sphalerite reasonably, the basic principle of generative process was applied to the simultaneous leaching of sphalerite in the presence of MnO_2. It was confirmed by experimental results that both mental ions and electric energy could be obtained in the simultaneous electrogenerative leaching process. The leaching cell had the open circuit potential about 1.0 V, about 2000 C of electric quantity was obtained, the optimal leaching ratio of Zn^{2+} and Mn^{2+} was 48.5, 39.6% respectively, after electrogenerative leaching for 11 h.

Keywords: *electrogenerative leaching, MnO_2, simultaneous, sphalerite*

Introduction

Electrogenerative leaching process is a newly-developed technique in hydrometallurgy. In order to utilize the chemical energy in leaching process reasonably and simplify the purification process, Wang *et al.* [1, 2] had completed experimental studies of electrogenerative leaching of galena and nickel concentrate with $FeCl_3$. Recently, some very interesting studies about the leaching of a series of MnO_2-sulfide mineral couples in acid media, such as MnO_2-ZnS [3], MnO_2-$CuFeS_2$ [4, 5], MnO_2-FeS_2 [6–8] have been reported, the leaching rate of the mineral couples are considerable high, even though the leaching rate of the MnO_2 or sulfide mineral itself under the same condition is small. So it should be very promising for the electrogenerative leaching of sphalerite in the presence of MnO_2. The electrode reaction of the oxidant was as follow:

$$MnO_2(s)+4H^+(aq)+2e=Mn^{2+}(aq)+2H_2O$$
$$\varphi \textit{ vs. SHE}=1.224\text{ V} \quad (1)$$

Sphalerite (ZnS) was oxidized according to:

$$ZnS(s)=Zn^{2+}(aq)+S(s)+2e$$
$$\varphi \textit{ vs. SHE}=0.264\text{ V} \quad (2)$$

accordingly, the cell reaction was obtained:

$$MnO_2(s)+ZnS(s)+4H^+(aq)= Mn^{2+}(aq)+2H_2O+Zn^{2+}(aq)+S(s)$$
$$\Delta_r G_m^\theta = -186.4\text{ kJ mol}^{-1} \quad (3)$$

Based on $W_{max}=\Delta_r G$, under reversible condition, a potential energy of 186.0 kJ would be liberated as electric work when 1 mol ZnS leaching performed in a simultaneous electrogenerative cell.

Experimental

A dual cell system was used in this study. The sphalerite (Zn 61.39 mass%) and chemical-grade MnO_2 (Mn 54.82 mass%) were taken as the electrode material. Two kinds of structures were adopted for sphalerite electrode. A mixture of 2.0 g sphalerite and 0.12 g acetylene black was put into a rectangular nylon filter bag with surface area about 5 cm^2, then a claviform graphite electrode (φ0.7 cm) was inserted as conductor. A mixture of 2.0 g sphalerite and 0.12 g acetylene black was put into a columnar filter bag (φ2.35 cm), then a claviform graphite electrode (φ2.3 cm) was inserted as conductor. A mixture of 2.0 g MnO_2 and 0.06 g acetylene black was put into a columnar filter bag (φ2.35 cm), then a claviform graphite electrode (φ2.3 cm) was inserted as conductor. Two mini-stirrers were used for agitating and water-bath thermostat for heating. Each of half-cell potentials was measured *vs*. the saturated calomel electrode (SCE), and the output voltages of the leaching cell were measured with a digital voltmeter. The current was measured with a low resistance milliammeter.

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Results and discussion

Influence of NaCl concentration

The influence of NaCl concentration on simultaneous electrogenerative leaching of sphalerite and MnO_2 was similar to the system of electrogenerative leaching with $FeCl_3$ [1]. Taken the maximum output current (I_{max}) as a measure of electrogenerative leaching rate, logI_{max}–log[NaCl] curve can be derived as shown in Fig. 1. The linear regressive equations in 0.1~0.5 mol L^{-1} can be expressed as logI_{max}= 2.31+0.32log[NaCl], R=0.99. It indicates that the rate of electrogenerative leaching of sphalerite is directly proportional to $[NaCl]^{0.32}$ at relatively lower concentration and deviate from this order at higher NaCl concentration.

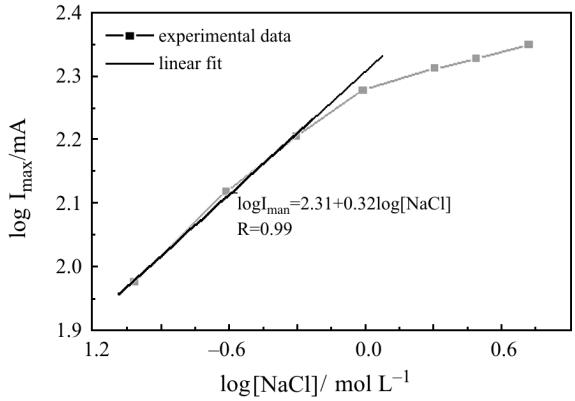

Fig. 1 Influence of NaCl concentration on the simultaneous electrogenerative leaching system. in 2.0 mol L^{-1} HCl catholyte and x mol L^{-1} NaCl, (x=0.1, 0.25, 0.50, 1.0, 2.0, 3.0, 5.0) anolyte, at 304 K and 500 r.p.m.

Influence of H^+ concentration

Hydrogen ion is in the reaction (1), so a series of experiments was conducted to evaluate the effect of H^+ concentration on the simultaneous electrogenerative leaching process. The experimental results indicated that the change of H^+ concentration affected the polarization of cathode. Figure 2 presented the graph of logI_{max} *vs*. log[H^+] with the slope about 0.53.

Influence of electrode structure

As the external resistance was varied from an infinitely high value (open circuit) down to very low value, the output voltage (V) continuously decreased, and the maximum output power was obtained when the external resistance equals 9.9 Ω. So the elctrogenerative leaching was performed under a constant external resistance of 9.9 Ω. The relations of output voltage and output current *vs*. the leaching time for rectangular filter bag electrode and columnar

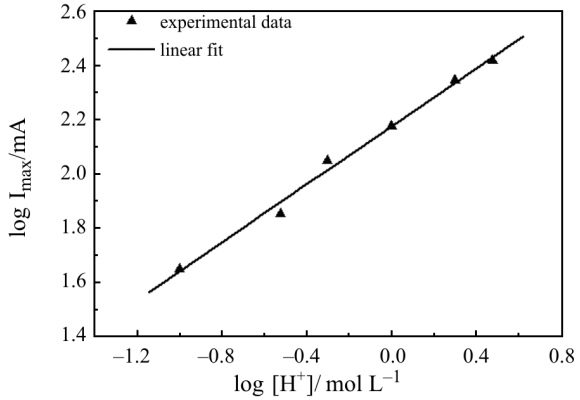

Fig. 2 Influence of H^+ concentration on the simultaneous electrogenerative leaching system in 3.0 mol L^{-1} NaCl anolyte and x mol L^{-1} HCl (x=0.1, 0.3, 0.5, 1.0, 2.0, 3.0) catholyte, at 304 K and 500 r.p.m.

filter bag electrode were listed in Fig. 3. After simultaneous electrogenerative leaching for 11 h, leaching ratio of Zn^{2+} and Mn^{2+} were 26.2 and 30.8%, respectively, for rectangular filter bag electrode. For columnar filter bag electrode, leaching ratio of Zn^{2+} and Mn^{2+} were 48.5 and 39.6%, respectively.

Kinetics of the simultaneous electrogenerative leaching system

Integrate the *I-t* curves in Fig. 3, the results were shown in Fig. 4. It is indicated that the process gained about 1400–2000 C of electric quantity at 304 K after simultaneous electrogenerative leaching for about 11 h. The curves were satisfied with an equation of $Q=\int_0^t I\mathrm{d}t=a+bt-ct^2$ specified as following:

A: $Q = 0.244 + 2.265t - 1.863\cdot10^{-6}\,t^2$, R=0.9999

B: $Q = 3.265 + 3.200t - 4.585\cdot10^{-4}\,t^2$, R=0.9999

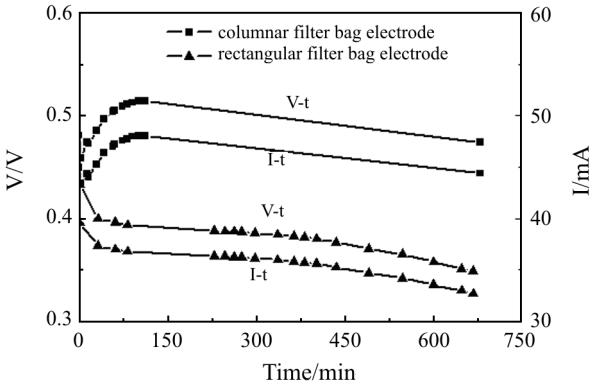

Fig. 3 The *V-I-t* curves of the simultaneous electrogenerative system in 3.0 mol L^{-1} NaCl anolyte and 2.0 mol L^{-1} HCl catholyte, at 304 K and 500 r.p.m.

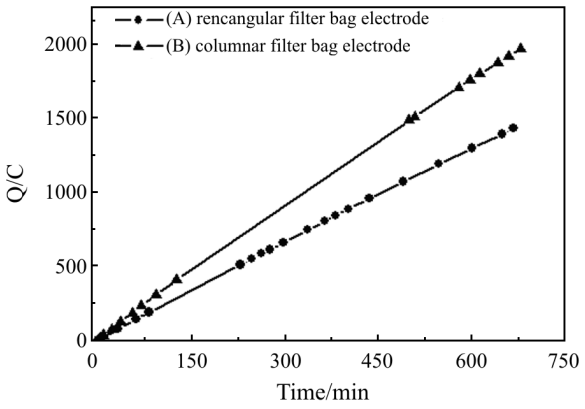

Fig. 4 The *Q-t* curves of the simultaneous electrogenerative system, in 3.0 mol L^{-1} NaCl anolyte and 2.0 mol L^{-1} HCl catholyte, at 304 K and 500 r.p.m.

According to $Q=\int_0^t I\mathrm{d}t=a+bt-ct^2$, $\frac{\mathrm{d}Q}{\mathrm{d}t}=k=b-2ct$.

When t=0, $k_{(t=0)}=b$. The value of b expresses the rate of output power increasing with time. $\frac{\mathrm{d}^2Q}{\mathrm{d}t^2}=2c$, and the value of c expresses degree of deviation of *Q-t* curves or degree of electrode polarization.

Conclusions

- Electrogenerative leaching with acidic MnO_2 via the cell of (–) ZnS(*s*), NaCl(*aq*) || HCl(*aq*), MnO_2, C(*s*) (+). The leaching cell had the open circuit potential about 1.0 V, and the leaching ratio of Zn^{2+} and Mn^{2+} was 48.5 and 39.6%, respectively, after electrogenerative leaching for about 11 h under the optimal conditions.
- Electrode with different structure has the different output power. It is necessary to make more proper electrode, which lead the application of simultaneous electrogenerative leaching in hydrometallurgical processes.
- The rate of simultaneous electrogenerative leaching of sphalerite and MnO_2 was directly proportional to $[NaCl]^{0.32}$ at relatively lower concentration and over 0.5 mol L^{-1}, the NaCl concentration has weaker effect on the process.
- Increase of H^+ concentration influence the cathodic polarization, and the graph of $\log I_{max}$ *vs*. $\log[H^+]$ has the slope about 0.53.
- Kinetics of the simultaneous electrogenerative leaching system was set forth simply and the coefficients in equation are clarified.

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