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ELECTROGENERATIVE LEACHING FOR SPHALERITE-MnO_2 IN THE PRESENCE OF *ACIDITHIOBACILLUS FERROOXIDANS*

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A dual cell system was used to study the electrogenerative leaching sphalerite-MnO_2 under the conditions of presence and absence of *Acidithiobacillus ferrooxidans* (*A. ferrooxidans*). The polarization of anode and cathode, and the relationship between the electric quantity (*Q*) and some factors, such as the dissolved Zn^{2+}, Fe^{2+}, the time in the bio-electro-generating simultaneous leaching (BEGSL) and electro-generating simultaneous leaching (EGSL), were studied.

The results show that the dissolved Zn^{2+} in the presence of *A. ferrooxidans* is nearly 60% higher than that in the absence of *A. ferrooxidans*; the electrogenerative quantity in the former is about 134% more than that in the latter. A three-electrode system was applied to study anodic and cathodic self-corrosion current, which was inappreciable compared with the galvanic current between sphalerite and MnO_2. The accumulated sulfur on the surface of sulfides produced in the electrogenerative leaching process could be oxidized in the presence of *A. ferrooxidans*, and the ratio of biological electric quantity reached to 31.72% in 72 h.

Keywords: *A. ferrooxidans, electrogenerative leaching, sphalerite*

Introduction

Hydrometallurgical treatment of sphalerite minerals have been reported [1–4]. Some new technology such as the electrogenerative leaching [4, 5] has been applied to the leaching of sulfides. In the process, the Gibbs free energy could transform to an applicable electrical work and the leaching products were acquired simultaneously. Instead of the produced substances that pollute environment in traditional leaching, such as gaseous H_2S and SO_2 [6], the new technique would not only precipitate the element sulfur, but also simplify the purified process of leaching solution [7]. Wang *et al.* [8] used the technology in the simultaneous leaching of chalcopyrite concentrate with MnO_2. Xiao *et al.* [9] pointed out that the accumulated sulfur covering on the surface of leached sulfides inhibit the anodic reaction and reduce the output of electric energy in EGSL greatly. As a result, it is necessary to develop a proper technique, which could be employed to eliminate the accumulated sulfur on the surface of the sulfides.

Acidithiobacillus ferrooxidans (*A. ferrooxidans*) plays an important role in the aspect of the biochemical treatment of sulfur and oxidation of ferrous ions into ferric ones. Under normal aerobic conditions, the bacteria can utilize ions in solution as an energetic substance and can also obtain energy from direct oxidation of the sulfur. If the microbes be added into anodic electrolyte of the electrogenerative leaching cell, and oxidize the produced sulfur to sulfuric acid in the sulfide leaching system, the electrogenerative leaching resistance will be decreased largely.

A. ferrooxidans were used to the simultaneous electrogenerative leaching system in this paper. We study the electrogenerative process of sphalerite-MnO_2 in the presence of *A. ferrooxidans*, by means of the antitheses study between the BEGSL and the EGSL.

Experimental

Materials

The selected sphalerite was a natural hand-sorted ore from a domestic mine. Its element analysis was listed in Table 1.

The XRD analysis showed that ZnS and FeS coexist in the minerals.

Table 1 Chemical composition of sphalerite (mass%)

Element	Zn	S	Fe	Sn	Si
Mass%	51.54	29.74	12.27	0.33	4.45

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Electrogenerative system

The cell was made of PVC, which was divided into two compartments connected by anion membrane. 200 milliliters of catholyte and anolyte were used in each compartment. The electrode of anode was sphalerite-acetylene black paste electrode: the sphalerite-containing mixture was compacted in an acid-resisting nylon filter net with aperture size 45 μm, in which the bacteria could get to the surface of sulfide mineral and the dissociated ions could diffuse freely. The electrode of cathode was MnO_2-acetylene black paste electrode which was made in the same way of anode. The electrodes were attached to carbon rods used as current collectors. Two air-blowing tubes were inserted into anolyte and catholyte, to supply the oxygen for bacteria and to agitate. The pH values were measured with a PHS-3C digital acidometer. Each of half cell potentials was measured *vs.* saturated calomel electrode (SCE) using a digital voltmeter and the voltage output of the leaching cell were measured with a digital voltmeter as well. The current was measured with a low resistance amperometer. The concentration of oxygen was measured with a Degussa oxygen meter. All of the measured instruments were calibrated before each run.

The solutions were prepared using AR reagents and distilled water. The bacteria culture medium were consisted of $(NH_4)_2SO_4$ 3.0 g L^{-1}, KCl 0.1 g L^{-1}, K_2HPO_4 0.5 g L^{-1}, $MgSO_4\cdot 7H_2SO_4$ 0.5 g L^{-1} and $Ca(NO_3)_2$ 0.01 g L^{-1}. For comparison, the medium was taken as anolyte of EGSL and the same nutrient medium with exponential growth phase bacteria was taken as anolyte of BEGSL. The concentration of oxygen in the solution was 5.9 mg L^{-1}. A pure strain of *A. ferrooxidans* that could breed on sphalerite was obtained from Hunan Province of China.

Self-corrosion measurements

A three-electrode system with a working electrode of MnO_2 or sphalerite-acetylene black paste, a platinum counter and a saturated calomel electrode (SCE) reference was used for self-corrosion measurements. Polarization was measured with the scanning rate of 0.1 mV s^{-1} by the CHI660B electrochemical workstation.

Results and discussion

Anodic and cathodic polarization in EGSL and BEGSL

The Evans diagram, anodic and cathodic polarization, and interior resistance of the cell are used to study the controlling factor in EGSL and BEGSL processes. Generally, the bigger the value of resistance is, the greater the effect on the leaching reaction [4]. Figure 1 shows the Evans diagram of EGSL and BEGSL for sphalerite –MnO_2 system.

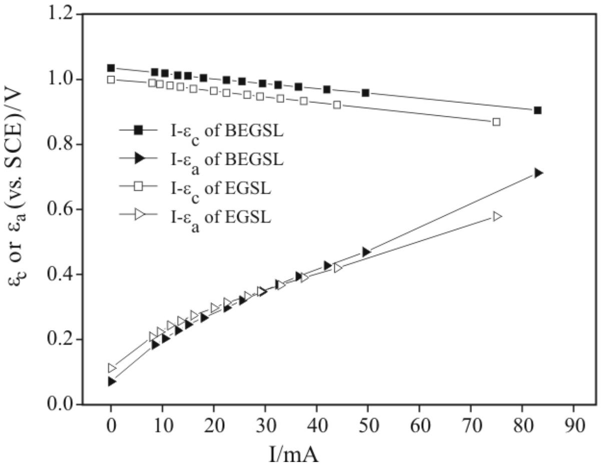

Fig. 1 The Evans diagram of EGSL and BEGSL for sphalerite–MnO_2

Polarization is defined as:

$$P=\frac{d\varepsilon}{dI}=\frac{\eta}{I} \tag{1}$$

where η is the over-potential, and *I*, the galvanic current. As is seen from Fig. 1, the currents increase with the over-potential of cathode η_c and the over-potential of anode η_a.

The polarization of anode and cathode is P_a and P_c, respectively.

$$P_a=\frac{\eta_a}{I} \tag{2}$$

$$P_c=\frac{\eta_c}{I} \tag{3}$$

$$\varepsilon_c-\varepsilon_a=\eta_c+\eta_a+IR=IP_c+IP_a+IR \tag{4}$$

$$I=\frac{\varepsilon_c-\varepsilon_a}{P_c+P_a+R} \tag{5}$$

R in Eqs (4) and (5) is interior resistance of the electrogenerative leaching system. The over-potentials of anode and cathode increase with decreasing of galvanic voltage in 36 h for EGSL and BEGSL processes similarly. P_a, P_c, *R*, and *J* (density of *I*) are listed in Table 2.

It is seen from Table 2 that the value of P_a and *R* are smaller in the beginning due to the electro-catalytic property of the electrode [10]. Compared with EGSL system, the polarization P_a comes to steady-value about 19~22 Ω with decreasing of the galvanic current in BEGSL system as the process is going on. This could be attributed to the fact that elemental sulfur accumulated in the anodic electrode inhibits the

Table 2 P_a, P_c, R and J of EGSL and BEGSL for sphalerite-MnO_2 system in 36 h

Process	Time/ h	P_c/ Ω	P_a/ Ω	R/ Ω	J_c/ mA cm^{-2}
BEGSL	0	1.75	7	2.64	9.11
	12	6.58	19.04	3.58	8.41
	24	8.05	21.19	3.89	7.83
	36	14.81	22.53	3.51	7.48
EGSL	0	1.54	8.04	1.21	10.25
	12	5.46	22.51	2.92	5.53
	24	7.84	28.63	2.63	4.86
	36	15.47	35.17	2.45	3.73

reaction in EGSL system, while be oxidized by oxygen with the promotion of *A. ferrooxidans* in BEGSL system. The decrease of acidity in the solutions of the two systems might be the reason for the increase in polarization P_c.

Self-corrosion for pyrite and MnO_2 electrodes

In addition to the galvanic interaction in EGSL and BEGSL system, there also exists the self-corrosion in two electrodes, respectively. The predominance of the two effects could be estimated from the values of the galvanic current and self-corrosion current [11]. A convenient way to determine the self-corrosion is to plot Tafel curves of the individual half-cells. The Tafel curves of sphalerite anode with or without *A. ferrooxidans* and MnO_2 cathode in 1M H_2SO_4 solution are listed in Fig. 2.

The self-corrosion potential E_{corr}, self-corrosion current density J_{corr}, and polarization resistance R_p obtained from the Tafel curves are listed inTable 3.

For sphalerite, J_{corr}, as seen from Table 3 is negligible compared with the galvanic current density J showed in Table 2. For MnO_2, the J_{corr} is almost same magnitude as the galvanic current. Consequently, the galvanic interaction for sphalerite predominates over their individual self-corrosion whether in EGSL or BEGSL processes.

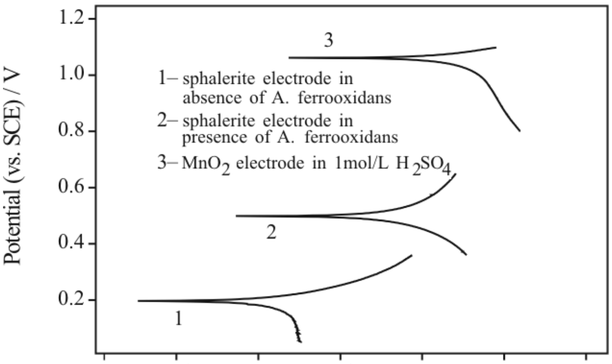

Fig. 2 Tafel curves

Table 3 E_{corr}, J_{corr} and R_p calculated from Tafel curves

Electrode	E_{corr} (*vs.* SCE)/V	J_{corr}/ mA cm^{-2}	R_p/Ω
Sphalerite (with *A. ferrooxidans*)	0.499	0.42	77
Sphalerite (germfree)	0.197	0.0087	1034
MnO_2	1.062	1.12	17

Electric quantity and leaching ratio in EGSL and BEGSL processes

Assume that the all-transferred charge is due to S^{2-} to S^0 and is considered as the theoretical electric quantity (TEQ), which can be calculated by the Faraday's law. However, the measured electric quantity (MEQ) in BEGSL process is larger than the theoretical one. This means that the transferred charge is not only S^{2-} to S^0 but also part of S^0 to sulfate group that is called as biological electric quantity (BEQ). The biological electric quantity is defined as the difference between the measured value and the theoretical one. The ratio of biological electric quantity to the measured value can be used to predict the progress of BEGSL process. Figure 3 gives the relationships between the measured electric quantity and reaction time in 12 h for EGSL and BEGSL processes.

As observed from Fig. 3, the measured electric quantity in EGSL and BEGSL processes is linear with respect to time respectively.

It is shown from the slopes of the straight lines that *A. ferrooxidans* accelerating the oxidative reaction result in the increase of the measured electric quantity. Nevertheless, the advantages in BEGSL are unremarkable in 12 h. Table 4 shows the relationship between time and such factors as the dissolved ratio of Zn^{2+} and Fe^{2+}, TEQ and MEQ in EGSL after 12 h.

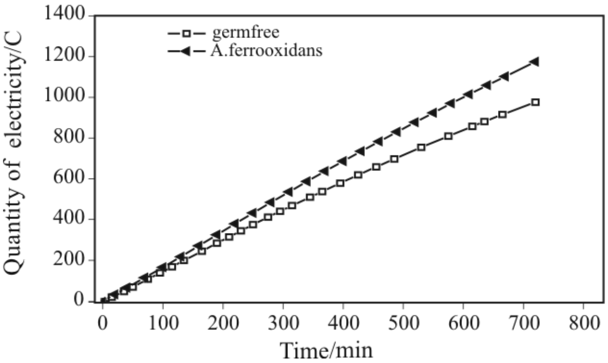

Fig. 3 The relationships between the measured electric quantity and time in 12 h for EL and BEGSL

Table 4 Relationship between time and such factors as dissolved Zn^{2+}, Fe^{2+}, TEQ and MEQ in EGSL after 12 h

Time/h	Zn^{2+}/%	Fe^{2+}/%	TEQ/C	MEQ/C
12	22.21	32.56	975.96	976.35
24	32.54	49.54	1445.73	1451.55
36	39.02	58.02	1722.03	1667.55

Table 5 Relationship between time and such factors as dissolved Zn^{2+}, Fe^{2+}, TEQ, MEQ and ratio of BEQ in BEGSL after 12 h

Time/h	Zn^{2+}/%	Fe^{2+}/%	BEQ/C	Ratio of BEQ/%
12	27.12	35.76	1158.58	1.36
24	39.58	48.13	1656.72	17.86
36	47.46	60.15	2007.16	30.93
48	52.69	69.73	2253.38	34.88
60	58.12	77.16	2487.99	33.88
72	62.13	84.17	2672.73	31.72

Table 5 gives the relationship between time and the dissolved ratio of Zn^{2+} and Fe^{2+}, BEQ and ratio of BEQ in BEGSL process.

It can be seen from Tables 4 and 5 that the amount of Zn^{2+}, Fe^{2+} and the output electric quantity in BEGSL are larger than that in EGSL. After 24 h in BEGSL, the ratio of BEQ is 17.86%, which shows that the bacterial oxidation on the surface of sphalerite has initiated. Subsequently, the increase in the ratio of BEQ with the increase in time is up to 31.72% for 72 h. The dissolved ratio of Zn^{2+} in the presence of *A. ferrooxidans* is nearly 60% higher than that in the absence of *A. ferrooxidans*; the electro-generative quantity in the former is about 134% more than that in the latter.

Conclusions

The electrogenerative simultaneous leaching of sphalerite and MnO_2 in the presence of *A. ferrooxidans* was studied in this paper. It could be concluded:

- The galvanic current for the sphalerite electrode in EGSL and BEGSL processes is predominates over its self-corrosion current.
- The leaching ratio and the electric quantity output in BEGSL system are larger than that in EGSL system, and the ratio of biological electric quantity is as high as 31.72% for 72 h BEGSL, the dissolved ratio of Zn^{2+} and the electro-generative quantity in the presence of *A. ferrooxidans* is nearly 60 and 134% more than that in the absence of *A. ferrooxidans*, respectively.
- Sphalerite is oxidized to ions and sulfur element both in EGSL and in BEGSL. But in BEGSL process, the sulfur element is further oxidized by oxygen in promotion of *A. ferrooxidans*.

Acknowledgements

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