

Mechanism of electro-generating leaching of chalcopyrite-MnO₂ in presence of *Acidithiobacillus thiooxidans*

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Abstract: A dual cell system with chalcopyrite anode and MnO₂ cathode was used to study the relations between time and such data as the electric quantity and the dissolution rates of the two minerals in the electro-generating leaching (EGL) and the bio-electro-generating leaching (B EGL), respectively. The results showed that the dissolution rates for Cu²⁺ and Fe²⁺ in BEGL were almost 2 times faster than those in EGL, and nearly 3 times for Mn²⁺; the electric output increased nearly by 3 times. The oxidation residue of chalcopyrite was represented by TEM and XRD, whose pattern was similar to that of the raw ore in EGL. The mechanism for leaching of CuFeS₂-MnO₂ in the presence of *Acidithiobacillus thiooxidans* was proposed as a successive reaction of two independent sub-processes for the anode. The first stage, common to both processes, is dissolution of chalcopyrite to produce Cu²⁺, Fe²⁺ and sulfur. The second stage is subsequent oxidization of sulfur only in BEGL, which is the controlling step of the process. However, the dissolution of MnO₂ lasts until the reaction of chalcopyrite stops or the ores exhaust in two types of leaching.

Key words: chalcopyrite; MnO₂; bio-oxidation; electro-generative leaching

1 Introduction

The electro-generating leaching (EGL) [1–3] has been applied to sulfides. In the process, substantively, the Gibbs free energy is transformed to an applicable electrical work [4] and the products are simultaneously leached. In order to complete EGL, a galvanic cell with anolyte and catholyte rooms separated by an anion membrane which allows anions to migrate freely is designed [3–6]. The compact sulfide powder and MnO₂ powder are used as the anode and cathode, respectively. The new technique not only can simplify the purification of the leached solution, but also can produce element sulfur instead of gaseous H₂S [7] and SO₂ [8] that pollute environment in the traditional leaching.

There are some reports on hydrometallurgical treatment of the chalcopyrite minerals [3, 9–14], including EGL of CuFeS₂-MnO₂ [3, 9]. XIAO et al [9] have pointed out that sulfur produced in EGL covers the surface of the leached sulfides, thwarting anodic reaction taking place

more and greatly reducing the electric energy output. The rates of corrosion of the two minerals in EGL were much higher than their self-corrosion rates [10–11]. It is also shown [12] that the sulfur film covered on the mineral surface passivated the anode. TAKAMI et al [15] presented that the elemental sulfur could be removed by the *Acidithiobacillus ferrooxidans* (*A. ferrooxidans*) in EGL of ZnS-MnO₂.

A. thiooxidans plays an important role in the biochemical treatment of sulfur [16–17]. The bacteria can obtain energy from oxidation of sulfur substrate [18–19] and make covered sulfur on the surface of minerals oxidized and removed. However, little work on leaching of chalcopyrite in the presence of *A. thiooxidans* is reported, especially the mechanism of bio-oxidization for the mineral is still indistinct.

In this study, the authors aim to explore the mechanism of BEGL for CuFeS₂ in the presence of *A. thiooxidans* by analysis of the relations between time and such data as the electric quantity and the dissolution rate of Cu²⁺, Fe²⁺, and Mn²⁺ in a galvanic cell with *A. thiooxi-*

dans, and by the evidence of SEM and XRD for oxidation remains of the mineral.

2 Experimental

2.1 Minerals

Chalcopyrite with 75 μm in size was naturally hand-sorted from a domestic mine. The XRD analysis shows that CuFeS_2 is predominant, and PbS and SiO_2 coexist. The results of element analysis are listed in Table 1. Manganese dioxide was commercial reagent (Shanghai Chemical Regents Industries, Ltd., China).

Table 1 Chemical composition of chalcopyrite (mass fraction, %)

Cu	Fe	S	Zn	Pb	SiO_2
29.06	25.96	30.46	1.72	8.95	4.46

2.2 Set and electrode for EGL

The cell frame placed in water bath was made of PVC, which was divided into anolyte and catholyte compartments, each of 200 mL, connected by an anion membrane, as shown in Fig.1. The membrane allowed anions to migrate freely[5–6], and blocked up cations.

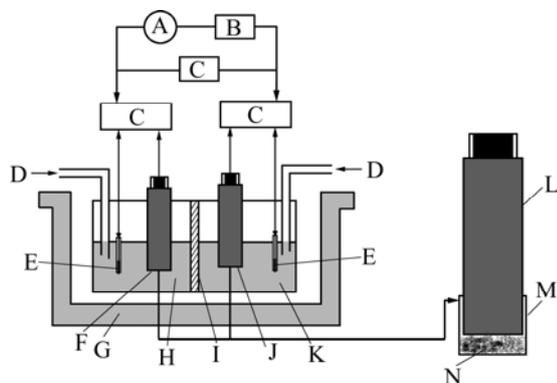


Fig.1 Schematic diagram of experimental apparatus: A—Amperemeter; B—Variable resistor; C—PHS-3C digital acidometer; D—Air-blowing tube; E—Saturated calomel electrode; F—Anode; G—Isothermal water bath; H—Anolyte; I—Anion membrane; J—Cathode; K—Catholyte; L—Carbon pole; M—Filtering cloth; N—Concentrate powder (chalcopyrite or MnO_2)

Two electrodes are made of the powders of chalcopyrite and MnO_2 , respectively. Air-blowing tubes were separately inserted into the anolyte and catholyte rooms to agitate and to supply oxygen for bacteria. The pH value, electrode potentials (vs SCE) and output voltage of the cell were measured with a PHS-3C digital acidometer, the output current with an amperemeter and the concentration of oxygen with a Degussa oxygen meter. All of the measured instruments were calibrated

before each run.

2.3 Solutions and bacteria

The solutions were prepared using AR reagents and distilled water. The bacteria culture medium consisted of $(\text{NH}_4)_2\text{SO}_4$ 3.0 g/L, KCl 0.1 g/L, K_2HPO_4 0.5 g/L, $\text{MgSO}_4 \cdot 7\text{H}_2\text{SO}_4$ 0.5 g/L and $\text{Ca}(\text{NO}_3)_2$ 0.01 g/L. For comparison, the medium was acidified first to pH 1.8 by H_2SO_4 as the anolyte of EGL, and the same nutrient medium with exponential growth phase bacteria was used as the anolyte of BEGL. Oxygen in the solution was 5.9 mg/L. A pure strain of *A. thiooxidans* that could breed on chalcopyrite was from Hubei Province of China.

3 Results and discussion

3.1 Relations between electric quantity, dissolved metal ion rate and time

Each run was started under open-circuit, and the measurement of electric output was under the closed-circuit with 8Ω load, which corresponds to the maximum power output[6]. The relation between the measured electric quantity (MEQ) and time is almost linear in EGL and BEGL, as shown in Fig.2. The fitting equations and correlation coefficient R are as follows:

$$Q(\text{EGL}) = 17.36 + 0.797t, R = 0.998$$

and

$$Q(\text{BEGL}) = 30.74 + 0.915t, R = 0.999$$

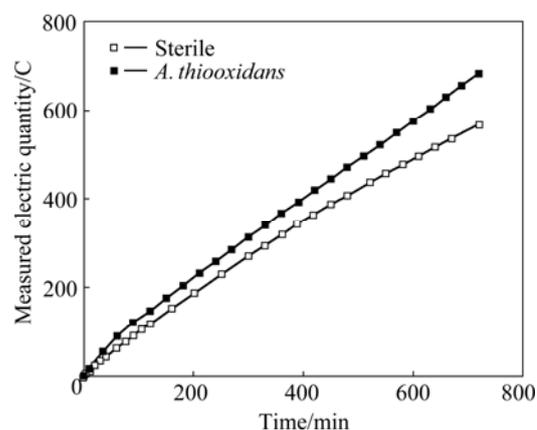


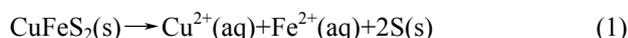
Fig.2 Relations between MEQ and time for 12 h in EGL and BEGL

From the slopes of straight lines it can be seen that *A. thiooxidans* accelerates the oxidation of ores, resulting in the increase of MEQ. But the advantage is unremarkable in 12 h.

As well known, 1 mol CuFeS_2 , theoretically, produces 1 mol Cu^{2+} , 1 mol Fe^{2+} and 2 mol S^0 in disorganization. Accordingly, it is reasonable to consider the total element sulfur $n(\text{S}^0)$ generated amounts to the

dissolved $n(\text{Cu}^{2+})$ and $n(\text{Fe}^{2+})$. Assume that the generated current is from S^{2-} to S^0 , which is taken as the theoretic electric quantity (TEQ) and can be calculated based on $n(\text{Cu}^{2+})$, $n(\text{Fe}^{2+})$ and Faraday's law. The MEQ can be obtained by measuring current and time. Both TEQ and MEQ in EGL should be equal. However, MEQ in BEGL for 96 h is about 1 572 C larger than that in TEQ. This means that the part of S^0 discharges to form the sulfate group, which is called as the biologic electric quantity (BEQ). The ratio of BEQ to MEQ (RBTM) can predict the progress of BEGL. Table 2 listed the dissolution rate of Cu^{2+} , Fe^{2+} and Mn^{2+} , TEQ and MEQ in both processes for 12 h, and RBTM in BEGL.

As observed from Table 2, very small difference between TEQ and MEQ in EGL indicates that the anodic dissolution of chalcopyrite accords with the theoretical analysis and the reaction is as follows:



It can also be seen from Table 2 that the dissolution rates for Cu^{2+} and Fe^{2+} in BEGL were almost 2 times faster than those in EGL, and nearly 3 times for Mn^{2+} ; the electric output increased nearly by 3 times. After 12 h of BEGL, RBTM was 8.13%, which shows that the sulfur oxidation on the surface of chalcopyrite had initiated. Subsequently, the increase in the ratio was up to 44.24% as time lasted for 96 h, indicating that the part of S^0 continuously discharged to form sulfate group.

The dissolved rate of Mn^{2+} was only 26.11% in EGL, whereas up to 81.06% in BEGL. Therefore, the dissolution of MnO_2 in this system depends on the behaviors of the chalcopyrite, and progresses all along until the reaction occurring on the ores stops.

3.2 XRD analysis

Fig.3 shows the XRD patterns of the untreated and

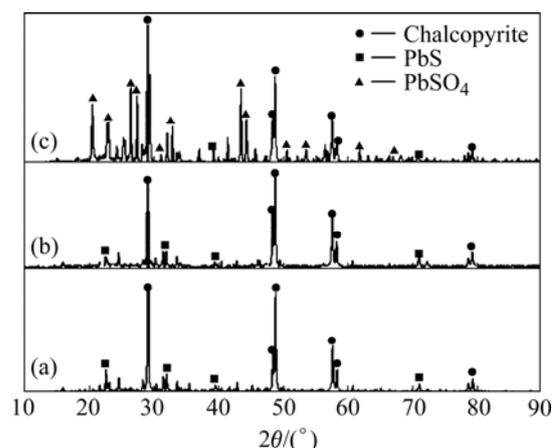


Fig.3 XRD patterns of chalcopyrite: (a) Before EGL; (b) After EGL; (c) After BEGL

treated chalcopyrite. It can be seen that the phases before and after EGL process are similar, and impurity PbS exists in the residue. However, PbS in BEGL was oxidized to insoluble PbSO_4 , covering the surface of the unreacted ores. The XRD pattern of the leach residue still has the peak of chalcopyrite. Accordingly, the chalcopyrite in BEGL should contain less insoluble impurity to make the dissolution rate of valuable metals increase much.

3.3 SEM images of oxidation debris of chalcopyrite

The SEM images of the oxidation debris in EGL and BEGL are shown in Fig.4, where it can be seen that a large quantity of sulfur floccules on the surface of the ores after EGL and the clear surface of the ores after BEGL. The results of the element analysis by atomic-absorption spectro-photometry (AAS) are listed in Table 3, where it can also be seen that, compared with EGL, the decrease of the element S and the increase of Cu and

Table 2 Dissolved rate of valuable metals, TEQ and MEQ in both processes for 12 h, and RBTM in BEGL

Process	Time/h	Dissolution rate/%			TEQ/C	MEQ/C	RBTM/%
		Cu^{2+}	Fe^{2+}	Mn^{2+}			
EGL	12	17.01	16.53	13.62	593.76	597.3	—
	24	27.82	25.93	22.47	951.48	986.1	—
	36	32.61	31.18	26.11	1129.18	1145.3	—
BEGL	12	18.08	17.32	15.55	626.43	681.9	8.13
	24	27.36	24.96	27.85	925.25	1221.7	24.27
	36	32.46	29.76	39.67	1 101.27	1740.1	36.71
	48	37.82	35.19	49.53	1 292.42	2172.3	40.50
	60	42.43	39.86	57.92	1 456.85	2539.5	42.63
	72	47.94	44.57	64.79	1 637.62	2841.9	42.38
	84	53.07	49.06	73.69	1 807.9	3230.7	44.04
96	57.64	54.32	81.06	1 982.11	3554.7	44.24	

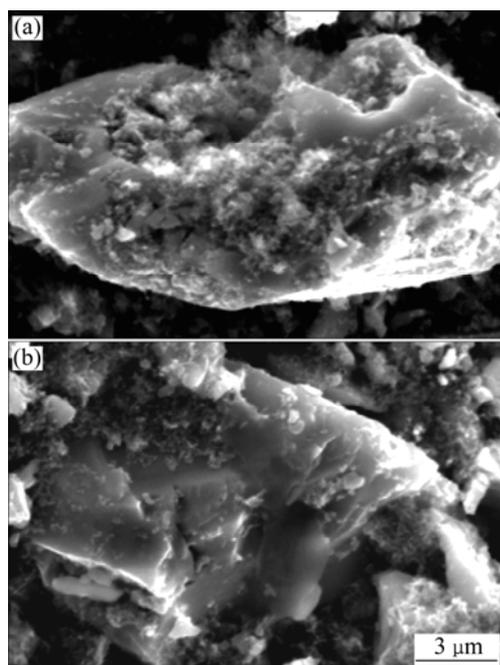


Fig.4 SEM images of oxidation debris of chalcopyrite: (a) After EGL; (b) After BEGL

Table 3 EDS results of chalcopyrite before and after leaching (mole fraction, %)

Element	Untreated	After EGL	After BEGL
Cu	32.490 7	20.553 2	27.535 5
Fe	34.044 1	22.575 3	24.681 7
S	33.465 2	56.871 5	47.782 7
Pb	0.783 4	0.645 2	1.127 3

Fe take place after BEGL, indicating that the produced sulfur is partly oxidized in the process.

3.4 Mechanism of electro-generating for chalcopyrite in presence of *A. thiooxidans*

The behaviors of the chalcopyrite in BEGL in 12 h are similar to those in EGL regarding dissolution rates of Cu^{2+} , Fe^{2+} and S[5], but RBTM for the former is smaller. The XRD patterns and SEM images of the residue for long-time leaching indicate that sulfur is partly oxidized in the presence of *A. thiooxidans*. Accordingly, the reaction mechanism in BEGL could be proposed as a successive reaction of two independent sub-processes. First chalcopyrite dissolves and produces Cu^{2+} , Fe^{2+} and the elemental sulfur as shown by reaction (1), and second the elemental sulfur is subsequently oxidized to the sulfate group by oxygen via the promotion of *A. ferrooxidans* according to reaction (2):



The rate of reaction (1) is faster than that of reaction (2) in BEGL by comparison of RBTM. In the first 12 h

in BEGL, the ratio is only 8.13%, showing that most of the discharge is based on reaction (1). As the ratio was up to 44.24%, the sulfur was still not completely oxidized, and became another resistance except insoluble PbSO_4 . The second stage appears to be the controlling step of BEGL because the oxidation by the promotion of bacteria is generally slow.

4 Conclusions

A dual cell system with chalcopyrite anode and MnO_2 cathode was used to study the electric quantity and the dissolution rate of the two minerals in EGL and BEGL. The results showed that the dissolution rates for Cu^{2+} and Fe^{2+} in BEGL were almost 2 times faster than those in EGL, and nearly 3 times for Mn^{2+} ; the electric output increased nearly by 3 times, and the ratio of BEQ to MEQ is as high as 44.24% in the presence of *A. thiooxidans* for 96 h. The oxidation residue of the chalcopyrite was represented by TEM and XRD, whose patterns are similar to those of the raw ore in EGL, and a large quantity of sulfur floccules deposited on the surface of the ores. The mechanism for leaching of $\text{CuFeS}_2\text{-MnO}_2$ in the presence of the bacteria is proposed as a successive reaction of two independent sub-processes for the anode. The first stage, common to both processes, is the dissolution of chalcopyrite on the surface to produce Cu^{2+} , Fe^{2+} and sulfur. The second stage is the subsequent oxidation of sulfur in BEGL, which is the controlling step of the process. However, the dissolution of MnO_2 lasts until the dissolution reaction of the chalcopyrite stops or the ores exhaust.

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