

DYNAMICS IN SIMULTANEOUS BIO-ELECTRO-GENERATIVE LEACHING FOR PYRITE-MnO₂*

L. Xiao^{1,4}, Y. Q. Li^{1,4}, S. F. Wang², Z. Fang¹ and G. Z. Qiu^{3**}

¹College of Chemistry and Chemical Engineering, Central South University, Changsha, Hunan 410083, China

²College of Chemistry and Environmental Engineering, Changsha University of Science and Technology, Changsha, Hunan 410076 China

³School of Resources Processing and Bioengineering, Central South University, Changsha, Hunan 410083, China

⁴Hunan Industrial University, Zhuzhou, Hunan 412000, China

The principle for the electro-generative simultaneous leaching (EGSL) is applied to simultaneous leaching of pyrite-MnO₂ in this paper. A galvanic system for the bio-electro-generative simultaneous leaching (BEGSL) has been set up. The equation of electric quantity vs. time is used to study the effect of produced sulfur on electro-generative efficiency and quantity. It has been shown that the resistance decreased in the presence of *Acidithiobacillus thiooxidans* (*A. thiooxidans*) with the increase of electro-generative efficiency. The effects of temperature and grain size on rate of ferrous extraction from pyrite under the conditions of presence and absence of *A. thiooxidans* were studied, respectively. The changes in the extraction rate of Fe²⁺ as particle size in presence of *A. thiooxidans* were more evident than that in the absence, which indicated that the extraction in bio-electro-generative leaching was affected by particle size remarkably. Around the optimum culture temperature for *A. thiooxidans*, the bigger change in the conversion rate of Fe²⁺ was depending on temperature. The transferred charge in BEGSL including part of S⁰ to sulfate group in the presence of (*A. thiooxidans*) which is called as biologic electric quantity, and the ratio of biologic electric quantity reached to 58.10% in 72 h among the all-transferred charge.

Keywords: *A. thiooxidans*, electro-generative-leaching, pyrite

Introduction

Pyrite is a kind of resource of abundant sulfide mineral, frequently associated with other valuable sulfide, gold and coal. It is important to research into hydrometallurgical treatments of pyrite in coal processing, extractive metallurgy and acid mine drainage [1–8]. Besides, the Gibbs free energy could transform to an applicable electrical work and leaching products simultaneously are acquired [9, 10] when the mineral is disaggregated, for example, in the electro-generative simultaneous leaching (EGSL) and bio-electro-generative simultaneous leaching (BEGSL). The EGSL for sulfides, such as ZnS [10], PbS [11], CuFeS₂ [12] and FeS₂ [13] has been investigated. It is also shown by a leaching experiment for chalcopyrite [12] that the sulfur film forms on the mineral surface during anodic dissolution, presenting the passivity regions. Takami [14] proposed that the removal of elemental sulfur might improve the galvanic reaction rate, and dissolution rates were enhanced by the *Acidithiobacillus ferrooxidans* (*A. ferrooxidans*) in

the simultaneous leaching system of zinc sulfide and manganese dioxide.

Acidithiobacillus thiooxidans (*A. thiooxidans*) also plays an important role in the biochemical treatment of sulfur [14]. The bacteria can directly obtain energy from oxidation of the substrate of sulfur [15–17] and make the accumulated sulfur on surface of minerals be oxidized and removed. However, few works have been reported on dynamics for the leaching of pyrite in presence of *A. thiooxidans*, and the process of bio-oxidization for FeS₂ with this bacterium is still indistinct. This study is intended to obtain the electro-generative mechanism for FeS₂ anode in presence of *A. thiooxidans*.

In this work, a dual cell set with *A. thiooxidans* is used to investigate BEGSL. The BEGSL dynamics of FeS₂ in the presence of *A. thiooxidans* will be studied by the relationship between time and such data as galvanic electric quantity and dissolved rate of Fe²⁺, and Mn²⁺, as well as by the effect of grain size and temperature on the dissolved rate of pyrite.

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** Author for correspondence: xiaoli_csu@163.com

Experimental

Minerals

The selected pyrite was a natural hand-sorted ores from a domestic mine. The XRD analysis showed that FeS₂ was predominant in the ores, and four kinds of size fraction, 12.14, 27.31, 46.85 and 72.34 μm were selected. The element analysis was listed in Table 1. The manganese oxide was commercial reagents (Shanghai Chemical Regents Industries, Ltd.).

Set and electrodes for electro-generative leaching

The cell putting in water bath was made of PVC, which was divided into anolyte and catholyte compartments, each of 200 mL, connected by an anion membrane, showed in Fig. 1. The membrane allowed of anions migrating freely [5, 6], and blocked up Fe²⁺ from FeS₂ in anode room to enter into catholyte and act with MnO₂ directly.

The anode and cathode, showed in Fig. 1, made of powders of pyrite and MnO₂ respectively. Two air-blowing tubes were inserted into two compartments, respectively, 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 ampere meter and the concentration of oxygen with a Degussa oxygen meter. All of the measured instruments were calibrated before each run.

Table 1 Chemical composition of pyrite (mass fraction/%)

Composition/ mass%	Fe	S	Al ₂ O ₃	Pb	SiO ₂
	46.40	49.30	0.52	0.1	0.98

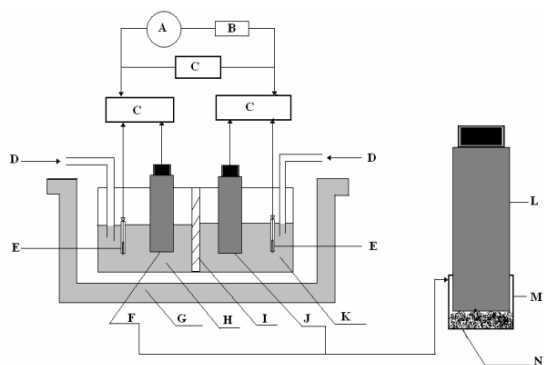


Fig. 1 Schematic diagram of experimental apparatus; A – ampere meter, B – variable resistor, C – PHS-3C digital acidometer, D – air blowing tube, E – saturated calomel electrode, F – anode, G – isothermal water bath, H – anolyte, I – anion membrane, J – cathode, K – catholyte, L – carbon pole, M – filtering cloth, N – concentrate powder (pyrite or MnO₂)

Solutions and bacteria

The solutions were prepared using AR reagents (Hunan Normal University Chemical Regents Industries, Ltd.) and distilled water. The bacteria culture medium consisted of S 10 g L⁻¹, (NH₄)₂SO₄ 3.0 g L⁻¹, KCl 0.1 g L⁻¹, K₂HPO₄ 0.5 g L⁻¹, MgSO₄·7H₂O 0.5 g L⁻¹ and Ca(NO₃)₂ 0.01 g L⁻¹. To compare BEGSL with EGSL, the medium without sulfur was acidified first to pH 1.8 by H₂SO₄ as anolyte of EGSL, and the same nutrient medium with exponential growth phase bacteria was used as anolyte of BEGSL. Oxygen concentration in the solution was 5.9 mg L⁻¹.

The bacterial culture from Hubei Province of China was a pure strain of *A. thiooxidans* that was suitable to growth on chalcopyrite ores.

Results and discussion

Relationship between measured electric quantity and time for EGSL and BEGSL

Each run was first set up under the open-circuit, then the measure of time and electric quantity output was under the circuit-closed conditions of the constant exterior resistance 8 Ω corresponding to the maximum powder was selected for the next electro-generative experiments to ensure the maximum power of the galvanic cell.

As observed from Fig. 2, the measured electric quantity *vs.* time in EGSL and BEGSL processes is polynomial fitted respectively, and the equations $Q = \int Idt = at + bt + ct^2$ are given as follows:

$$Q(\text{EGSL}) = 25.9027 + 1.41899t - 3.95808 \cdot 10^{-4}t^2$$

$$R = 0.99335$$

and

$$Q(\text{BEGSL}) = 4.86551 + 1.44136t - 1.62637 \cdot 10^{-4}t^2$$

$$R = 0.99973$$

where $dQ/dt = k = b + 2ct$, when $t \approx 0$, $k = b$, which is the amplitude of the increase of electric quantity with the

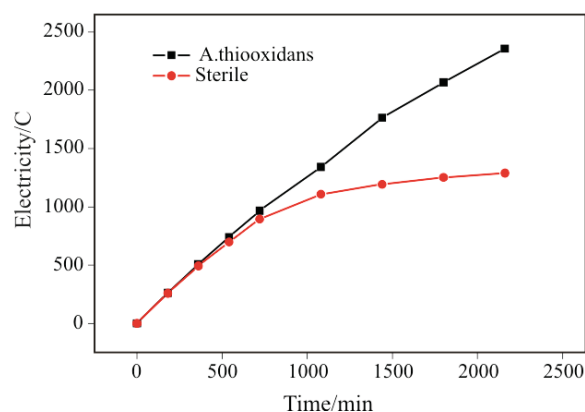


Fig. 2 Relationships between the measured electric quantity and time in 36 h for EGSL and BEGSL

increase of time, represents the electro-generative efficiency. The $d^2Q/dt^2=2c$, which is the degree of curve deviating straight line due to intermediate product sulfur thwarting electro-generation, is used to analysis the effect of bacteria on ores. From Fig. 2 that *A. thiooxidans* accelerate the oxidative reaction resulting in the increase of the fitted factors *b* and *c*. This means the electro-generative efficiency is higher and the degree of curve deviating straight line is smaller in BEGSL than those in EGSL.

Effect of grain size on ferrous extraction

The ores with four various grain sizes were used to study the effect of grain size on ferrous extraction. The output voltage and current obviously decreased for the pyrite with four sizes in 12 h whether or not inoculate the bacteria in anolyte, and the falling rate of the current in the presence of *A. thiooxidans* was similar to that in the absence of the bacteria. Sample every 30 min to analyze the conversion ratio of Fe^{2+} in anolyte.

It can be seen from Figs 3 and 4 that the changes in the extraction ratio as particle size in presence of *A. thiooxidans* were more evident than that in the absence of the bacteria, which indicated that the effect of the particle size on the ferrous extraction in BEGSL was more remarkable. Furthermore, the effect of the bacteria on conversion of ferrous was larger than that without it under the same conditions of grain size of ores and temperature, which indicated that *A. thiooxidans* could promote the oxidization of part of sulfur produced in the electro-generative leaching.

Experimental results in Fig. 3 showed that in BEGSL, the maximum conversion of ferrous for 12 h, 28.19%, came from the ores with grain size of 27.31 μm , that is to say, the optimum particle size should be 27.31 μm when the bacteria was used in the

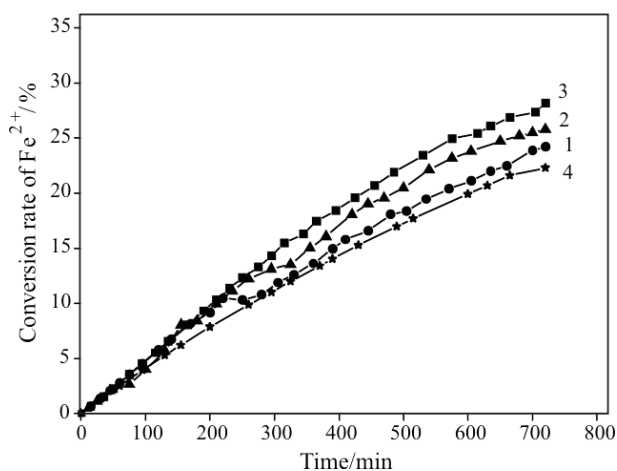


Fig. 3 Relationship between conversion ratio of Fe^{2+} and time with *A. thiooxidans*; 1 – 72.34; 2 – 46.85; 3 – 27.31; 4 – 12.14 μm

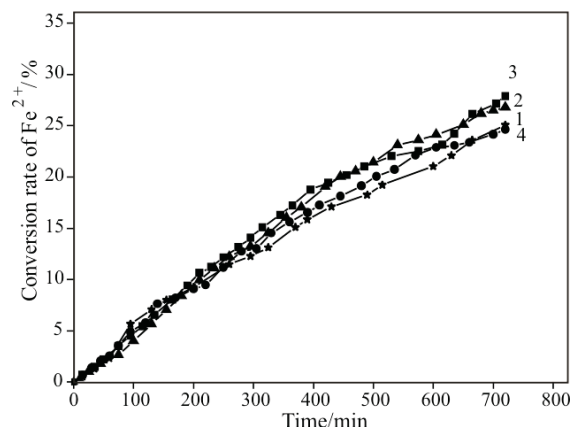


Fig. 4 Relationship between conversion ratio of Fe^{2+} and time without bacteria; 1 – 72.34; 2 – 46.85; 3 – 27.31; 4 – 12.14 μm

electro-generative leaching. The particle size favored the bacteria that oxidized sulfur on the ore surface. The increase of the extraction ratio with the decrease of the particle size ranged from 72.34 to 27.31 μm , indicating that the sulfur-containing product layer may be more oxidized in presence of *A. thiooxidans* in the small particle size range. However, when the particle size was 12.14 μm , the bacteria had little influence on the extraction.

Effect of temperature on ferrous extraction

As already mentioned, the five temperature points, 299, 301, 303, 305 and 307 K were favored of *A. thiooxidans*. The study has been made of the effect of temperature on extraction of ferrous in two systems, both BEGSL and EGSL, at these temperatures. The conversion of ferrous for 36 h in BEGSL and EGSL was measured.

The extraction ratio increased from 31.31 to 41.27% as the temperature changed from 299 to 307 K in BEGSL. The relatively big conversion ratio of ferrous and its dependence on temperature were in

Table 2 Ferrous extraction ratio for 36 h in BEGSL and EGSL

Temperature/K	<i>A. thiooxidans</i>	Ferrous extracted/%
299	inoculated	31.31
299	sterile	31.03
301	inoculated	34.39
301	sterile	34.18
303	inoculated	39.45
303	sterile	38.11
305	inoculated	40.12
305	sterile	38.46
307	inoculated	41.27
307	sterile	39.13

Table 3 The relationship of time, the dissolved ratio of ferrous and manganese ion, TEQ and MEQ in EGSL

Time/h	Dissolved ratio of Fe ²⁺ /%	Dissolved ratio of Mn ²⁺ /%	TEQ/C	MEQ/C
12	27.11	21.26	924.55	933.4
24	35.01	27.13	1142.01	1144.3
36	38.11	32.07	1225.72	1289.1

Table 4 the relationship of time, the dissolved ratio of ferrous and manganese ion, TEQ, MEQ, BEQ and ratio of BEQ in BEGSL

Time/h	Dissolved ratio of Fe ²⁺ /%	Dissolved ratio of Mn ²⁺ /%	MEQ/C	BEQ/C	Ratio of BEQ/%
12	28.19	23.68	965.4	63.88	6.62
24	35.17	39.65	1764.6	639.86	36.26
36	39.45	52.18	2358.6	1096.99	46.51
48	42.84	65.39	3039.0	1668.97	54.92
60	46.93	70.08	3514.2	2013.37	57.29
72	51.12	80.16	3902.0	2267.18	58.10

BEGSL. It would be explained by the fact that *A. thiooxidans* could promote the oxidation of sulfur. The experiments of EGSL showed that the extraction ratio of ferrous gradually increased with temperature, indicating that temperature has little effect on the dissociation of pyrite because no bacteria could oxidize sulfur formed at this case.

Electric quantity and leaching ratio in EGSL and BEGSL processes

Assume that the all-transferred charge is due to S₂²⁻ to S⁰ and is considered as the theoretic 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 theoretic one. This means that the transferred charge is not only S₂²⁻ to S⁰ but also part of S⁰ to sulfate group that is called as biologic electric quantity. The biologic electric quantity (BEQ) is defined as the difference between the measured and the theoretic one. The ratio of biologic electric quantity to the measured can be used to predict the progress of BEGSL process. But, the advantages in BEGSL are unremarkable in 12 h. The leaching time in both processes further lasted until the output current was below 5 mA. Table 3 shows the relationship between time and such indexes as the dissolved ratio of ferrous and manganese ion, TEQ and MEQ in EGSL after 12 h. Table 4 gives the BEQ, MEQ and ratio of biologic electric quantity (ratio of BEQ) to the measured one in BEGSL process.

Compared Table 3 with Table 4, it can be seen that the amount of ferrous and manganese ions and the output electric quantity in BEGSL are larger than that in EGSL. The dissolved Fe²⁺ in the presence of

A. thiooxidans is nearly 40% higher than that in the absence of *A. thiooxidans*; the electro-generative quantity in the former is about 200% more than that in the latter. After 12 h in BEGSL, the ratio is of BEQ 6.62%, which shows that the bacterial oxidation on the surface of pyrite has initiated. Subsequently, the increase in the ratio of BEQ with the increase in time is up to 58.10% for 72 h, which indicates that the transferred charge due to the bacteria is more than that of EGSL process.

Conclusions

- The electro-generative efficiency is higher in BEGSL than those in EGSL; the resistance of electro-generation decreases in BEGSL.
- The effect of the particle size on the ferrous extraction in BEGSL is more remarkable; the effect of the bacteria on conversion of ferrous was larger than that without it under the same conditions of grain size of ores and temperature.
- The extraction ratio of ferrous gradually increases with temperature in BEGSL, but temperature has little effect on the dissociation of pyrite in EGSL because no bacteria could oxidize sulfur formed at this case.
- The dissolved Fe²⁺ in the presence of *A. thiooxidans* is nearly 40% higher than that in the absence of *A. thiooxidans*; the electro-generative quantity in the former is about 200% more than that in the latter; the transferred charge due to the bacteria is more than that of EGSL process in the last stage of BEGSL.

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