

Electro-generative mechanism for simultaneous leaching of pyrite and MnO₂ in presence of *A. ferrooxidans*

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Abstract: A dual cell system was used to study the output power, output voltage, galvanic polarization of anode and cathode, and the relationship between the electric quantity (Q) and some factors, such as the dissolved Fe²⁺ magnitude, the time in the electro-generative simultaneous leaching with bacteria (BEGSL) and without bacteria (EGSL). A three-electrode system was adopted to study their individual self-corrosion current, which was smaller compared with the galvanic current. The results show that the output power and voltage in BEGSL are higher than those in EGSL. The accumulated sulfur on the surface of sulfides produced in BEGSL can be oxidized by *A. ferrooxidans*, and the ratio of biologic electric quantity reaches 51.50% in 72 h. The first stage both in EGSL and in BEGSL is the dissolution of pyrite on the surface to ferrous ion and sulfur element, which was oxidized by *A. ferrooxidans* in the further procedure.

Key words: pyrite; MnO₂; bio-oxidation; simultaneous leaching; electro-generation

1 Introduction

Many sulfides of metal such as galena, sphalerite, chalcopyrite, and pyrite, are semiconductors. When two kinds of such minerals contact each other in an electrolyte, a galvanic couple, where the mineral of lower rest potential as anode, and that of higher rest potential as cathode forms. Manganese dioxide is also a semiconductor with much higher rest potential than all sulfides mentioned above, so that a galvanic couple in which both the minerals would dissolve simultaneously can form, when it contacts with any of the sulfides.

The simultaneous leaching of metal oxides and sulfides, such as ZnS-MnO₂[1–2], CuFeS₂-MnO₂[3–5], and FeS₂-MnO₂[6–10] has been investigated. RATH et al[2] have examined the galvanic interaction between sphalerite and MnO₂ and observed that the rates of corrosion of the two minerals are much higher than their self-corrosion rates in the individual anodic and cathodic insides. Similarly, the galvanic current between CuFeS₂-MnO₂[5] and FeS₂-MnO₂[10] in dilute sulfuric

acid solutions has also been reported as high as about 2.40 and 1.7 mA/cm², respectively. But little work has been reported on simultaneous leaching with electro-generation. Therefore, the study has been done on the electro-generatively simultaneous leaching (EGSL) of MnO₂ and sulfide minerals[11–13].

It is well known that chemical energy releases as heat in the oxidation leaching of sulfide. If the process is carried out by electro-generation, the heat released can transform to useful electrical energy. XIAO et al[12] have pointed out that the surface of leached sulfides covered by the accumulated sulfur, thwarting the anodic reaction to continue and greatly reducing the output of electric energy in EGSL. It is also shown by a leaching experiment for chalcopyrite[5] that the sulfur film forms on the mineral surface during anodic dissolution, presenting the passivity regions. TAKAMI et al[14] have proposed that the removal of elemental sulfur may improve the galvanic reaction rate, and dissolution rates are enhanced by the *Acidithiobacillus ferrooxidans* (*A. ferrooxidans*) in the simultaneous leaching system of zinc sulfide and manganese dioxide.

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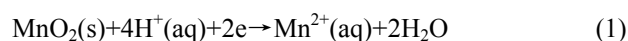
A dual cell set and *A. ferrooxidans* were used to the simultaneous leaching with electro-generation in this work, which was called as bio-electro-generative simultaneous leaching(BEGSL). The electro-generative mechanism of FeS₂-MnO₂ in the presence of *A. ferrooxidans* was studied, by the galvanic electric quantity and BEGSL was compared with the electro-generative simultaneous leaching(EGSL).

2 Experimental

2.1 Principle

In the simultaneous leaching of FeS₂-MnO₂ in dilute HCl, it has been confirmed that there are two corrosion couples, MnO₂/Fe²⁺ and FeS₂/Fe³⁺, which depend on each other[9]. The corrosion reactions of the couples are as follows:

To MnO₂/Fe²⁺,
Cathode:



Anode:



To FeS₂/Fe³⁺,
Cathode:



Anode:



and/or



2.2 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 the size was (17.8±5.3) μm. The element analysis is listed in Table 1. The manganese oxide was commercial reagents (Shanghai Chemical Regents Industries, Ltd.).

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

Fe	S	Al ₂ O ₃	Pb	SiO ₂
46.40	49.30	0.52	0.1	0.98

2.3 Set and electrodes for electro-generative leaching

The set used was an electrolysis cell made of PVC in water bath, which was divided into two compartments, anolyte and catholyte, each of 200 mL, connected by anion membrane, across which anions migrated freely, and the ferrous ions dissolved from FeS₂ in anode room

did not act MnO₂ directly in cathode room. The dissolution was electrochemical in nature and followed the principles of corrosion, i.e. reactions (4) or (5) for anode and reaction (1) for cathode.

The anode and cathode were made of the powders of pyrite and MnO₂, respectively. Two air-blowing tubes were inserted into anolyte and catholyte, respectively, to supply the oxygen for bacteria and to agitate. The pH value, the electrode potentials (vs SCE) and the output voltage of the leaching cell were measured with a PHS-3C digital acidimeter, 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.

2.4 Solutions and bacteria

The bacteria culture medium consisted of (NH₄)₂SO₄ 3.0 g/L, KCl 0.1 g/L, K₂HPO₄ 0.5 g/L, MgSO₄·7H₂O 0.5 g/L and Ca(NO₃)₂ 0.01 g/L. To compare BEGSL with EGSL, the medium was acidified first to pH 1.8 by H₂SO₄, and then taken as anolyte of EGSL, and the same nutrient medium with exponential growth phase bacteria was used as anolyte of BEGSL.

The bacterial culture used was a pure strain Yunnan 3 (PQ321745) of *A. ferrooxidans* that was suitable for growth on pyrite ores and was obtained from Yunnan Province of China.

The solutions used for the present experiments were prepared using AR reagents and distilled water. Oxygen concentration in the solution was measured to be 5.9 mg/L.

2.5 Self-corrosion measurements

A three-electrode system with a working electrode of MnO₂ or pyrite-graphite paste, a platinum counter and a saturated calomel(SCE) reference was used for self-corrosion measurements. Polarization was measured with the scanning rate of 0.1 mV/s by the CHI660B electrochemical workstation with a computer. All potentials presented in this work were against SCE.

3 Results and discussion

3.1 Galvanic current-power-potential

The galvanic current, power, and potential in BEGSL and EGSL were measured under the condition of the various exterior loads. Each run was first set up under the open-circuit, then the voltage and current outputs were measured under the circuit-closed conditions of changing the exterior resistance from 1 000 to 0 Ω. When the exterior load approached zero, the current was maximum and the galvanic potential was minimum due to the interior resistance of solution, ion membrane and

electrode.

The results are shown in Fig.1, which indicates that the useful power and galvanic potential in the presence of *A. ferrooxidans* are higher than those in the absence of the bacteria. The load of 8 Ω corresponding to the maximum powder was selected for the next electro-generative experiments to ensure the maximum power of the galvanic cell.

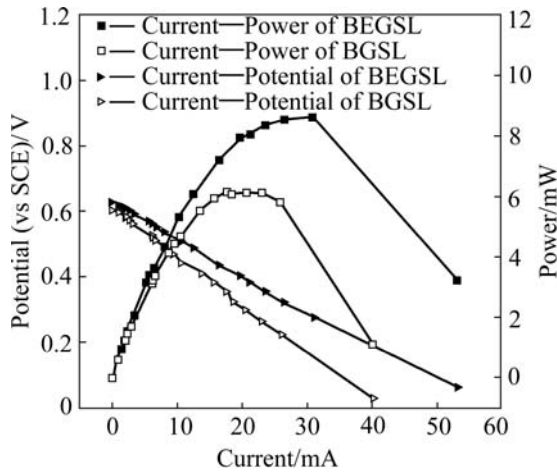


Fig.1 Output current—power—potential of EGSL and BEGSL for pyrite-MnO₂

3.2 Anodic and cathodic polarizability in EGSL and BEGSL

The Evans diagram, anodic and cathodic polarization, and interior resistance of the cell were used to study the control factor in EGSL and BEGSL processes. Generally, the bigger the value of resistance, the greater the effect on the leaching reaction.

As shown from Fig.2, the currents increase with the over-potential of cathode Δε_c and the over-potentials anode Δε_a. We define polarization as

$$P = \frac{d\varepsilon}{dI} = \frac{\Delta\varepsilon}{I} \tag{6}$$

where Δε is the over-potentials, and I is the galvanic

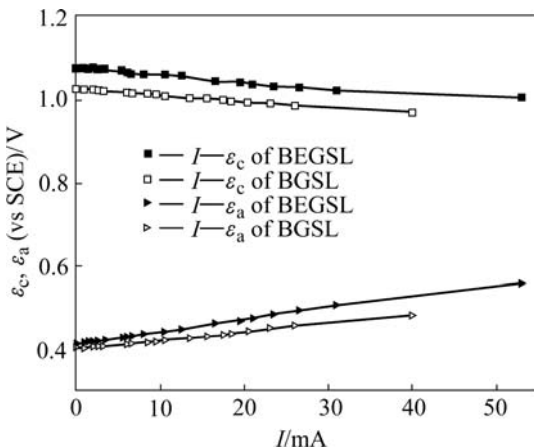


Fig.2 Evans diagram of EGSL and BEGSL for pyrite-MnO₂

current.

The polarizations of anode and cathode are P_a and P_c:

$$P_a = \frac{\Delta\varepsilon_a}{I}; \quad P_c = \frac{\Delta\varepsilon_c}{I} \tag{7}$$

$$\varepsilon_c - \varepsilon_a = \Delta\varepsilon_c + \Delta\varepsilon_a + IR = IP_c + IP_a + IR \tag{8}$$

$$I = \frac{\varepsilon_c - \varepsilon_a}{P_c + P_a + R} \tag{9}$$

where R is the interior resistance and P_a, P_c, R and I are listed in Table 2. The over-potentials of anode and cathode increase with the decrease of galvanic voltage for 36 h in SLEG and BEGSL processes.

Table 2 P_c, P_a, R and J of EGSL and BEGSL for pyrite-MnO₂

Process	Stage	P _c /Ω	P _a /Ω	R/Ω	J/(mA·cm ⁻²)
BEGSL	Initial	1.68	2.97	7.81	6.42
	12 h	6.05	10.93	5.58	4.45
	24 h	11.8	11.94	4.41	3.73
	36 h	11.87	11.96	4.13	3.31
EGSL	Initial	1.46	2.04	11.96	5.38
	12 h	11.07	16.25	4.97	2.48
	24 h	13.28	27.86	4.46	1.45
	36 h	15.25	45.14	4.61	0.83

It can be seen from Table 2 that the interior resistance R is larger than P_a and P_c when the leaching is initiated, and follows by drop to a steady value. Perhaps, the reason is that the interface resistance between electrolyte and pyrite decreases as the reaction comes to steady state.

Another important feature of polarization reflects to the data of different stages (see the columns 3, and 4 in Table 2). P_a and P_c are smaller at first due to the electric catalytic activity of acetylene black [15–16]. Compared with EGSL, the polarization P_a comes to a steady-value about 10–11 Ω with the decrease of the galvanic current in BEGSL process as the reactions are continued. This could be attributed to the fact that elemental sulfur accumulated in the anodic electrode stops reaction in EGSL, while be oxidized by *A. ferrooxidans* in BEGSL. The increase of polarization P_c in both processes might be the reason for the decrease in acidity of the solution.

3.3 Self-corrosion for pyrite and MnO₂ electrodes

In addition to the galvanic current in EGSL and BEGSL, there also exists the self-corrosion in two electrodes, respectively. Comparison of the galvanic current flow with the self-corrosion current could estimate which one is predominant. A convenient way to determine the self-corrosion is to plot Tafel curves of the individual half-cells. The Tafel curves of pyrite anode

with or without *A. ferrooxidans* and MnO_2 cathode in 1 mol/L H_2SO_4 are shown in Fig.3. E_{corr} , J_{corr} , and R_p obtained from the Tafel curves are listed in Table 3.

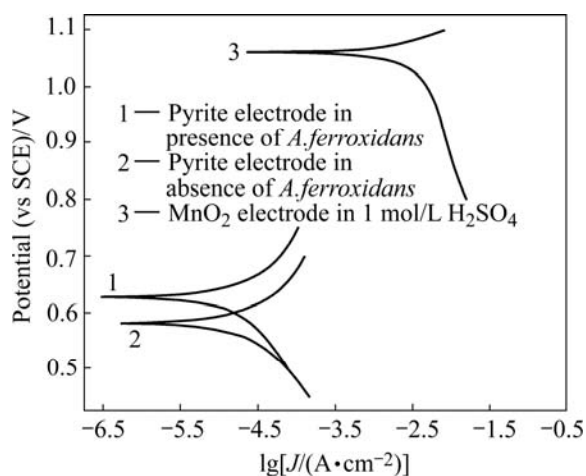


Fig.3 Tafel curves

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

System	E_{corr} (vs SCE)/V	J_{corr} /(mA·cm ⁻²)	R_p/Ω
Pyrite without bacteria	0.627	0.004 9	1840
Pyrite with bacteria	0.553	0.087 0	92
MnO_2	1.062	1.120 0	17

For pyrite, the self-corrosion current J_{corr} as seen from Table 3 is negligible compared the galvanic current I shown in Table 2, and for MnO_2 , the self-corrosion current almost same magnitude as the galvanic current. Accordingly, the galvanic interaction for pyrite predominates over their individual self-corrosion whether in EGSL or BEGSL processes.

3.4 Electric quantity and leaching ratio in EGSL and BEGSL processes

Assuming that the all-transferred charge is due to S_2^{2-} to S^0 and is considered 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 S_2^{2-} to S^0 but also part of S^0 to sulfate group that is called as biologic electric quantity (BEQ). BEQ is defined as the difference between the measured and the theoretic one. The ratio of BEQ to the MEQ can be used to predict the progress of BEGSL process. Fig.4 shows the relationships between the MEQ and reaction time for 12 h in EGSL and BEGSL processes.

It can be seen from Fig.4, the MEQ in EGSL and BEGSL processes is linear with respect to time respectively, and the equations are given as follows:

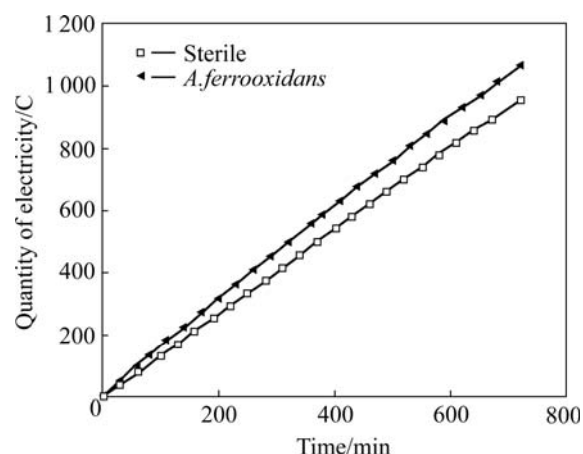


Fig.4 Relationship between measured electric quantity and time in 12 h for EGSL and BEGSL

$$Q(\text{EGSL})=0.966\ 51+1.333\ 36\ t, R=0.999\ 93 \quad (10)$$

and

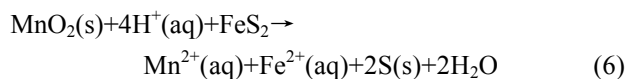
$$Q(\text{BEGSL})=17.760\ 77+1.478\ 49\ t, R=0.999\ 65 \quad (11)$$

From the slopes of the straight lines it can be seen that *A. ferrooxidans* accelerate the oxidative reaction resulting in the increase of the MEQ. 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 4 shows the relationship between time and such indexes as the dissolved ferrous and manganese ion ratio, TEQ and MEQ in EGSL after 12 h. Table 5 lists the BEQ and rate of BEQ to the measured one in BEGSL process.

Table 4 Relationship between time and such indexes as dissolved ferrous and manganese ion rate, TEQ and MEQ in EGSL after 12 h

Time/h	Dissolving rate of $\text{Fe}^{2+}/\%$	Dissolving rate of $\text{Mn}^{2+}/\%$	TEQ /C	MEQ /C
12	28.91	21.26	924.55	933.4
24	35.71	27.13	1 142.01	1 144.3
36	40.11	32.07	1 282.72	1 289.9

As observed from Table 4, the difference between TEQ and MEQ is very small, indicating that the proceed reaction in EGSL accords with reaction (4). The overall reaction in EGSL is as follows:



Comparing Table 4 with Table 5, it can be seen that the amount of ferrous and manganese ions and the output

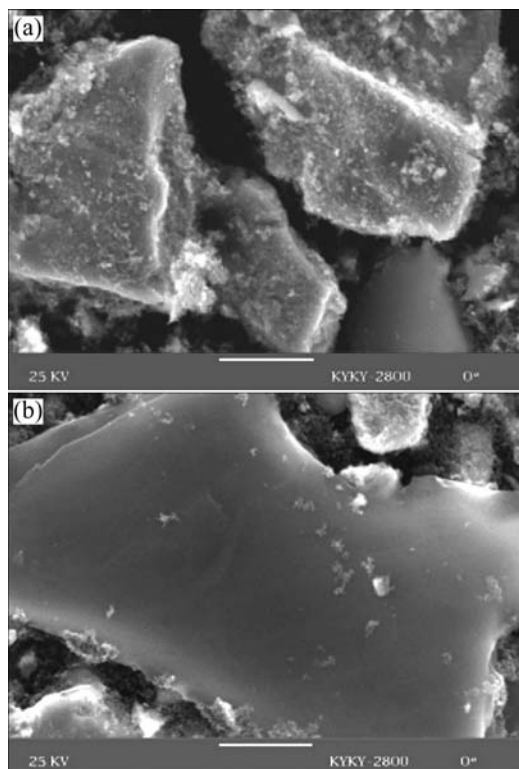
Table 5 Relationship between time and such indexes as dissolved ferrous and manganese ion rate, BEQ and rate of BEQ in BEGSL after 12 h

Time/h	Dissolving rate of Fe ²⁺ /%	Dissolving rate of Mn ²⁺ /%	BEQ/C	Rate of BEQ/%
12	28.07	23.68	166.12	18.51
24	35.76	39.65	587.09	33.92
36	39.48	52.18	1 026.13	44.83
48	44.05	65.39	1 459.58	50.89
60	49.41	70.08	1 468.16	48.16
72	52.13	80.16	1 769.98	51.50

electric quantity in BEGSL is larger than that in EGSL. After 12 h in BEGSL, the ratio is 18.51%, which shows that the bacterial oxidation on the surface of pyrite has initiated. Subsequently, the increase in the ratio of BEQ with the increase of time, is up to 51.50% for 72 h, which indicates that the transferred charge due to the bacterial oxidation is more than that of EGSL process.

3.5 Mechanism of electro-generation for pyrite in presence of *A. ferrooxidans*

Fig.5 shows the SEM images of the oxidation debris after 24 h in BEGSL and EGSL to study the changes occurring on the surface of pyrite.

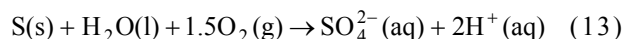
**Fig.5** SEM images of oxidation debris for pyrite: (a) EGSL; (b) BEGSL

It can be seen from Fig.5 that there is an obvious difference of the oxidation debris of pyrite in EGSL and BEGSL. For the EGSL, a large quantity of floccules accumulate on the surface of the ores, while for BEGSL with few floccules. The mole fraction of Fe and S atoms measured by AAS is listed in Table 6. The increase of element S and the decrease of Fe compared with that before leaching, and the quantity of element S in the sample of EGSL for 24 h is larger than that in BEGSL, which indicates that the produced sulfur is oxidized by *A. ferrooxidans* in BEGSL process.

Table 6 Mole fraction of main element for pyrite before and after leaching

Leaching condition	x(Fe)/%	x(S)/%
Before leaching	34.984 4	64.989 2
EGL	30.187 9	69.453 6
B EGL	32.165 8	67.321 9

The data of SEM leached residues indicate that the reaction mechanism in BEGSL could be supposed as a successive reaction of two independent sub-processes. First is that the pyrite dissolves and produces the ferrous ion and elemental sulfur as shown in reaction (4), and second is that elemental sulfur is consecutively oxidized by *A. ferrooxidans* to sulfate group according to the following reaction:



As mentioned above, the rate of BEQ in the second stage is low, and the sulfur accumulates on anode in BEGSL, which appears to be the controlling step in BEGSL process.

4 Conclusions

1) The electric power and galvanic potential in the presence of *A. ferrooxidans* are higher than those in the absence of the bacteria.

2) The galvanic current for the pyrite electrode in EGSL and BEGSL processes predominates over its self-corrosion process.

3) The leaching rate and the electric quantity output in BEGSL are larger than those in EGSL, and the rate of BEQ is as high as 51.50% for 72 h BEGSL, which indicates that the charge transferred by the bacterial oxidation is more than that of pure EGSL process.

4) The mechanism in BEGSL process is determined by two independent sub-processes: pyrite is oxidized to sulfur in the initial stage of oxidation, elemental sulfur is

oxidized to sulfate group by *A. ferrooxidans* in the following step, and the latter one is the controlling step.

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