

# Galvanic interaction between galena and pyrite in an open system \*

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**Abstract** Galvanic interactions between sulfide minerals have very important influences on hydrometallurgical processes, the supergene enrichment of sulfides and the formation of acid mine drainage. By changing the concentrations of  $\text{Fe}^{3+}$ , the pH values, status of the flowing of the solution and the solution salinity (e. g. the concentrations of  $\text{Na}_2\text{SO}_4$ ) and monitoring the galvanic currents and potentials, studies were conducted in this work on the galvanic interaction between pyrite acting as the anode and galena acting as the cathode. The results indicated that the concentrations of  $\text{Fe}^{3+}$ , pH values and the flowing of the solution exhibit a great effect on the galvanic interaction of galena-pyrite couple, while the salinity of the solution has only a slight influence on the interaction. The experiments also revealed that in case cracks exist on the surface of pyrite electrode, the potential of pyrite will decrease so sharply as to be lower than that of galena under the same experimental condition. The experimental results were explained in terms of the Butler-Volume equation and the theory of mixed potential.

**Key words** pyrite; galena; galvanic interaction; acid mine drainage; flowing medium

## 1 Introduction

Most sulfide minerals in nature have perfect conductivity and possess semiconducting properties. Galvanic corrosion may occur when two sulfide minerals with different potentials are connected together in the solution. The mineral with the higher potential acts as a cathode, where the reduction reaction occurs and the mineral is galvanically protected, whereas the mineral with the lower potential becomes an anode, where the oxidation reaction takes place and the dissolution of the mineral is intensified.

Galvanic interactions usually occur in many mineral-processing systems, especially in floatation (da Silva et al., 2003) and leaching (Madhuchhanda et al., 2000), and the galvanic interaction may affect the efficiency of metallurgy. Sui et al. (1995) carried out dissolution experiments on the four independent minerals of pyrite, pyrrhotite, galena and sphalerite, as well as on their galvanic couples, and found that metal ion production with minerals in pairs was different from that for single minerals, and the amount of metal ions in the solution followed a galvanic interaction model; oxidation of the anodic mineral was enhanced, leading to an increase in metal ions in the so-

lution compared to the mineral alone, while the cathodic mineral was protected from oxidation.

Many geological processes in nature are also related to galvanic interactions between sulfide minerals, such as the supergene enrichment of sulfide ore deposits (Thornber, 1975a, b; Sato, 1992) and the formation of acid mine drainage (Subrahmanyam and Forssberg, 1993). Sikka et al. (1991) studied the geochemistry of secondary copper minerals from the Malanjkhand porphyry copper deposit in India and found that the secondary alteration was mainly due to the galvanic interaction between pyrite and chalcopyrite. The lower potential primary chalcopyrite altered progressively to form minerals by depletion of Fe and S and enrichment of Cu. Li Heping (1995) described in detail the general characteristics and mechanisms of galvanic interactions which occur ubiquitously in the various spheres of the Earth, and experimentally studied the relationship between the electromotive force (EMF) of galvanic cells composed of sulfide minerals and the elastic stress on the mineral surface. Current mine pollution caused by acid mine drainage has attracted ever increasing attention, which is principally attributed to acids and heavy metals derived from the oxidation of sulfide minerals (Wang Jizhong et al., 2005), primarily the oxidation of pyrite (Lowson, 1982; Salomons, 1995; Banks et al., 1997; Naicker et al., 2003), while galvanic interactions between pyrite and other sulfide minerals will affect the generation process of acid mine drainage (Subrahmanyam and

Forsberg, 1993). Using cyclic voltammetry with carbon paste electrodes containing mineral particles (CPE-Mineral), Cruz et al. (2001) studied the influence of mineral impurities in pyrite on the overall reactivity of generating acid mine drainage. The results showed that when pyrite samples contained sphalerite, galena and other impurities, due to galvanic effects, the oxidation of pyrite would be protected until these impurities were consumed. Considering the influence of galvanic effects on the production of acid mine drainage, Shelp et al. (1995, 1996) proposed an *in-situ* electrochemical technology to ameliorate acid mine drainage problems. The study indicated that the proposed electrochemical approach of employing scrap iron as the sacrificial anode was a technically feasible and practical method of ameliorating acid mine drainage.

The pyrite-galena galvanic couple is one of the most common and most important galvanic cells both in the field of hydrometallurgy and in nature, which has been widely documented by many scholars. Holmes and Crundwell (1995) quantitatively studied the galvanic interaction between galena and pyrite using the rotating ring-disc electrodes and proposed a mathematical model to obtain a prediction of the magnitude of galvanic interaction. Making use of synthetic mixtures of galena and pyrite, Pecina-Treviño et al. (2003) investigated the effect of galvanic interaction of the mixtures on the floatation response of these two minerals. In the galvanic interactions discussed above, pyrite was always acted as the cathode and its oxidation process was protected. However, the authors found in their practice that in case there had cracks on the surface of pyrite electrode, the potential of pyrite would decrease so sharply as to be lower than that of galena under the same experimental condition. When galvanic interaction occurs between pyrite with cracks and galena, pyrite will act as the anode of the galvanic couple and the dissolution will be accelerated. In order to gain a better understanding of the kinetics of galvanic interaction between galena and pyrite, this work dealt with the influences of the concentrations of  $\text{Fe}^{3+}$  and  $\text{Na}_2\text{SO}_4$  and the solution pH values on the galvanic currents and potentials of the galvanic interaction between pyrite anode and galena cathode. In addition, a simulating experiment was made on the effects of the flowing of solution medium, just like the flowing of mine water, on the rate of galvanic interaction.

## 2 Samples and experimental methods

Experimental samples of single crystalline pyrite and polycrystalline galena were collected from the Huize Pb-Zn deposit in Yunnan Province, China. The

mineral electrodes were cut from massive mineral specimens to obtain cylindrical samples, 8 mm in diameter, and the working surface area was  $0.5 \text{ cm}^2$  for each mineral electrode. Then a copper wire was soldered onto one side of the cylinder. After that, the sample was mounted in a Teflon tube with the working surface exposed, and the central part of the tube was sealed with epoxy resin. These arrangements proofed the electrode against the effects of possible leaks, and only the working surface of the mineral electrode could contact with the solution. The electrodes were polished to mirror surface stage by stage, and it is observed that there were cracks on the pyrite electrode surface. Reflected light microscopy indicated that the polished mineral electrodes were pure pyrite and pure galena. The mean composition given by electron microprobe (EMP) analysis was: Fe 46.89 wt% and S 52.96 wt% for pyrite; and Pb 85.83 wt% and S 13.91 wt% for galena. Before each run, the electrode surface was repolished and washed repeatedly with acetone and distilled water.

Solutions were prepared from analytical grade reagents and doubly distilled water. The volume of the solution was 250 mL for each run (except for the experiments under flowing conditions). Sulfuric acid and sodium hydroxide solution were used to obtain the desired pH value of the solution.

In the experiments a HP-34401A Model high precision digital multimeter (input impedance  $> 10 \text{ G}\Omega$ ) was used to measure the galvanic potentials and currents. The multimeter was controlled by a computer to collect data one time per minute. The pyrite and galena mineral electrodes were electrically connected to each other through the multimeter to measure the galvanic current. The galvanic potential was measured against a calomel reference electrode (SCE) and the potentials quoted in this work are on SCE scale. The schematic diagram of experimental equipment under flowing condition is shown in Fig. 1. Throughout the experiments of measuring both potentials and currents, the galena electrode was connected with the positive input terminal of the multimeter. All experiments were carried out at  $25 \pm 1 \text{ }^\circ\text{C}$  with the solution exposed to the atmosphere.

## 3 Results

### 3.1 Electrode potential of pyrite with cracks

The variation of electrode potential with time for pyrite with cracks in  $0.01 \text{ mol/L Fe}_2(\text{SO}_4)_3$  solution is shown in Fig. 2. For comparison, the figure also presents the potential variations measured in this work of galena and pyrite with perfect surface. It is indicated

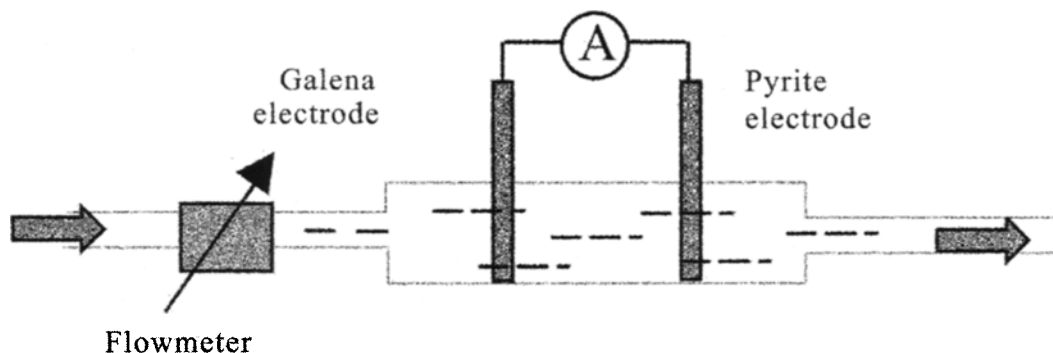


Fig. 1. Schematic diagram of the experimental equipment under flowing condition.

that when there have cracks on the surface of pyrite electrode, the electrode potential of pyrite will decrease, even so sharply as to be lower than that of galena electrode under the same condition. Therefore, when the pyrite with cracks couples with galena to form a galvanic cell, pyrite will no longer act as a cathode, instead it will become an anode and the dissolution is favoured. Meanwhile, galena will act as a cathode and the oxidization is protected. Li Heping et al. (1998) studied the potential variation of pyrite electrode in the saturated KCl solution with the applied elastic stresses. The results demonstrated that the application of elastic stresses on pyrite surface led to the storage of elastic energy within the lattice of pyrite and the free energy increased so that the potential of pyrite decreased according to the galvanic thermodynamics. In stress-induced corrosion of metallic materials it has also been found that the existence of cracks in metals will cause the localized stress to be concentrated on the point of

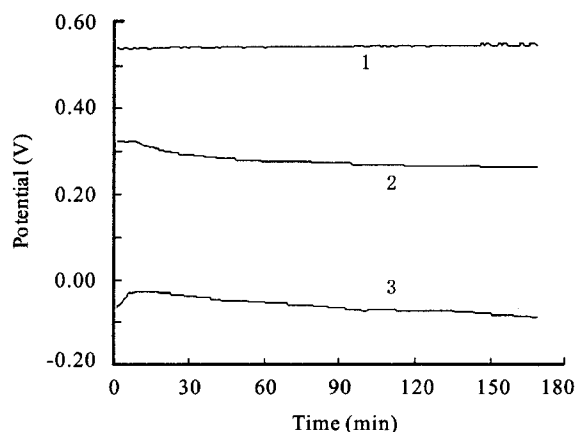


Fig. 2. Variations of potential with time for pyrite and galena in 0.01 mol/L  $\text{Fe}_2(\text{SO}_4)_3$  solution. 1. Pyrite with perfect surface; 2. galena; 3. pyrite with cracks.

cracks (Xiao Jimei and Cao Chunan, 2002). At this

location, the electrode potential is obviously reduced. Remarkable reduction of the potential of pyrite with cracks, as observed in this experiment, may be attributed to the same mechanism.

### 3.2 Effect of $\text{Fe}_2(\text{SO}_4)_3$ concentrations on galena-pyrite galvanic interaction

Figures 3 and 4 show the variations of current density and mixed potential with time for the galvanic interaction between pyrite and galena in 0.01 and 0.0001 mol/L  $\text{Fe}_2(\text{SO}_4)_3$  solutions at pH = 1.78. It can be seen from the figures that both the galvanic current density and galvanic potential in 0.01 mol/L  $\text{Fe}_2(\text{SO}_4)_3$  solution are larger than those in 0.0001 mol/L  $\text{Fe}_2(\text{SO}_4)_3$  solution. Figure 5 presents the variations of potential with time for galena, pyrite and galena-pyrite couple in 0.01 mol/L  $\text{Fe}_2(\text{SO}_4)_3$  solution. It is apparent that the potential of galena is maximal, while the potential of pyrite with cracks is minimal, with the mixed potential of galena-pyrite galvanic couple being intermediate. In addition, in case galena electrode existed in 0.01 mol/L  $\text{Fe}_2(\text{SO}_4)_3$  solution individually, it was not long before black coatings forming on the surface, whereas when galena coupled to pyrite with cracks, no coating was observed on galena surface.

### 3.3 Effect of solution pH on galena-pyrite galvanic interaction

The variations of galvanic current density and galvanic potential with time for galena-pyrite couple in 0.1 mol/L  $\text{Na}_2\text{SO}_4$  solutions at pH values of 1.82 and 6.63 are presented in Figs. 6 and 7, respectively. It is apparent that the galvanic current density in  $\text{Na}_2\text{SO}_4$  solution at pH = 6.63 is larger than that in  $\text{Na}_2\text{SO}_4$  solution at pH = 1.82, while the galvanic potential in

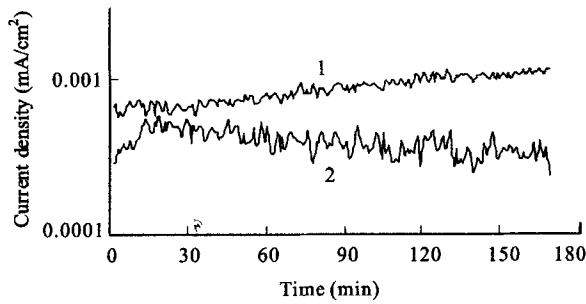


Fig. 3. Variations of galvanic current density with time for galena-pyrite couple in  $Fe_2(SO_4)_3$  solutions of different concentrations at  $pH = 1.78$ . 1. 0.01 mol/L; 2. 0.0001 mol/L.

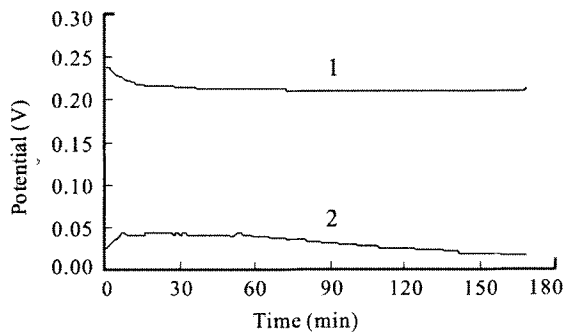


Fig. 4. Variations of galvanic potential with time for galena-pyrite couple in  $Fe_2(SO_4)_3$  solutions of different concentrations at  $pH = 1.78$ . 1. 0.01 mol/L; 2. 0.0001 mol/L.

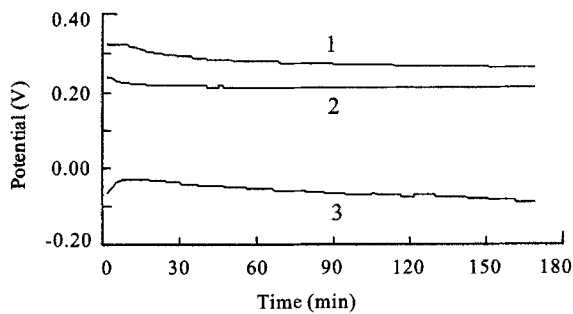


Fig. 5. Variations of potential with time for galena, pyrite and galena-pyrite galvanic couple in 0.01 mol/L  $Fe_2(SO_4)_3$  solution. 1. Galena; 2. galena-pyrite couple; 3. pyrite with cracks.

$Na_2SO_4$  solution at  $pH = 1.82$  is higher.

### 3.4 Effect of $Na_2SO_4$ concentrations on galena-pyrite galvanic interaction

Figures 8 and 9 present the variations of current

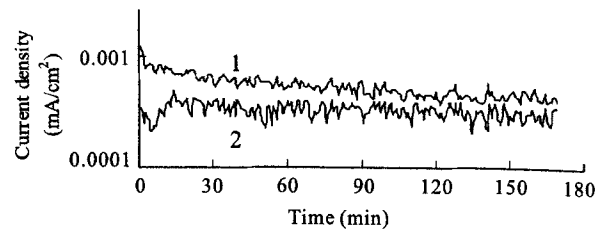


Fig. 6. Variations of galvanic current density with time for galena-pyrite couple in 0.1 mol/L  $Na_2SO_4$  solution at different  $pH$  values. 1.  $pH = 6.63$ ; 2.  $pH = 1.82$ .

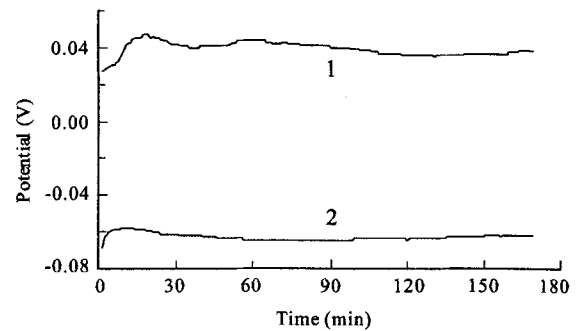


Fig. 7. Variations of galvanic potential with time for galena-pyrite couple in 0.1 mol/L  $Na_2SO_4$  solution at different  $pH$  values. 1.  $pH = 6.63$ ; 2.  $pH = 1.82$ .

density and mixed potential with time between pyrite and galena in 0.1 and 0.001 mol/L  $Na_2SO_4$  solutions. From the figures it can be seen that the galvanic current densities are generally close to each other and the galvanic potentials are slightly variable with increasing  $Na_2SO_4$  concentration.

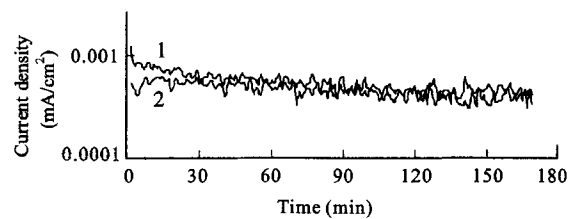


Fig. 8. Variations of galvanic current density with time for galena-pyrite couple in  $Na_2SO_4$  solutions of different concentrations. 1. 0.1 mol/L; 2. 0.001 mol/L.

### 3.5 Effect of solution flowing on galena-pyrite galvanic interaction

Figure 10 shows the variations of galvanic current density with time for galena-pyrite couple in 0.1 mol/L  $Na_2SO_4$  solution. It is indicated that the flowing of solution greatly enhanced the galvanic current density in comparison with that under the static condition.

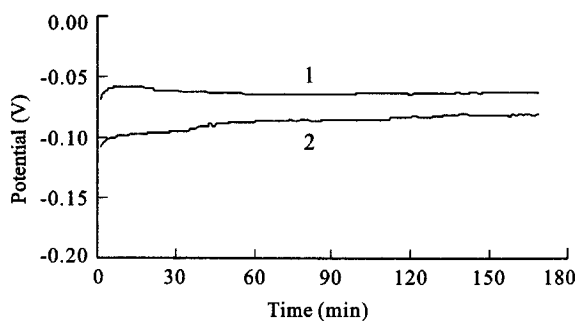


Fig. 9. Variations of galvanic potential with time for galena-pyrite couple in  $\text{Na}_2\text{SO}_4$  solutions of different concentrations. 1. 0.1 mol/L; 2. 0.001 mol/L.

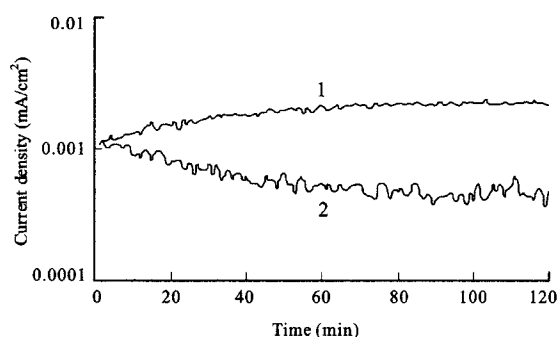


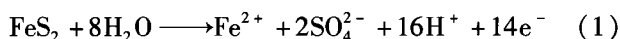
Fig. 10. Variations of galvanic current density with time for galena-pyrite couple in 0.1 mol/L  $\text{Na}_2\text{SO}_4$  solution. 1. Flow rate: 120 L/h; 2. static condition.

## 4 Discussion

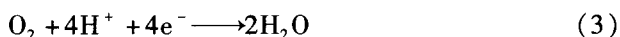
In the course of pyrite crystal growth and its long-term geological evolution there will form many defects in pyrite crystal, and reactions will firstly occur in these locations with high surface energy (Lasaga and Blum, 1986; Mckibben and Barnes, 1986). When pyrite electrode with cracks coupled with galena electrode to form a galvanic cell, pyrite acted as the anode and galena became the cathode. In the experiments galena electrode was connected with the positive input terminal of the multimeter, because galena had a higher potential, so the galvanic current density of all the galvanic interactions is of positive value, just in conformity with the measured results. When galena electrode existed alone in 0.01 mol/L  $\text{Fe}_2(\text{SO}_4)_3$  solution, there would form black coatings on the surface before long. Such black coatings were analyzed to be  $\text{PbSO}_4$ . Lin (1997) also found in the etching experiment that the oxidation of galena led to the precipitation of lead sulfate. But in case galena coupled to pyrite with cracks in 0.01 mol/L  $\text{Fe}_2(\text{SO}_4)_3$  solution, there was no black coating on galena surface during the experi-

ment. The reason is that the oxidization of galena cathode was protected in this galvanic interaction. In addition, according to the mixed potential theory (Holmes and Crundwell, 1995; Cao Chunan, 2004), the galvanic potential should be intermediate between the potentials of anode and cathode. The measured galvanic potential of galena-pyrite couple shown in Fig. 5 is truly larger than the potential of pyrite and smaller than the potential of galena.

Galvanic interaction between pyrite and galena belongs to a spontaneous reaction. This work only considered the oxidation reaction of the anode and the reduction reaction of the cathode. In this study pyrite acts as the anode, and the anodic half-reaction occurring on pyrite surface is expressed as follows:



Galena acts as the cathode, on the surface of which occurs the reduction reaction of oxidants. The oxidants involved in the experiments are  $\text{Fe}^{3+}$  and dissolved oxygen (DO). The cathodic half-reaction is expressed as follows:



The overall reaction behaves as the oxidative dissolution of pyrite. Using electrochemical methods, Holmes and Crundwell (2000) investigated reactions (1), (2) and (3) individually, and gave their Butler-Volmer equations as follows:

$$i_{\text{FeS}_2} = k_{\text{FeS}_2} [\text{H}^+]^{-1/2} \exp\left(\frac{\alpha_{\text{FeS}_2} FE}{RT}\right) \quad (4)$$

$$i_{\text{Fe}} = k_{\text{Fe}^{2+}} [\text{Fe}^{2+}] \exp\left(\frac{\alpha_{\text{Fe}} FE}{RT}\right) - k_{\text{Fe}^{3+}} [\text{Fe}^{3+}] \exp\left(\frac{-(1-\alpha_{\text{Fe}}) FE}{RT}\right) \quad (5)$$

$$i_{\text{O}_2} = -k_{\text{O}_2} [\text{O}_2] [\text{H}^+]^{0.14} \exp\left(\frac{-(1-\alpha_{\text{O}_2}) FE}{RT}\right) \quad (6)$$

where  $i$  is the current density of each reaction;  $k$  is the rate constant;  $\alpha$  is the transfer coefficient and generally  $\alpha_{\text{FeS}_2} \approx \alpha_{\text{Fe}} \approx \alpha_{\text{O}_2} = 1/2$ ;  $F$  is the Faraday constant;  $E$  is the potential of each reaction;  $R$  is the universal gas constant; and  $T$  is the temperature. In this work the influence of activity coefficient is negligible, so the concentration is used to replace the activity in the dis-

cussion.

According to the Faraday's law (Guo Hetong and Tan Qixian, 2000), the mass of the material involved in the electrochemical reaction is in direct proportion to the quantity of electricity passing through the electrode. So the current density is usually to embody the rate of the reaction (Holmes and Crundwell, 2000). According to the mixed potential theory, the galvanic interaction occurs at the mixed potential,  $E_g$ , at which the anodic current density,  $i_a$ , due to the processes occurring on pyrite surface, is equal to the cathodic current density,  $i_c$ , due to the processes occurring on galena surface, also is equal to the galvanic current density,  $i_g$  (Holmes and Crundwell, 2000):

$$i_a = -i_c = i_g \quad (7)$$

In the absence of  $Fe^{3+}$  in solution, dissolved oxygen is the only oxidant, and according to the mixed potential theory, it is clear that the following condition holds at the galvanic potential,  $E_g$ :

$$i_{FeS_2} = -i_{O_2} = i_g \quad (8)$$

Substitution of Eqs. (4) and (6) into Eq. (8) gives the following expressions for the galvanic potential and galvanic current density:

$$E_g = \frac{RT}{F} \ln \left( \frac{k_{O_2} [O_2] [H^+]^{0.64}}{k_{FeS_2}} \right) \quad (9)$$

$$i_g = k_{FeS_2}^{1/2} k_{O_2}^{1/2} [O_2]^{1/2} [H^+]^{-0.18} \quad (10)$$

In the presence of ferric ions and oxygen in the solution, both reaction (2) and reaction (3) take place on galena electrode surface. The condition that the anodic current density is equal to the cathodic current density gives the following expression:

$$i_{FeS_2} = -(i_{O_2} + i_{Fe}) = i_g \quad (11)$$

Substituting Eqs. (4), (5) and (6) into Eq. (11) and rearranging the resulting equation, the following explicit expressions are obtained for the galvanic potential and current density in the presence of both ferric ions and dissolved oxygen:

$$E_g = \frac{RT}{F} \ln \left( \frac{k_{Fe^{3+}} [Fe^{3+}] + k_{O_2} [O_2] [H^+]^{0.14}}{k_{Fe^{2+}} [Fe^{2+}] + k_{FeS_2} [H^+]^{-1/2}} \right) \quad (12)$$

$$i_g = k_{FeS_2} [H^+]^{-1/2} \left( \frac{k_{Fe^{3+}} [Fe^{3+}] + k_{O_2} [O_2] [H^+]^{0.14}}{k_{Fe^{2+}} [Fe^{2+}] + k_{FeS_2} [H^+]^{-1/2}} \right)^{1/2} \quad (13)$$

According to Henry's law, under certain temperature and equilibrium conditions the solubility of gas in the solution is in direct proportion to the equilibrium partial pressure. Experiments in this work were carried out in an open system, so the DO concentrations in the solution can be described by:

$$[O_2] = k_H \cdot P_{O_2} \quad (14)$$

where  $k_H$  is Henry's Law constant, and  $P_{O_2}$  is the pressure of  $O_2$  on the surface of the solution. In the system open to  $O_2$ , the partial oxygen pressure is a constant, so it can be considered that the DO concentrations in the solution are a constant under the experimental conditions.

In 0.1 mol/L  $Na_2SO_4$  solutions at pH values of 1.82 and 6.63, the concentrations of  $O_2$  are a constant. According to Eqs. (9) and (10), it is clear that in case the concentrations of  $H^+$  increase, the galvanic potential,  $E_g$ , will increase, whereas the galvanic current density,  $i_g$ , will decrease. The measured galvanic current density and potential for galena-pyrite couple shown in Figs. 6 and 7 are in consistency with the above analysis.

In 0.01 and 0.0001 mol/L  $Fe_2(SO_4)_3$  solutions at pH = 1.78, the concentrations of  $H^+$  and  $O_2$  are both constants. From Eqs. (12) and (13), it can be seen that the galvanic potential,  $E_g$ , and the galvanic current density,  $i_g$ , tend to increase with increasing  $Fe^{3+}$ , just in accord with the variations of galvanic current density and potential for galena-pyrite couple shown in Figs. 3 and 4.

As for the galvanic interaction between galena and pyrite in 0.1 and 0.001 mol/L  $Na_2SO_4$  solutions, there only changed the concentrations of inert electrolyte in the solution. According to Eqs. (9) and (10), it can be seen that there will be only minor effects on the whole galvanic interaction. As illustrated by Figs. 8 and 9, the galvanic current density and potential for galena-pyrite couple vary very slightly.

Under the conditions of solution flowing, the galvanic interaction between galena and pyrite in 0.1 mol/L  $Na_2SO_4$  solution is greatly affected by the diffusion of dissolved oxygen in the solution, and the current density on the electrode surface can be approximately expressed as (Holmes and Crundwell, 1995; Cao Chunan, 2004):

$$i = \frac{4FD}{\delta} ([O_2]_b - [O_2]_s) \quad (15)$$

where  $D$  is the diffusion coefficient;  $\delta$  is the thickness of the diffusion layer;  $[O_2]_b$  is the concentration of dissolved oxygen in the bulk solution; and  $[O_2]_s$  is the concentration of dissolved oxygen on the electrode surface. The tangential flow of the solution on the electrode surface makes the diffusion layer thickness reduced. So the galvanic current density under flowing condition will be larger than that under static condition according to Eq. (15). What's more, due to the flowing of the solution, the resultants on the electrode surface will be carried away steadily, while the reactants will be continuously supplemented. From Eqs. (4) and (6) it can be seen that both the reduction of  $H^+$  in the resultants of Eq. (1) and the increment of  $O_2$  and  $H^+$  in the reactants of Eq. (3) will lead to an increase in current density of the galvanic interaction. The measured galvanic current density for galena-pyrite couple shown in Fig. 10 in the flowing solution is surely larger than that in the static solution, which implicates that the flowing of mine waters, surface waters and even underground waters will obviously enhance the galvanic interaction between galena and pyrite.

## 5 Conclusions

In case there are cracks on the surface of pyrite electrode, the potential of pyrite will decrease, even so sharply as to be lower than that of galena under the same experimental condition. When pyrite with cracks couples to galena to form a galvanic cell, pyrite will act as the anode of the galvanic couple and the dissolution will accelerate. As for the galvanic interaction between galena and pyrite with cracks, both the increment of  $Fe^{3+}$  in the solution and the flowing of the solution will enhance the galvanic potential and the rate of galvanic interaction; the rise of solution pH values will lead to the increase of reaction rate and the decrease of galvanic potential; while the increase of solution salinity (e. g. the concentrations of  $Na_2SO_4$ ) only has little influence on the galvanic interaction between galena and pyrite.

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**Correction of error in printing:**

In the paper entitled “Research on the direction of secondary migration of oil by making use of nitrogen compounds as tracers in the No. 6 area of the Melut Basin” which appears in the No. 2 (2006) of Chinese Journal of Geochemistry, there is an error in printing, i. e. , “Melut Basin” , which actually refers to “Muglad Basin”.