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Electrochemical investigation of the mechanism of aqueous oxidation of pyrite by oxygen

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Abstract

The aqueous oxidation of pyrite in air-equilibrated HCl solutions was investigated at various temperatures (30 and 40 ºC), pH values (2 to 5) and sulfate concentrations (0.001 to 0.5 M). It was found that the oxidation current densities (i_{ox}) increase when the temperature and sulfate concentration increase. The rate dependence on sulfate concentration indicates that during the oxidative dissolution of pyrite an activated complex of ionic nature is formed on mineral surface, and sulfate is not involved in the rate determining step of pyrite oxidative dissolution.

Keywords: pyrite oxidation; sulfate; potentiodynamic polarization; cyclic voltammetry ; electrochemical impedance spectroscopy

1. Introduction

The aqueous oxidation of pyrite (FeS_2) is very important in the formation of acid mine drainage, in mineral processing and in the geochemical cycling of iron and sulfur, and therefore has been investigated in a large number of studies.[1-4] The rate of pyrite aqueous oxidation can be affected by all chemical species presents in the solutions.[1] It was reported that the presence of sulfate inhibit the rate of the pyrite aqueous oxidation.[5] This inhibiting effect increases when the sulfate concentration ($[SO_4^{2-}]$) increases. Other studies however suggested that the sulfate ion

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does not influence the rate of aqueous oxidation of pyrite.[1] As sulfate is a reaction product of aqueous oxidation of pyrite its concentration will steadily increase during the mineral oxidation and hence it is important to know the effect of this ion on the overall oxidation reaction.

In the present study the potentiodynamic polarization curves, cyclic voltammetry and electrochemical impedance spectroscopy, were used to investigate the influence of sulfate on aqueous oxidation of pyrite in various conditions.

2. Experimental

Reagent grade chemicals and distilled water were used to prepare the experimental solutions. The pH of air-equilibrated HCl solutions was measured at experimental temperature with a combined electrode connected to a pH/millivoltmeter Consort C538. The electrode was calibrated against two commercial buffers (pH 4.01 and 7.00). The sulfate concentration ($[SO_4^{2-}]$) was set to desired value by dissolving Na_2SO_4 to the air-equilibrated HCl solutions. A detailed description of pyrite used in this study can be found in a previous paper.[6]

A three-electrode cell (Zahner KMZ3) was used for potentiodynamic polarization (PP), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) studies. The electrochemical cell was connected to an electrochemical workstation (Zahner Zennnium) controlled by PC. The working electrode was a rectangular pyrite sample encapsulated in epoxy resin. The exposed surface area of the working electrode was 1 cm^2. Prior to experiments, the working electrode was polished with 600, 2000 and 3000 grade SiC papers, then immersed for 1 min in 1 M HNO_3, washed with distilled water, dried with acetone and immersed in the experimental solution. The counter electrode was a Pt foil and as reference electrode we used a saturated calomel electrode (SCE).

The potentiodynamic polarization measurements were carried out with a scan rate of 1 mV/s. The potential range was -0.25 V to 0.25 V versus open circuit potential (OPC). The electrochemical impedance spectroscopy experiments were carried out at OCP with a signal of 10 mV amplitude at frequencies ranging from 10 mHz to 3 MHz. Cyclic voltammetric curves (2 cycles per experiment) were recorded at a scan rate of 0.1 V/s, in positive direction and between -1 and 1 V.

All potentials were measured against SCE and converted to the standard hydrogen electrode (SHE). The analysis of experimental data was performed using the Thales (Zahner) software.

3. Results and discussion

Table 1 shows all of the electrochemical kinetic parameters obtained by Tafel analysis of potentiodynamic polarization data. The potentiodynamic polarization curves for pyrite immersed in air-equilibrated HCl solutions at different pH values at 30 °C, and in the absence and presence of SO_4^{2-} (as Na_2SO_4) are shown in Fig. 1. It can be observed that both in the presence and absence of SO_4^{2-} the oxidation potential (E_{ox}) decreases when the pH of air-equilibrated solutions increases. Oxidation current densities (i_{ox}) determined by Tafel analysis increase when the pH of solutions increases from 2 to 3. A subsequent increase in pH does not produce a decrease of i_{ox}. i_{ox} is closely related to rate of aqueous oxidation of pyrite. It is important to note that in the presence of SO_4^{2-} both E_{ox} and i_{ox} increase.

As we can see from Table 1 both temperature and $[SO_4^{2-}]$ are important parameters which influence the rate of aqueous oxidation of pyrite by oxygen. When the temperature or $[SO_4^{2-}]$ increase, i_{ox} (i.e., rate of aqueous oxidation of pyrite) increases. The temperature dependence of the rate of aqueous oxidation of pyrite is in good agreement with the results of the previous studies and indicates that the rate-determining step of pyrite oxidative dissolution is a surface reaction.[1,7,8] The dependence of rate on $[SO_4^{2-}]$ suggests that, on the one hand, during the oxidative dissolution of pyrite an activated complex of ionic nature is formed[9] and, on the other hand, SO_4^{2-} is not involved in the rate determining step of FeS_2 oxidative dissolution.

Fig. 3 presents the cyclic voltammetry curves for pyrite electrode in air-equilibrated HCl solutions at 30 °C and pH 2, in the presence and absence of SO_4^{2-} (0.01 M). The cyclic voltammetry curve for pyrite in the absence of SO_4^{2-} is magnified and presented in the small windows within Fig. 2. From Fig. 2 we can observe that in the presence of SO_4^{2-} the rate of aqueous oxidation of pyrite increases (the anodic peaks). Also, the cathodic current densities undergo an important increase when SO_4^{2-} is inserted in the system. This behavior indicates that both anodic (pyrite

oxidation) and cathodic (pyrite reduction to H_2S) reactions of pyrite involve activated complexes of ionic nature. These complexes are stabilized by the ionic species (Na_2SO_4) added to air-equilibrated HCl solutions.
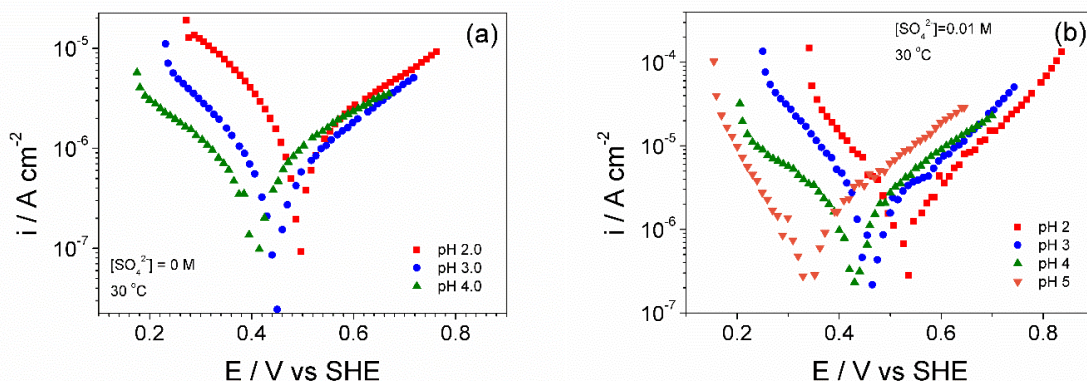

Fig. 1. Potentiodyamic polarization curves for pyrite electrodes in air-equilibrated solutions at 30 ^{o}C, pH ranging between 2 and 5, in the (a) absence and (b) presence of SO_4^{2-} (0.01 M).

Table 1. Electrochemical kinetic parameters obtained by Tafel analysis for pyrite electrode in air-equilibrated HCl solutions at pH between 2 and 5, [SO_4^{2-}] ranging from 0.001 M to 0.5 M, 30 ^{o}C and 40 ^{o}C. ba and bc are anodic and cathodic Tafel slopes.

[SO_4^{2-}]	pH	Temperature, ^{o}C	i_{ox}, μA cm^{-2}	E_{ox}, V	ba, V/dec	bc, V/dec
0.001	3	40	1.84	0.463	0.171	-0.132
0.1	3	40	1.96	0.481	0.139	-0.108
0.5	3	40	2.33	0.460	0.159	-0.091
0.001	3	30	0.87	0.501	0.138	-0.095
0.01	3	30	0.99	0.468	0.171	-0.111
0.1	3	30	1.30	0.473	0.158	-0.089
0.5	3	30	1.55	0.479	0.168	-0.114
0.01	2	30	1.40	0.524	0.174	-0.119
0.01	4	30	1.27	0.424	0.209	-0.187
0.01	5	30	1.06	0.333	0.218	-0.829
0	2	30	1.23	0.498	0.307	-0.193
0	3	30	0.51	0.457	0.260	-0.204
0	4	30	0.44	0.417	0.235	-0.258

Nyquist plots for pyrite immersed in air-equilibrated HCl solutions at 30 °C and pH 2 in the presence and absence of SO_4^{2-} (0.01 M) are presented in Fig. 4. In the absence of SO_4^{2-} a well-defined capacitive loop is visible at low and medium frequencies and a small and irregular capacitive loop appears at high frequencies. In the presence of SO_4^{2-} the capacitive loop situated at high frequencies is missing. The capacitive loop situated at low and medium frequencies can be assigned to double layer capacitance.[10] The small capacitive loop presents at high frequencies (the small windows within the Fig. 4) can be attributed to the formation of an inhomogeneous layer on pyrite surface during its oxidation. The layer is likely to be composed of elemental sulfur. It acts as dielectric of the capacitor consisting of pyrite and the solution.[10] Although a surface layer is formed on pyrite surface the experimental results does not indicate that the overall rate of pyrite oxidative dissolution is controlled by a diffusion process.
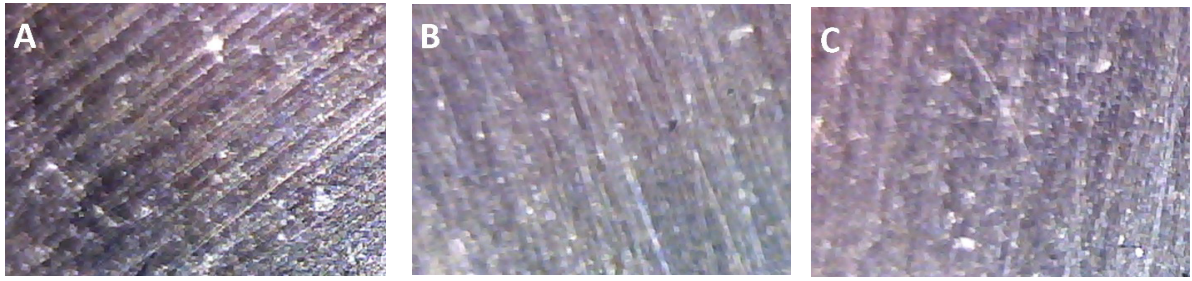
Fig. 2. Micrograph (x200) of (A) unreacted pyrite electrode and reacted at pH 3 in the (B) absence and (C) presence of SO_4^{2-} (0.01 M) at 30 ^{o}C.
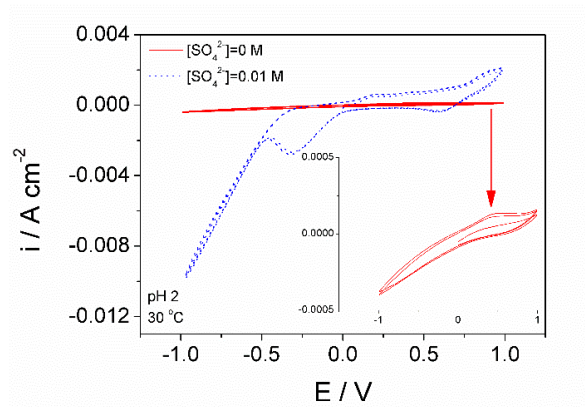

Fig. 3. Cyclic voltammetry curves for pyrite at 30 ^{o}C, pH 2, in the presence and absence of SO_4^{2-} (0.01 M).
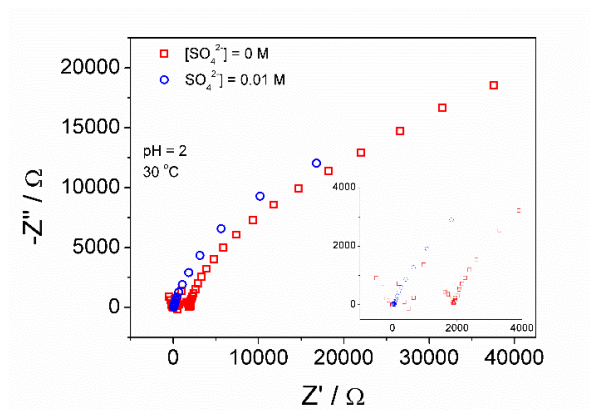

Fig. 4. Nyquist curves for pyrite electrodes in air-equilibrated solutions at 30 ^{o}C, pH 2, in the absence and presence of SO_4^{2-}.

4. Conclusions

The pyrite oxidative dissolution in the absence and presence of SO_4^{2-} was studied by electrochemical techniques. The experimental results indicate that the rate of aqueous oxidation of pyrite (i.e., i_{ox}) increases when the temperature and $[SO_4^{2-}]$ increase. The rate dependence on $[SO_4^{2-}]$ indicates that during the oxidative dissolution of pyrite an activated complex of ionic nature is formed. In addition the experimental results indicate that SO_4^{2-} is not involved in the rate determining step of pyrite oxidative dissolution. In the absence of sulfate, EIS measurements indicate the formation of an inhomogeneous product layer on pyrite after immersion in oxygen-bearing solution.

Acknowledgements

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