



Natural versus synthetic pyrrhotite oxidation by dissolved oxygen

Research article

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Abstract

The reaction of pyrrhotite with dissolved oxygen was studied at pH 2.5 and 25°C by electrochemical methods (potentiodynamic polarization, Electrochemical Impedance Spectroscopy (EIS) or Cyclic Voltammetry (CV)). It was found that there are differences between the reactivity of the natural and synthetic pyrrhotite, respectively. The natural pyrrhotite is more resistant to oxidation than the synthetic counterpart. The lower reactivity of the natural pyrrhotite can be explained by the formation of a higher amount of S(0) on its surface. EIS spectra indicate that the characteristics of the pyrrhotite/solution interface are essentially identical for both natural and synthetic pyrrhotite electrodes.

Keywords: pyrrhotite, oxygen, oxidation

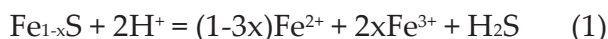
1. INTRODUCTION

Pyrrhotite (Fe_{1-x}S , $0 < x \leq 0.2$ [1]) is formed in oxygen-poor environments. When pyrrhotite is extracted from these environments,

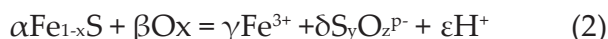
through mining activities, and come into contact with the oxygen dissolved in water, it is oxidized, the reaction contributing to acid mine drainage formation.

Compared to pyrite (FeS_2), pyrrhotite can undergo not only oxidative dissolution but also non-oxidative dissolution [2-4].

The non-oxidative dissolution of pyrrhotite can be represented by the global reaction:



The oxidative dissolution of pyrrhotite [2-8] can be schematized as follows:



Ox represents the oxidizing species, $\text{S}_y\text{O}_z\text{P}^-$ are the oxidation products of sulfur, and α , β , γ , δ and ε are the stoichiometric coefficients of the reactants and products.

The oxidative dissolution supposes several non-oxidative and oxidative steps. These steps of the reaction mechanism, reaction intermediates and reaction products are not fully known [2,5].

In order to obtain new information related to the aqueous oxidation of pyrrhotite with dissolved oxygen, we have investigated the oxidation process for both synthetic and natural pyrrhotite by electrochemical methods.

2. EXPERIMENTAL

Aqueous solutions saturated with air, with a pH of 2.5 and a temperature of 25°C, were used for the experiments. The solutions pH was measured with a Consort electrode. The electrochemical experiments were carried out with a Zahner Zenium electrochemical workstation in a three-electrode cell. The electrodes used were:

- working electrode \equiv parallelepiped pieces of natural pyrrhotite (po) or synthetic pyrrhotite (sy po).

- reference electrode \equiv saturated calomel electrode (SCE);
- the counter electrode \equiv Pt foil;

The following types of electrochemical measurements were carried out:

- Potentiodynamic polarization;
- Electrochemical Impedance Spectroscopy (EIS);
- Cyclic Voltammetry (CV).

In potentiodynamic polarization experiments, the potential range was between -0.250 V and $+0.250$ V relative to the open circuit potential (OCP). The scanning speed was 1 mV/s.

Impedance measurements were performed in the frequency range 100 kHz and 10 mHz. The amplitude of the AC signal was 10 mV.

The potential range in which the cyclic voltammograms were recorded was between -1 V and $+1$ V.

3. RESULTS AND DISCUSSION

It was found that the open circuit potential (OCP) is constant over time, which demonstrates the stability of the electrode surface (Figure 1).

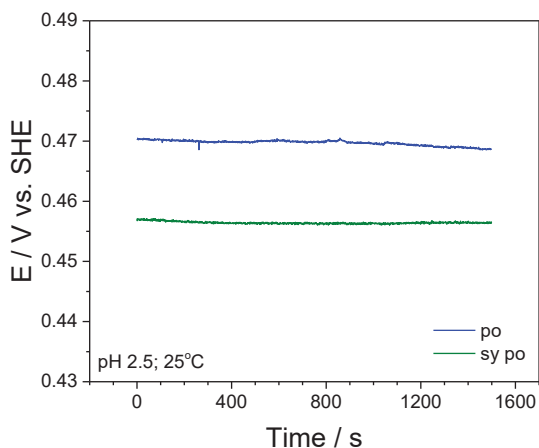


Figure 1. The OCP during 25 minutes after the immersion of the pyrrhotite electrodes in the aerated solutions. SHE = standard hydrogen electrode

The results of potentiodynamic polarization experiments for the two electrodes (i.e., natural pyrrhotite (po) and synthetic pyrrhotite (sy po)) are presented in Figure 2.

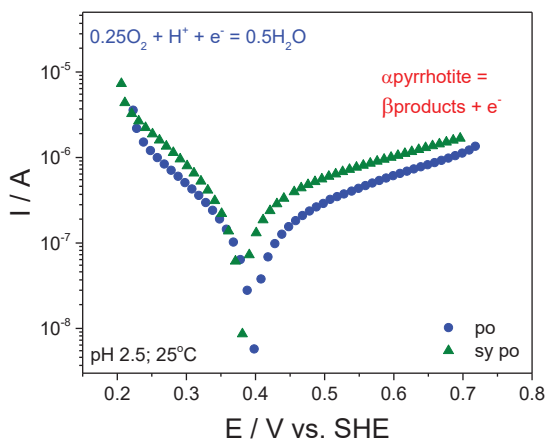


Figure 2. Potentiodynamic polarization curves obtained for po and sy po electrodes. Experimental conditions: aerated solutions, pH 2.5 and 25°C. SHE = standard hydrogen electrode

From the analysis of Figure 2, we find that the oxidation currents (I) registered for natural pyrrhotite (po) are lower than those registered in the case of synthetic pyrrhotite (sy po) indicating that the reactivity of sy po is higher than that of po. It should be mentioned that the surface of the two pyrrhotite electrodes exposed to the oxidizing solutions was identical.

The results obtained from the EIS measurements are presented in the form of Nyquist diagrams (Figure 3). The shape of the impedance spectra (po and sy po) assumes an arc of circle followed by a straight line with a slope of approximately 45°.

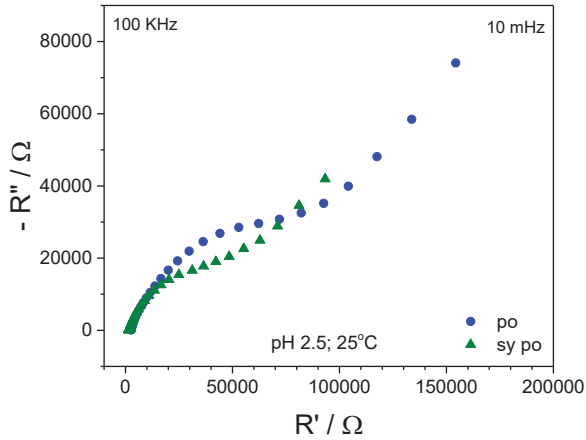


Figure 3. Nyquist plots of po and sy po electrodes. Experimental conditions: aerated solutions, pH 2.5 and 25°C

From Figure 3 it is clear that, in the case of both pyrrhotite samples, the characteristics of the mineral/solution interface are essentially identical. It is also important to note that a Warburg diffusion element can be associated with the straight line with a slope of approximately 45° in Figure 3 [9]. This fact indicates that in the oxidative dissolution of pyrrhotite samples is involved a diffusion process.

Figure 4 shows the results of the Cyclic Voltammetry experiments with the pyrrhotite electrodes. A first peak observed is produced by the oxidation of sulfur in pyrrhotite from S(-II) to elemental sulfur (P1). Further, with the increase in potential, we can observe the oxidation of the mineral to sulfate (P2) [2]. It is important to note the prominent P1 peak recorded in the case of natural pyrrhotite. The formation of a higher amount of S(0) on the po surface can explain its lower reactivity (i.e. its lower oxidation rate) with respect to that of sy po. The most important process in the cathodic zone is that of oxygen reduction.

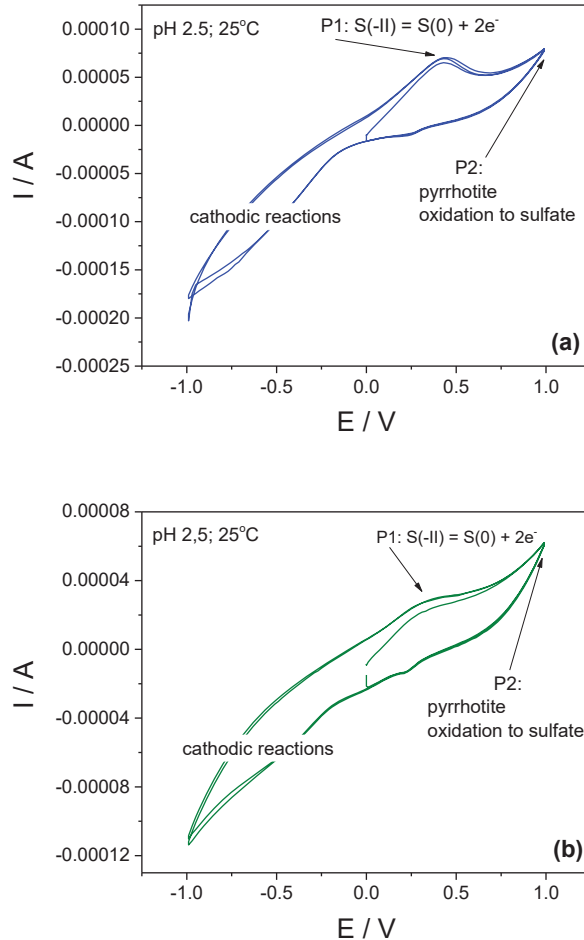


Figure 4. Cyclic voltammograms of (a) po and (b) sy po

4. CONCLUSION

The main conclusions that emerge from the study are the following:

- There are clear differences regarding the reactivity of the two pyrrhotite samples: the natural pyrrhotite sample is more resistant to oxidation than the synthetic pyrrhotite;

- The lower reactivity of po compared to that of sy po can be explained by the formation of a higher amount of S(0) on the mineral surface.

- The EIS spectra of both pyrrhotite samples include an arc of circle plus a straight line with a slope of approximately 45° (to which a Warburg diffusion element can be associated), meaning that the properties of the pyrrhotite/oxidizing solution interface are essentially identical for the two pyrrhotite samples.

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