



The effect of temperature on the kinetics of the ferric-ferrous redox couple on pyrite



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ABSTRACT

This article presents two methods for the study of ferric-ferrous reaction kinetics on the surface of an electro-active electrode. The working electrode in this study was a high quality bulk pyrite mineral, and the experimental results have been collected in a 0.5 M sulfuric acid solution within a temperature range of 22 to 65 °C. Two electrochemical methods, based on mixed potential theory, are introduced to isolate the Fe(II)/Fe(III) reaction from the other interfering reactions of pyrite oxidation and oxygen reduction, and to study its kinetics. The two methods use chronoamperometry or cyclic voltammetry for the kinetics analysis. By subtracting the current density of pyrite oxidation in an Fe-free acidic solution from that in an Fe-containing solution the Fe(II)/Fe(III) kinetics were isolated and studied.

Tafel behavior was established by both chronoamperometry and cyclic voltammetry to analyze the kinetics of the Fe(II)/Fe(III) redox reactions. The results showed that the exchange current densities increased slightly with temperature, however they remained in the order of 10^{-5} A cm⁻². The activation energy for Fe(II) oxidation and Fe(III) reduction on the pyrite surfaces was calculated to be 102.0 and 32.7 kJ mol⁻¹, respectively. Anodic transfer coefficients also increased by increasing temperature from 0.24 to 0.39. Electrochemical impedance spectroscopy measurements showed a typical two-step pyrite oxidation process. The EIS measurement under different temperature showed that the predominant reaction in an Fe-free solution is pyrite oxidation, which has a large R_{ct} value, starting from 4200 Ω at 22 °C and decreasing to 1490 Ω at 65 °C. Meanwhile the R_{ct} values in an Fe-containing solution reduces from 1760 to 511 Ω by increasing the temperature from 22 °C to 65 °C, as the Fe(II)/Fe(III) redox reaction is the predominant reaction. The diffusion coefficients of Fe(II) during pyrite polarization was related to the Warburg impedance and calculated to be 1.9×10^{-6} cm² S⁻¹ at 22 °C and increases to 7.1×10^{-6} cm² S⁻¹ at 65 °C.

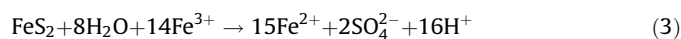
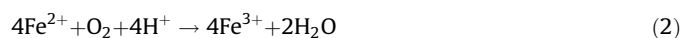
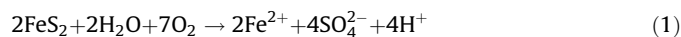
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1. Introduction

Pyrite, an abundant sulfides mineral in the nature, is commonly considered as a valueless gangue mineral frequently associated with other valuable sulfide minerals such as chalcopyrite, or metals such as gold, or coal [1]. Pyrite oxidation has been the subject of extensive research in view of gold metallurgy, as oxidation of pyrite is the initial step to break down the pyrite lattice and expose the encapsulated fine gold particles [2].

Fe(III) ion and dissolved oxygen (DO) have generally been considered as the two most important oxidants with respect to pyrite oxidation, having been studied extensively in previous research [3,4]. Previous studies have shown that the Fe(III) ion and

DO collaboratively participate in pyrite oxidation in nature; the process is a relatively complex process, and the mechanism is still under debate [5]. Nevertheless, the process of pyrite oxidation can be viewed as a series of reactions amongst pyrite, ferrous, ferric and oxygen in which pyrite is initially oxidized by the dissolved oxygen in water forming ferrous (Eq. (1)), and then the ferrous also is oxidized by the dissolved oxygen to form ferric (Eq. (2)). The ferric, produced by reaction 2, then could potentially oxidize pyrite (Eq. (3)) and convert to ferrous.



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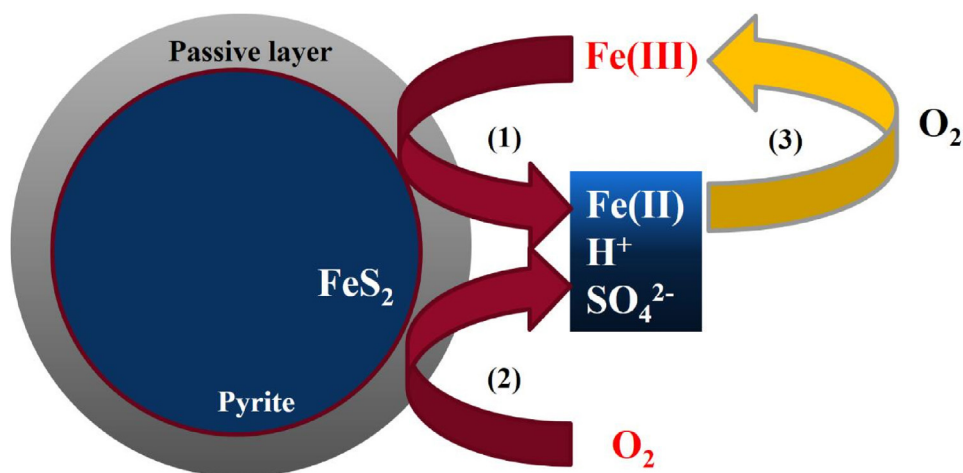


Fig. 1. Schematic graph of pyrite oxidation in nature.

Fig. 1 summarizes the three reactions involved in pyrite oxidation. As shown in Fig. 1, the Fe(II)/Fe(III) oxidation–reduction reaction functions as a bridge for pyrite oxidation. It is clear from Fig. 1 that the Fe(II)/Fe(III) redox reaction kinetics plays an important role in pyrite oxidation and its kinetics is worth to be investigated and better understood.

There have been numerous studies concerning the kinetics and mechanism of oxidative pyrite dissolution by DO and ferric. In earlier kinetics studies of pyrite oxidation, researchers have tried to measure the ferric and DO reduction rates to calculate the pyrite electro-dissolution rate. Reaction rates available from previous studies suggest that the kinetics of pyrite oxidation strongly correlates with Eh (Fe(II)/Fe(III) ratio and/or DO concentration), which is consistent with an electrochemical reaction mechanism. Another studies have attempted to quantify the kinetics of oxidative pyrite dissolution via electrochemical methods [6]. Mixed potential theory is often applied to interpret the collected electrochemical data.

However, most electrochemical research regards pyrite oxidation as solely an electrochemical corrosion process, a combination of sulfide oxidation to elemental sulfur, sulfate or other oxidized forms of sulfur, and ferric and DO reduction. Unfortunately, most researchers have given minimum or no attention to the kinetics of ferric/ferrous redox reaction on the surface of pyrite, despite the fact that this electrochemical couple reaction is shown to play an important role on the oxidative dissolution of pyrite. The ferrous oxidation half-cell reaction on pyrite surface is the rate-limiting step for oxidative pyrite dissolution process [7]. Although it was shown that Fe(II) oxidation by DO is very slow, except when subjected to high pressures and temperatures as in the autoclave processes, recent findings have shown that pyrite in an Fe(II) containing solution can significantly boost the Fe(II) oxidation reaction owing to its catalytic effect on the reaction. And yet the kinetics of Fe(II) oxidation was studied not in an electrochemical method [8].

The iron ions reduction-oxidation reactions kinetics on pyrite surfaces was studied by the authors very recently [9]. However the studies before that mostly had focused on the kinetics of couple reactions on noble electrodes such as platinum, and few superficially oxidized metals such as titanium [10–13]. The challenge with the ferric/ferrous reaction kinetics measurements on the surface of sulfide minerals are explained elsewhere [10].

In this study, two electrochemical techniques are applied to shed light on the electrochemistry of Fe(II)/Fe(III) on the pyrite surface. Important kinetic parameters including equilibrium potential, exchange current density, and charge transfer

coefficients of the iron couple reactions as well as the activation energy of the reaction were measured and calculated on the surface of a bulk pyrite mineral electrode. To better understand the chemistry of Fe(II)/Fe(III) during the atmospheric oxidation process of pyrite, the effect of temperature was explored. It is believed that the analysis of the Fe(II)/Fe(III) reaction at elevated temperatures would generate valuable kinetic information for industrial practice. Atmospheric oxidation of pyrite at elevated temperatures has become a research hotspot due to low capital costs, in comparison to other oxidation methods [14]. There have been numerous studies about pyrite oxidation at high temperature, however, most of the research conducted also investigated high pressures as experienced in autoclaves [15].

2. Experimental

2.1. Pyrite electrode fabrication

The pyrite sample used in this study was high purity natural pyrite, 99.5% FeS₂, originating from Navajún, Spain. The chemical analysis of the pyrite mineral is presented in Table 1.

The process for the preparation of the pyrite electrodes with an exposed surface area of 0.5 cm², is explained elsewhere [10].

2.2. Electrochemical test set-up

Electrochemical experiments were carried out by an GSTAT302N potentiostat (Metrohm) controlled by Nova software (Version 2.0). All electrochemical tests were carried out in a corrosion cell, which was water jacketed to allow for thermostatic temperature control by a Cole-Parmer Polystat Heated Circulating Bath (± 1 °C). The electrochemical analysis was conducted with a traditional three electrodes system. The pyrite electrode prepared [10] was used as the working electrode in the experiments. A graphite rod counter electrode and a silver-silver chloride

Table 1
Elemental analysis of the pyrite mineral by inductively coupled plasma – optical emission spectrometry (ICP-OES).

| Sample | Ag (ppm) | Au (ppm) | K% | Ca% | Mg% | Pb% | Cr% |
|--------|----------|----------|------|------|------|------|--------|
| Pyrite | <5.0 | 1.0 | 0.02 | 0.29 | 0.05 | 0.01 | 0.05 |
| Sample | Fe% | Mn% | Na% | Ni% | P% | Ti% | S% |
| Pyrite | 45.78 | 0.03 | 0.02 | 0.05 | 0.02 | 0.01 | 53.601 |

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