

Pyrite oxidation in air-equilibrated solutions: An electrochemical study



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ABSTRACT

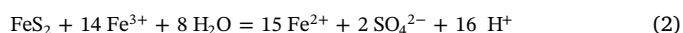
Oxidative dissolution of pyrite (FeS₂) in air-equilibrated solutions was investigated with electrochemical techniques (polarization measurements and electrochemical impedance spectroscopy) at different solution pH (1 to 5) and temperatures (25 to 40 °C). We have found that, at a given temperature, the oxidation current density (*j*_{ox}) varies only slightly from initial pH 1 to 4, but was significantly lower at initial pH 5, while oxidation potential (*E*_{ox}) decreases when pH increases. At the investigated temperatures, the reaction order with respect to hydrogen ions has been found to be zero, suggesting that H⁺ is not involved into the rate-determining step of the oxidation rate. The *j*_{ox} values increase with temperature, whereas *E*_{ox} potentials are hardly affected by temperature from 25 to 40 °C. Activation energies (*E*_a) were estimated from polarization data and vary between 57 ± 28 kJ/mol (initial pH 5) and 19 ± 3 kJ/mol (initial pH 4). The obtained values indicate that the rate-determining step of the overall oxidative dissolution of FeS₂ involves a surface reaction. The importance of surface reaction is also supported by the electrochemical impedance spectroscopy measurements which show that interfacial transfer of electrons is dominated by surface charge transfer and the elementary surface reaction which controls the mineral oxidative dissolution is the electron transfer from the conduction band of pyrite to adsorbed O₂.

1. Introduction

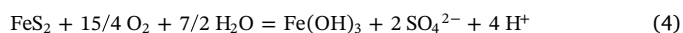
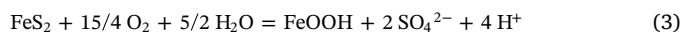
Pyrite (FeS₂) oxidation is important in a wide range of environmental processes and technological applications, and, as such, has been extensively investigated (Lowson, 1982; Rimstidt and Vaughan, 2003; Rickard and Luther, 2007; Murphy and Strongin, 2009). Knowledge of the oxidation mechanisms and rates are essential to better model biogeochemical cycling of iron and sulfur, formation of acid mine drainage (AMD), and mineral processing. Ferric iron (Fe³⁺) and oxygen (O₂) have been recognized as the most important oxidants of pyrite in natural systems (Lowson, 1982; Lehner et al., 2007). Early dissolution studies have demonstrated that Fe³⁺ is the most effective oxidant of pyrite, especially under acidic pH conditions. However, the dissolved concentration of this species steadily decreases with pH, thereby diminishing its relative importance (Nicholson et al., 1988). In contrast, O₂ is fairly abundant in most subsurface aerobic environments, hence it may be considered as a potent oxidant in AMD and hydrometallurgical processes (Williamson and Rimstidt, 1994). Pyrite oxidation by O₂ usually leads to endproducts such as dissolved sulfate, protons and Fe²⁺, according the mass balance equation



Furthermore, Fe²⁺ released by dissolution can be oxidized by O₂ to Fe³⁺ which acts as an oxidant of pyrite



Thus, a cycle appears in which Fe²⁺ is oxidized to Fe³⁺, and Fe³⁺ subsequently oxidizes pyrite, releasing additional protons and Fe²⁺ (Singer and Stumm, 1970). At near-neutral pH, Fe³⁺ precipitation somewhat hinders this Fe²⁺/Fe³⁺ cycling (Nicholson et al., 1990). The overall processes of pyrite oxidation can then be written as



The precipitated Fe(III) phases can inhibit the mineral oxidation by shielding the reaction center from the oxidant (O₂) (Nicholson et al., 1990; Perez-Lopez et al., 2007). Moses et al. (1987) reported that in the presence of dissolved O₂ and at pH > 3.9, thiosulfate and polythionate species are present in the reaction system. Also elemental sulfur was found on the reacted surface of pyrite at pH 2 in the presence of O_{2(aq)} (Demoisson et al., 2008; Sun et al., 2015; Qiu et al., 2016). However, other studies (e.g. Descostes et al., 2004; Gartman and Luther, 2014) did not detect all of these species, and so their formation is still somewhat controversial.

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Although the aqueous oxidation of pyrite in the presence of O₂ has been studied using several techniques, including spectroscopic (Bailey and Peters, 1976; Moses et al., 1987; Moses and Herman, 1991; Nesbitt and Muir, 1994; Caldeira et al., 2010), aqueous batch (Williamson and Rimstidt, 1994; Kamei and Ohmoto, 2000; Descostes et al., 2004; Gleisner et al., 2006) and electrochemical measurements (Ahlberg and Broo, 1997; Holmes and Crundwell, 2000; Liu et al., 2008; Savage et al., 2008; Liu et al., 2009; Constantin and Chirita, 2013), some key aspects (rate law, rate determining step(s), reaction intermediates and reaction products) of the pyrite oxidative dissolution under mildly acidic conditions in aerated solutions can be further clarified. Williamson and Rimstidt (1994) compiled the most reliable data available in the literature and derived a rate law of pyrite oxidation as a function of pH (over the pH range of 2–10) and concentration of dissolved O₂ ([O_{2(aq)}]). They showed that the rate of aqueous oxidation of pyrite by O₂ is inversely proportional to the concentration of protons (reaction order –0.11) and directly proportional to the square root of [O_{2(aq)}]. The experimental observations supported an electrochemical mechanism whereby anodic and cathodic reactions occur on the pyrite surface (Williamson and Rimstidt, 1994). Holmes and Crundwell (2000) further developed the electrochemical equations for anodic and cathodic reactions at the pyrite surface. By applying the condition that the net accumulation of electrons in pyrite is zero, they could derive a theoretical relationship for the rate of pyrite oxidative dissolution. This rate order could reproduce the reaction orders observed experimentally. In addition, several studies have demonstrated that the initial step of pyrite oxidation can be successfully investigated by electrochemical methods at the surface of pyrite electrodes (Peters and Majima, 1968; Biegler and Swift, 1979; Meyer, 1979; Ahlberg and Broo, 1997; Kelsall et al., 1999). The results of these studies can be translated directly in terms of pyrite interfacial potential and its impact on the dissolution rate and mechanism. Yet, most of these studies are restricted to acidic conditions and thus their applications to environmentally relevant conditions remain problematic.

The purpose of this study is to obtain the electrochemical kinetics parameters and identify the reaction pathway of pyrite oxidative dissolution in air-equilibrated solutions over pH range 1 to 5 and temperature range of 25 to 40 °C. The pH and temperature ranges thus extend the conditions previously investigated by Holmes and Crundwell (2000). The electrochemical parameters for pyrite oxidative dissolution (oxidation current densities, oxidation potentials, cathodic and anodic Tafel slopes) were determined by Tafel method (Brett and Oliveira Brett, 1993). Information about physical and chemical processes occurring in the pyrite/solution interface was provided by electrochemical impedance spectroscopy (EIS) (Bryson and Crundwell, 2014). Based on experimental results, we analyzed the interaction of pyrite with dissolved O₂ and identified the rate determining step as the electrons transfer from the conduction band of pyrite to O₂.

2. Materials and methods

Natural pyrite of unknown origin was used for electrochemical experiments. Pyrite chemical analysis was performed by combustion (sulfur) and ICP-OES (other elements) (S.C. Prospectiuni Geologice S.A.) and yielded a S:Fe atomic ratio close to 2. Impurities detected include Mn (52.8 mg/kg), Co (283.7 mg/kg), Ni (848.6 mg/kg); Cu (53.9 mg/kg) Zn (93.5 mg/kg) Pb (29.5 mg/kg) Cd (0.4 mg/kg) Ag (0.9 mg/kg) As (146.3 mg/kg), and Sb (1.0 mg/kg). X-ray diffraction confirmed the pyrite nature of the starting material, and showed the presence of only quartz as a detectable crystalline contaminant.

All electrochemical experiments were performed in a three-electrode cell with aerated distilled water adjusted to the desired initial pH (pH_i) by adding aliquots of HCl solutions. The working electrode was prepared from a pyrite monolith cut into a cubic shape and sealed with epoxy resin, exposing an area of 2 cm². Before each experiment, the working electrode was mechanically polished with emery paper (600,

2000 and 3000), immersed in 1 M HNO₃ for 60 s, rinsed several times with O₂-free distilled water and degreased with acetone. The reference electrode was a saturated calomel electrode (SCE) and the counter electrode was platinum foil. A Luggin capillary, positioned at 1 mm from the working electrode, was connected to the reference electrode via a 3 M KCl solution. All potentials in this paper are quoted relative to the Standard Hydrogen Electrode (SHE). Potentiodynamic polarization, EIS measurements and data analysis were carried out with an electrochemical workstation (ZAHNER Elektrik IM6e) controlled by Thales software. The initial pH (pH_i), the pH after the immersion of pyrite electrode (pH_{ai}) and the final pH (pH_f) of solutions were measured using a combination glass electrode connected to a pH/millivoltmeter (Consort C534). Before each measurement, the glass electrode was calibrated against two commercial buffers (pH 4.01 and pH 7.00).

For each experiment, the reactor was filled with 250 mL of desired solution, introduced in a thermostated water bath, and equilibrated with air at the desired temperature. No stirring was performed, except for the slow air bubbling. The working electrode was equilibrated in the oxidizing solutions for > 40 min to assure steady states. For the potentiodynamic polarization the potential was scanned from –250 mV below the open circuit potential (OCP) to 250 mV above OCP at a scanning rate of 1 mV/s, and the results were processed using the Thales software. First, the cathodic and anodic Tafel slopes (β_c and β_a) were determined from tangents to the linear regions of the cathodic and anodic curves. Next, the oxidation potential (E_{ox}) and oxidation current density (j_{ox}) (Table 1) were obtained from the intersection point of these tangents. The computational uncertainties on E_{ox} (± 0.007 V), current density (± 16%), cathodic and anodic Tafel slopes (± 0.04 and ± 0.025 V/dec, respectively) were obtained from duplicate tests performed at 30 °C and in the pH range of 1 to 5. Impedance measurements were carried out at OCP with a sinusoidal signal of 10 mV amplitude and over a frequency range of 10 mHz–3 MHz.

3. Results and interpretation

3.1. pH measurements

The pH_{ai} drift with respect to pH_i is within uncertainties. The deviation of pH_f with respect to pH_{ai} is also small at low pH_i (Fig. 1). At higher pH_i values of 4 and 5, the pH slightly drifts to higher values. This increase could be explained by the non-oxidative dissolution of S(-II) presents on the electrode surface (Kamei and Ohmoto, 2000) and/or the

Table 1
Summary of the electrochemical kinetic parameters for pyrite in aerated HCl solutions with pH in the range of 1.0 to 5.0 and at temperatures between 25 and 40 °C.

pH	Temperature/°C	j _{ox} /μA cm ⁻²	E _{ox} vs. SHE/V	β _a /V	β _c /V
1.0	25	1.04	0.561	0.17	–0.12
2.5	25	1.31	0.516	0.16	–0.14
3.5	25	0.72	0.460	0.18	–0.16
4.0	25	1.18	0.442	0.20	–0.19
5.0	25	0.23	0.366	0.17	–0.17
1.0	30	1.30	0.573	0.15	–0.11
2.5	30	1.32	0.520	0.18	–0.13
3.5	30	1.43	0.477	0.19	–0.17
4.0	30	1.23	0.459	0.19	–0.19
5.0	30	0.44	0.372	0.14	–0.16
1.0	35	1.73	0.569	0.17	–0.11
2.5	35	1.94	0.519	0.16	–0.13
3.5	35	1.43	0.468	0.18	–0.17
4.0	35	1.49	0.431	0.21	–0.22
5.0	35	0.31	0.354	0.08	–0.10
1.0	40	2.24	0.577	0.14	–0.11
2.5	40	1.82	0.524	0.15	–0.14
3.5	40	1.61	0.467	0.18	–0.17
4.0	40	1.67	0.427	0.17	–0.20
5.0	40	0.88	0.366	0.18	–0.18

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