



Mechanism of the cathodic process coupled to the oxidation of iron monosulfide by dissolved oxygen

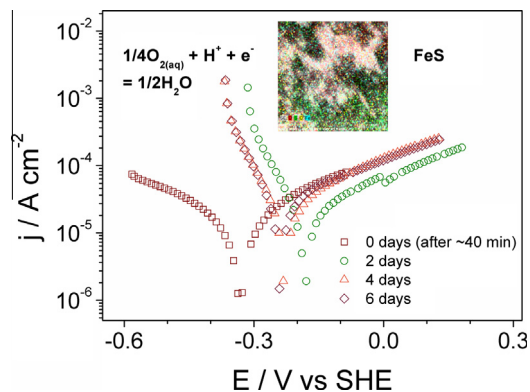


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GRAPHICAL ABSTRACT



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ABSTRACT

This study investigated the mechanism of iron monosulfide (FeS) oxidation by dissolved oxygen ($O_{2(aq)}$). Synthetic FeS was reacted with $O_{2(aq)}$ for 6 days and at 25 °C. We have characterized the initial and reacted FeS surface using Scanning Electron Microscopy coupled with Energy Dispersive X-ray (SEM/EDX) analysis, Raman spectroscopy and Fourier transform infrared spectroscopy (FTIR). It was found that during the aqueous oxidation of FeS new solid phases (disulfide, polysulfide, elemental sulfur, ferric oxyhydroxides and Fe_3O_4) develop on the mineral surface. The results of potentiodynamic polarization experiments show that after 2 days of FeS electrode immersion in oxygen bearing solution (OBS) at initial pH 5.1 and 25 °C the modulus of cathodic Tafel slopes dramatically decreases, from 393 mV/dec to 86 mV/dec. This decrease is ascribed to the change of the mechanism of electron transfer from cathodic sites to O_2 (mechanism of cathodic process). The oxidation current densities (j_{ox}) indicate that mineral oxidative dissolution is not inhibited by pH increase up to 6.7. Another conclusion, which emerges from the analysis of j_{ox} , is that the dissolved Fe^{3+} does not intermediate the aqueous oxidation of FeS. The results of electrochemical impedance spectroscopy (EIS) show that after 2 days of contact between electrode and OBS the properties of FeS/water interface change. From the analysis of the EIS, FTIR spectroscopy, Raman spectroscopy and SEM/EDX data we can conclude that the change of FeS/water interface properties accompanies the formation of new solid phases on the mineral surface. The new characteristics of the surface layer and FeS/water interface do not cause the inhibition of mineral oxidation.

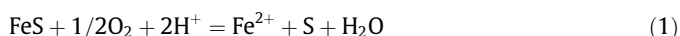
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1. Introduction

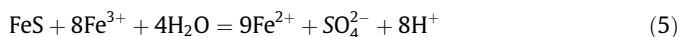
Iron monosulfide minerals (pyrrhotite, troilite and mackinawite) are present in various geological environments [1]. Also, iron monosulfide phases (FeS) can be present on the iron/steel surface as result of the reaction between H₂S (product of sulfate reduction [2]) and Fe²⁺ (product of iron/steel corrosion [3]). By its products of oxidation (ferric iron and protons), FeS oxidation can produce severe environmental problems [4,5]. In acidic media, the ferric iron is an effective oxidant which dissolves new amounts of FeS and other mineral sulfides [6] releasing toxic species such as Cu, Cd, Hg, Pb or As. Since the oxidation of FeS phases is fast (much faster than that of pyrite [7]), the understanding of the mechanism of aqueous oxidation of FeS is very important. Badica and Chirita [8] have shown that the aqueous oxidation of troilite by dissolved oxygen (O_{2(aq)}) occurs after an electrochemical mechanism. The oxidative dissolution of FeS in the presence of oxygen (the most common oxidant at the Earth's surface) generates a surface layer which incorporate ferric iron, oxygen, disulfide, polysulfide and elemental sulfur [4,9]. Also, FeS oxidation produces soluble species such as ferrous iron and sulfate:



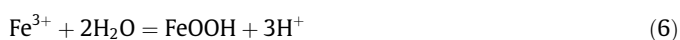
The aqueous oxidation of FeS is always accompanied by the non-oxidative dissolution, which is faster [4,10]:



The non-oxidative dissolution is an acid-consuming process. The released Fe²⁺ is oxidized by O_{2(aq)} to Fe(III). If the reaction occurs at acidic pH, the soluble Fe(III) (Fe³⁺) will oxidize FeS producing Fe²⁺ [11,12]:



As in the case of pyrite [13], it can appear a cycle in which the Fe²⁺ is oxidized to Fe³⁺, and the Fe³⁺ subsequently oxidizes the FeS and produces Fe²⁺. Fe²⁺/Fe³⁺ cycle can be interrupted at pH > 4 [4] (in many cases, the pH of oxidizing solutions) by the precipitation of Fe³⁺



The reactions (6) and (7) are acid-producing processes. The precipitation of Fe³⁺ can affect the oxidation of FeS by, on the one hand, the decrease of Fe³⁺ concentration [12], and, on the other hand, the hindering of the access of O_{2(aq)} to mineral surface [14]. Because the great majority of the experimental studies were performed in acidic media [4,15], the details of the reaction mechanism (the rate determining step(s), intermediates, reaction products, etc.) of FeS oxidation with O_{2(aq)} at high pH in aqueous media have not yet established.

In this paper, the aqueous oxidation of FeS in oxygen bearing solution (OBS) at initial pH 5.1 and 25 °C was studied by various techniques. At pH 5.1 the ferric iron solubility is very low (~10⁻¹¹ M) and it continues to decrease when pH increases up to 8 (10^{-12.26} M) [16]. Hence, in this pH range, Fe³⁺ cannot be the oxidant of FeS. To observe any behavioral changes, the aqueous oxidation of FeS was monitored by means of electrochemical techniques (potentiodynamic polarization and electrochemical impedance spectroscopy (EIS)) over a period of 6 days of FeS electrode immersion in OBS. The reaction products were analyzed using

chemical methods, Scanning Electron Microscopy coupled with Energy Dispersive X-ray (SEM/EDX) analysis, Raman spectroscopy and Fourier transform infrared spectroscopy (FTIR). For comparison, we carried out a series of electrochemical experiments with pyrite as electrode material.

2. Experimental

2.1. Materials

The characteristics of synthetic FeS (96 wt.% of troilite and 4 wt.% of elemental iron) and natural FeS₂ (pyrite) used in this study have been previously described in detail elsewhere [8,17–19]. All chemicals were of analytical grade and all solutions were prepared with distilled water.

2.2. Electrochemical experiments

The electrochemical measurements were performed in a standard three-electrode cell with an electrochemical workstation Zahner Elektrik IM6e. The working electrode (WE) was prepared by encapsulation of FeS (or FeS₂) in epoxy resin. Only one side, with the effective area of 0.5 cm² (or 1 cm² for the pyrite electrode) was exposed. It has been polished with 600, 2000 and 3000 grade silicon carbide paper. After polishing the electrode surface was rinsed with distilled water and acetone. The counter electrode was platinum foil, while reference electrode was saturated calomel electrode (SCE). The working electrode was immersed in OBS at initial pH 5.10 and 25 °C. The initial pH was adjusted to 5.10 by addition of diluted HCl, without any other background electrolyte. A constant flow of air was bubbled continuously through the solution. The initial pH and pH before each electrochemical measurement was measured with a combined glass electrode (Consort). Before each measurement the pH electrode was calibrated against two commercial pH buffers (pH 4.01 and pH 7.00).

Potentiodynamic polarization measurements were carried out with a scan rate of 1 mV/s in the potential range from –250 to +250 mV relative to the open circuit potential (OCP). Before the polarization measurement corresponding to 0 days, the electrode was allowed to equilibrate with the oxygen bearing solution for ~40 min. The electrochemical parameters (oxidation potential (E_{ox}), oxidation current density (j_{ox}), anodic and cathodic Tafel slopes (β_a and β_c)) were determined by analyzing the polarization data with Thales 3.16 software. EIS measurements were carried out at OCP over a frequency range of 3 MHz–10 mHz with a signal amplitude perturbation of 10 mV. The impedance data were validated using Z-HIT transform test (Fig. S1 of the Supplementary material) [8,17] and then fitted with an equivalent electric circuit using Thales software.

2.3. Aqueous batch experiment

In order to characterize the solid layer developed on the FeS surface during its aqueous oxidation the unreacted FeS powder and the residual solid resulted from an aqueous batch experiment were analyzed by FTIR spectroscopy. FeS powder was prepared by crushing in an agate mortar the same material used for the construction of WE. The specific surface area of the FeS powder was determined using BET method with a Micromeritics TriStar 3000 equipment and found to be 2.02 m²/g. The aqueous batch experiment was performed by the suspension of 1 g FeS powder in 0.5 L oxygen bearing HCl solution (initial pH 5.10) at 25 °C. The experiment lasted for 6 days, and a constant flow of air was bubbled continuously through the solution. At the end of aqueous batch experiments aliquots of suspension were removed with a

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