Oxidation of FeS by oxygen-bearing acidic solutions

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Abstract

Oxidation of FeS in oxygen-bearing acidic solutions was investigated at different temperatures (25 to 45 °C) and pH (2.75 to 3.45). The rate of the oxidative dissolution of FeS is strongly dependent on pH. The reaction order with respect to hydrogen ions has been found to be 1.03 ± 0.02 at 25 °C, and the apparent activation energy (Ea) is 41.6 ± 10.7 kJ mol⁻¹ at initial pH 3.00, suggesting that the FeS oxidative dissolution is controlled by the diffusion of oxidant species across a sulfur-rich layer (SRL) that undergoes chemical transformations leading to an increase in the mean number of sulfur atoms in polysulfide chains and the rearrangement of these chains. Fourier transform infrared spectroscopy and X-ray diffraction results obtained for the FeS samples reacted for 72 h at 25 °C and pH between 2.75 and 3.45 indicate the formation of goethite, of lepidocrocite, and of poorly ordered solid phases (assigned as SRL) on initial surfaces. The experimental data suggest a mechanism based on the protonation of FeS surfaces followed by oxidation of FeS by dissolved oxygen to produce Fe²⁺, S⁰, and S₂⁻. Fe²⁺ is unstable under oxidative conditions and transforms into Fe(OH)₃(s), goethite and lepidocrocite.

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1. Introduction

Sulfide minerals form one of the main groups of ore minerals, pyrite being by far the most abundant. Synthetic analogs, such as ZnS and CdS, are studied for their optical, electronic, and magnetic properties in solid-state electronics [1,2]. Hexagonal pyrrhotite (Fe₁₋₉S, 0 < q < 0.125), monoclinic pyrrhotite (Fe₁₋₉S, q = 0.125), and troilite (Fe₁₋₉S, 0 ≤ q < 0.05), generally named iron(II) monosulfides, are found in various natural environments in association with other valuable metal sulfide, together with coal or gold [3]. These minerals are thermodynamically stable under reducing conditions and are found in anoxic environments. They can be easily oxidized when they come into contact with aqueous fluids containing dissolved oxygen. Therefore, an understanding of the oxidative dissolution chemistry of iron(II) monosulfide is of interest for geochemistry, mineral processing, and treatment of resulting mineral wastes.

Because of its importance, the oxidative dissolution of iron(II) monosulfide has been studied using several experimental techniques, including aqueous batch experiments [4–8] and electrochemical [9–12] and spectroscopic studies [3,4,13–18].

There is general agreement that the surface of iron(II) monosulfide undergoes a sulfur enrichment as a result of preferential release of iron relative to sulfur on dissolution. This enrichment may be attributed to surface precipitation of S(0), according to

FeS + ½O₂(aq) + 2H⁺ = S(0) + Fe²⁺

or

FeS + 3/4O₂(aq) + 1/2H₂O = S(0) + FeOOH₃(s)

under more oxidative, iron(III)-promoting conditions.

The sulfur is incorporated into polysulfide chains (S₂⁻ₙ) and elemental sulfur (S⁰) [4]. The presence of S₂⁻ₙ and S⁰ was
proven by various spectroscopic studies of iron(II) monosulfide leached in anoxic [3,15,16] or air-equilibrated acidic solutions [6,13,14]. Jones et al. [19] found that after acid reaction the pyrrhotite surface partly restructures to a crystalline, defective tetragonal Fe₂S₃ phase in which linear chains of sulfur atoms have a S–S distance similar to elemental sulfur. Pratt et al. [4,14] analyzed with Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) a pyrrhotite surface reacted in air-equilibrated pH 3 H₂SO₄ solutions and HCl–H₂SO₄ acid mixtures, respectively. These techniques suggested the presence of several compositional layers including a surface coating of Fe(III)-oxyhydroxide, an underlying zone with a high S:Fe ratio and unreacted pyrrhotite.

According to findings by Janzen et al. [6] only a fraction (14 to 20%) of the sulfur component of pyrrhotite–troilite mixtures undergoes a complete oxidation generating sulfate ions:

\[
\text{FeS} + 2\text{O}_2 = \text{Fe}^{2+} + \text{SO}_4^{2-}.
\]

On the basis of sulfate production, they calculated activation energies ranging from 79.1 to 106 kJ mol⁻¹ at pH 2.5 for the oxygen oxidation of pyrrhotite–troilite mixtures. These activation energies are higher than those calculated on the basis of iron release, which range from 47.7 to 50 kJ mol⁻¹. However, the mineral samples used by Janzen et al. [6] were washed with 1 mol L⁻¹ HCl for 10 min before the kinetic tests. Acid washing dramatically alters the structure and composition of pyrrhotite or troilite surfaces [3,11,15–18], e.g., by creating a massive sulfur-rich layer (SRL) on mineral surfaces [16,17]. The formation of SRL is assigned to preferential dissolution of iron relative to sulfur. With the removal of iron from the FeS structure, monosulfide groups are oxidized to form polysulfide and elemental sulfur. Therefore, it is possible that the activation energies calculated on the basis of sulfate production reflect the kinetics of SRL oxidative dissolution, and not the kinetics of pyrrhotite or troilite oxidative dissolution. Pratt and Nesbitt [4] observed a rapid release of sulfate ions into solutions during the first 15 min of pyrrhotite dissolution in air-equilibrated acidic solutions. After this short period of time the sulfate concentration did not increase with reaction progress. Pratt and Nesbitt [4] concluded that the observed trend is the result of initially rapid dissolution of soluble iron sulfate existing on pyrrhotite [20,21], and that subsequent pyrrhotite oxidation is dominated by the oxidation of monosulfide groups into elemental sulfur and polysulfide, but not into sulfate.

These studies revealed that despite all of these efforts the main features of the iron(II) monosulfide oxidative dissolution remain unclear. For example, the nature of reaction products and stoichiometry are poorly understood. Also, very few data were collected to evaluate the reaction kinetics and mechanism under acidic pH.

To answer these questions, the iron(II) monosulfide (FeS) oxidation by oxygen-bearing acidic solutions can be followed by monitoring the changes in amounts of total dissolved iron and hydrogen ions. Indeed, it is well known that the total dissolved iron can be successfully used as a progress variable in solution at pH ≤ 4 (ferrous and ferric iron are soluble in acidic solutions), and proton concentration at pH ≥ 2.5 [22]. In contrast, at acidic pH most of the surface sulfide is oxidized into polysulfide and elemental sulfur rather than sulfate [4,6,18], and the reaction rate may be underestimated. Therefore the use of released sulfate is considered as an inappropriate progress variable.

The present work aimed at investigating the kinetics and mechanism of FeS oxidation by dissolved oxygen in acidic solutions as a function of pH (2.75 to 3.45) and temperature (25 to 45 °C). The changes in amounts of total dissolved iron and hydrogen ions were chosen to quantify the progress of the reaction. Additionally, Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) analyses were used to characterize the oxidation products of FeS.

2. Experimental

2.1. Characterization of FeS

Commercially available iron(II) monosulfide (FeS) in powder form (100 mesh, e.g., 149 µm, 99.9%) and packed under nitrogen was obtained from Aldrich. The surface area of particles was characterized by BET surface area analysis (Micromeritics ASAP2010) with Kr as adsorptive gas, and X-ray diffraction (Philips X’Pert diffractometer, CoKα radiation). A value of 0.345 ± 0.006 m² g⁻¹ was obtained for the surface area of the unreacted FeS powder. X-ray diffraction patterns revealed that the sample contained mostly 4 M pyrrhotite (Fe₇S₈) and troilite (FeS), together with minor amounts of pyrite (FeS₂), metal iron (Fe0), and elemental sulfur (S₈). No other solid phase could be detected.

2.2. Oxidation experiments and analytical determinations

All chemicals used were of analytical grade. Two sets of batch experiments were conducted. The first set investigated the kinetics of FeS oxidation by molecular oxygen in HCl solutions (10⁻⁴ to 10⁻³.45 mol L⁻¹) over 6 h of contact time (short-term experiments). The second set examined the kinetics of FeS oxidation by molecular oxygen under the same conditions with longer duration (72 h). The nature of solids at the end of these latter experiments was investigated. Reaction solutions were prepared by diluting reagent grade (Riedel–de Haen) hydrochloric acid (37%) with double-distilled water. Oxidation experiments were performed in Erlenmeyer flasks in contact with air and periodically shaken by hand. The flasks were filled with 250 mL of the desired reaction solution and then were immersed in a water bath held at constant temperature of 25, 35, or 45 (±0.1) °C. At the beginning of each experimental run, 0.5 g of FeS was added to a reaction solution that had been thermally equilibrated to the reaction temperature.

Periodically, a sample of 2 mL was extracted from the reaction solutions with a syringe connected to a 0.22-µm filter and analyzed for total dissolved iron (nFe) by spectrophotometry (2,2’-dipyridyl method, λ = 522 nm) on a SPECTOL 11 DDR spectrophotometer. The uncertainty in measured nFe was better than ±5% for amounts of dissolved iron above 10⁻⁴ mol L⁻¹.
The pH of solutions was measured at experimental temperature with a combination glass electrode (Ingold InLab 400; reported accuracy of ±0.01 pH units) connected to a pH/millivoltmeter (Mettler Delta 320). The combination electrode is specially designed for accurate temperature-compensated measurement of pH in solutions at ambient pressure and temperatures up to 50°C. Before each measurement, the pH electrode was standardized against two commercial pH buffers (Ingold 469863250, pH 4.01, and 469865250, pH 7.00). In two separate experiments the \( E_h \) of reaction solutions was monitored using a Pt electrode (ALASC Pt) coupled with a calomel reference electrode (ALASC ER 01) connected to a pH/millivoltmeter (Jenway 3305). The response of Pt electrode was checked before both experiments in Zobell’s solutions prepared from reagent grade salts (K₃Fe(CN)₆·3H₂O, K₃Fe(CN)₆, and KCl) and double-distilled water (\( E_h = 186 \text{ mV} / \text{SHE} \)). At the end of each long-term solution, the residual solution was discarded and FeS grains were sampled and stored in an evacuated and oxygen-free desiccator until analyzed by FTIR and XRD.

2.3. FTIR measurements

The FTIR spectra were collected with a FTS 40A Bio-Rad spectrometer. Samples were pressed as KBr pellets, and the FTIR spectra were recorded immediately after pellet preparation. Spectra were obtained in the 400 to 4000 cm\(^{-1}\) range with a resolution of 2 cm\(^{-1}\). Identification of different absorption bands on oxidized FeS surfaces was identified by comparison with a spectral database from sulfur and iron reference compounds of representative oxidation products [18,23–26].

2.4. X-ray diffraction of reacted samples

Samples for X-ray diffraction were reacted for 72 h at 25°C and pH 2.75 (DFeS1), 3.00 (DFeS2), and 3.45 (DFeS3), respectively. X-ray diffractograms were collected on a Philips PW3710 diffractometer, using a CuKα radiation, over a 4º–60º (2θ Cu) angular range, with an angular step of 0.02º 2θ Cu and a counting time of 1 s per step.

3. Results and interpretation

3.1. Effect of initial pH

The effect of initial pH on FeS dissolution was followed by monitoring the pH and the amount of total dissolved iron per unit of surface area (\( n_{Fe} \), in mmol m\(^{-2}\)) at 25°C (Figs. 1A–1D). During long-term dissolution experiments the pH increases up to pH 5 during the first 20 h (at initial pH 3.45) or 30 h (at initial pH of 2.75 and 3.00) of FeS dissolution, and then remains practically unchanged close to pH 5 (see Fig. 1B). As shown in Fig. 1C, \( n_{Fe} \) increases, but not regularly, during the first 6 h of FeS dissolution. When initial pH is 3.45, \( n_{Fe} \) increases up to 0.04 mmol m\(^{-2}\) (1 h), remains roughly constant between the first and the third hour of FeS oxidative dissolution (inhibition stage), and then increases again to 0.31 mmol m\(^{-2}\) (6 h). In contrast, at initial pH 3.00 \( n_{Fe} \) linearly increases up to 0.44 mmol m\(^{-2}\) (6 h). An inhibition period of iron release into solution is again observed during experiments conducted at initial pH 2.75, when \( n_{Fe} \) increases up to 0.08 mmol m\(^{-2}\) (1 h), remains roughly constant between the first and the second hour of FeS dissolution, and then increases again to 0.58 mmol m\(^{-2}\) (6 h). Fig. 1D reveals that the \( n_{Fe} \) continues to increase for approximately 20 h, and thereafter \( n_{Fe} \) remains roughly constant. Total dissolved iron amounts at initial pH of 2.75, 3.00, and 3.45 converge toward 1.41, 0.87, and 0.50 mmol m\(^{-2}\), respectively.

3.2. Effect of temperature

The influence of temperature on the FeS dissolution was studied at pH 3.00 by following pH and \( n_{Fe} \) values with time at 25, 35, and 45°C. As observed in Figs. 2A and 2B initial rates of \( n_{Fe} \) release and pH drift both increase with temperature. It is interesting to note that the trends in \( n_{Fe} \) observed at 35 and 45°C have parabolic shapes, as the release rate levels off after approximately 3 h of reaction. This long-term decrease in Fe release rate is paralleled by a constant increase in pH during each experimental run. In contrast, at 25°C the release rate of Fe is nearly constant during the 6 h of dissolution.

3.3. Solution \( E_h \)

The results of the two experiments designed to follow \( E_h \) variations during FeS dissolution are shown in Fig. 3. During the first 4 h, \( E_h \) continuously decreased with time from 597 to 509 mV/SHE and from 595 to 513 mV/SHE (initial pH 2.75 and 3.00, respectively). At initial pH 3.00, \( E_h \) continues to decrease after 4 h of FeS dissolution and attains 504 mV/SHE after 6 h of reaction. Instead, at initial pH 2.75, \( E_h \) first slightly increases at 519 mV/SHE after 4 h and then remains constant at 516 mV/SHE (6 h).

Despite the numerous possible redox couples in reaction, the evolution of \( E_h \) could be related to the equilibria between Fe\(^{2+}\) and amorphous Fe(OH)\(_{3(s)}\) (Fe(OH)\(_{3(amat)}\)) and between Fe\(^{2+}\) and goethite (\( \alpha\)-FeOOH\(_{3(s)}\)), according to

\[
E_h = 1.065 - 0.177 \log ([Fe^{2+}]) \quad (4a)
\]

and

\[
E_h = 0.74 - 0.177 \log ([Fe^{2+}]), \quad (4b)
\]

respectively (see Kamei and Ohmoto [27] and Neff et al. [28] for thermodynamic constants). Fig. 4 shows the theoretical equilibrium concentrations for Fe\(^{2+}\) at saturation with respect to Fe\(^{2+}\)/\( \alpha\)-FeOOH\(_{3(s)}\) and Fe\(^{2+}\)/Fe(OH)\(_{3(amat)}\) couples, respectively, for \( E_h = 500 \text{ mV} / \text{SHE} \). The solid rhombs in Fig. 4 represent log[Fe\(^{2+}\)] values ([Fe\(^{2+}\)] in mol L\(^{-1}\)) corresponding to experimental [Fe\(^{2+}\)] values measured after 6 h of oxidative dissolution at 25°C and initial pH 2.75, 3.00, and 3.45. It should be noted that for \( E_h = 500 \text{ mV} / \text{SHE} \), [Fe\(^{3+}\)] ≪ [Fe\(^{2+}\)], as can be simply estimated from the standard redox potential of the Fe\(^{3+}/Fe^{2+}\) couple (\( E_0^{0} = 770 \text{ mV} / \text{SHE} \)). Hence, we can assume that the experimental [Fe\(_{\text{total}}\)] equals [Fe\(^{2+}\)]. The log[Fe\(^{2+}\)] values fall below the equilibrium concentrations.
Fig. 1. pH and dissolved iron ($n_{\text{Fe}}$) variation during FeS oxidation at 25 °C and initial pH ranging from 2.75 to 3.45: (A) pH during short-term experiments; (B) pH during long-term experiments; (C) $n_{\text{Fe}}$ during short-term experiments; and (D) $n_{\text{Fe}}$ during long-term experiments.

Fig. 2. pH and dissolved iron ($n_{\text{Fe}}$) variation during FeS oxidation at initial pH 3.00 and under temperatures ranging from 25 to 45 °C: (A) pH; (B) $n_{\text{Fe}}$. 
of Fe$^{2+}/\alpha$-FeOOH$_{(s)}$ and Fe$^{2+}/$Fe(OH)$_3$(am) couples, indicating that solutions are close to saturation with respect to both solids. The differences between the theoretical [Fe$^{2+}$] (corresponding to Fe$^{2+}/\alpha$-FeOOH$_{(s)}$ equilibrium) and the measured [Fe$^{2+}$] clearly indicate that the equilibrium was not attained between Fe$^{2+}$ and $\alpha$-FeOOH$_{(s)}$ in the experimental solutions during the first 6 h of FeS oxidative dissolution. This disequilibrium can be explained by the slow oxidation kinetics associated with the conversion of dissolved ferrous iron to ferric iron by dissolved O$_2$ in acidic media. The increasing in both dissolved iron concentration and pH during the next hours of oxidative dissolution will create the necessary conditions for $\alpha$-FeOOH$_{(s)}$ and possibly Fe(OH)$_3$(am) precipitation. In fact, after approximately 30 h of dissolution, precipitates with the typical red-brown color of ferrihydrite become visible in the suspension.

### 3.4. FTIR spectroscopy

Fourier-transform infrared spectra (Fig. 5) show various features in the 400–1650 cm$^{-1}$ region, and broad bands around 3300 cm$^{-1}$. In general, OH stretch vibrations are observed in the region around 3300 cm$^{-1}$, including modes from water and other hydroxyl-bearing species such as ferric hydroxide or oxyhydroxide. The band at 3426 cm$^{-1}$ can be attributed to stretching modes of surface water molecules, while the shoulders at
3230, 3120, 3015, 2926, and 2854 cm\(^{-1}\) are due to stretching modes in Fe(OH)\(_{3(g)}\) and goethite [23]. The 1653 cm\(^{-1}\) band results from H–O–H deformation. The presence of carbonate ions is revealed by shoulders at 1456 and 740 cm\(^{-1}\) and bands at 1400 cm\(^{-1}\). The line at 740 cm\(^{-1}\) (present only in DFeS1, DFeS2, and DFeS3 spectra) can be also assigned to lepidocrocite [23]. The absorption bands observed in all spectra (unreacted FeS, DFeS1, DFeS2, and DFeS3) at 1200, 1167, 1115, 1022, 982, and 600 cm\(^{-1}\) clearly indicate the presence of sulfate on the FeS surface [24]. The shoulder bands at 1200 and 1456 cm\(^{-1}\) can be interpreted as respectively \(v_3\) and \(v_4\) frequencies of highly symmetrical \(SO_4^{2-}\) ions. The split of \(v_3\) vibration into a number of distinct vibrations (1167, 1115, 1022, and 982 cm\(^{-1}\)) is due to the perturbation of sulfate symmetry by its coordination with protons, ferrous and ferric iron [18,24–26]. The lines at 1115, 982, and 667 cm\(^{-1}\) can also be assigned to sulfite and thiosulfate coordinated to iron via oxygen [18,24].

The characteristic bands at 790 and 880 cm\(^{-1}\) are assigned to the Fe–O–H bending vibrations of Fe(OH)\(_{3(g)}\) and goethite [23,24]. According to Mikhlín et al. [18] the bands at 414 and 464 cm\(^{-1}\) can be assigned to elemental sulfur, polysulfide and disulfide species.

It is important to point out that the bands observed in the 900–4000 cm\(^{-1}\) region are more intense for unreacted FeS than for the reacted samples (DFeS1, DFeS2, and DFeS3). These observations suggest that the FeS sample is very hygroscopic and very reactive, undergoing a rapid process of oxidation during the preparation of FTIR pellets. This finding is in good agreement with the XPS studies by Buckley and Woods [21] and Mycroft et al. [20] showing that a pyrrhotite surface exposed to air is rapidly oxidized. The 1200–400 cm\(^{-1}\) region (Fig. 5) suggests that the unreacted surface of FeS mainly contains products of sulfur oxidation (the clear bands 1200, 1167, 1115, 1022, 982, 667, and 600 cm\(^{-1}\) assigned to sulfate, sulfite, and thiosulfate) and lesser products of iron oxidation (the flabby band 790 cm\(^{-1}\) assigned to Fe(OH)\(_{3(g)}\) and goethite). Also, it is evident that during pellet preparation the samples can adsorb CO\(_2\) from air. The signals of carbonate ions at 1456 and 740 cm\(^{-1}\) decrease after FeS dissolution, but shoulders at 740 cm\(^{-1}\) appear after the dissolution process. In the spectral region 400–900 cm\(^{-1}\) the reacted samples yield evident signals denoting the formation of Fe(OH)\(_{3(g)}\) and goethite on their surface after 72 h of oxidative dissolution. It is interesting to note that, according to Mikhlín et al. [18] (and references therein), the presence of a broad line at wavenumbers <800 cm\(^{-1}\) in the FTIR spectrum of their unreacted sample could be assigned to adsorbed water. This and the stronger signals observed for the unreacted sample at 1635 and 3426 cm\(^{-1}\), indicate that the surface of the initial sample is more hydrophilic than the surface of reacted samples. This is probably due to the formation of hydrophobic elemental sulfur and polysulfide species on the surface of reacted samples.

### 3.5. X-ray diffraction

Several features may be noted from the analysis of X-ray diffractograms collected for distinct reaction pH (Fig. 6). First, no contribution for \(\alpha\)-Fe(0) is observed after sample reaction, whatever the probed conditions. Second, the contribution of \(\alpha\)-S\(_8\) and of all iron sulfur compounds (pyrrhotite, trolite, pyrite) gradually decrease from DFeS1 to DFeS2 and to DFeS3. For example, the \(\alpha\)-S\(_8\) peaks at 3.863 and 3.457 Å can no longer be observed for DFeS3. Also, the amplitude of the pyrrhotite contribution at 2.054 Å is halved from DFeS1 to DFeS3. Third, goethite (diffraction peaks near 4.180 and 2.449 Å) and lepidocrocite contributions are clearly observed in all reacted samples, with the amplitude of goethite peaks increasing from DFeS1 to DFeS2 and to DFeS3. In addition, a broad band centered near 9 Å is observed for all reaction samples. This band presumably results from the formation of a poorly ordered solid phase. In conclusion, X-ray diffractograms confirm the presence of goethite, possibly lepidocrocite, and of poorly ordered solid phases in the reaction samples.

### 3.6. Dissolution rates

In order to determine the rate of FeS dissolution in hydrochloric solutions equilibrated with atmosphere, the amount of H\(^+\) “consumed” ([\(H^+\)]) was calculated from pH drifts, and plotted as a function of time (Figs. 7A and 7B). These plots show a decrease with time of the rate of proton removal from solution during the 6 h of oxidative dissolution. Plotting the data from Figs. 7A and 7B ([\(H^+\)]) against square root of time yields linear trends (Figs. 8A and 8B). These observations compare with those of Pratt and Nesbitt [4] and they suggest that the long-term kinetics of proton removal is mostly controlled by a slow, rate-limiting reaction of diffusion. The rate coefficients ([\(k_H\)]) derived from slopes of lines from Figs. 8A and 8B are given in Table 1. Obviously, \(k_H\) values increase with both increasing initial [H\(^+\)] and temperature. These trends are confirmed by plots of \(-\log(k_H)\) versus pH (Fig. 9) and \(-\ln(k_H)\)
versus 1/T (Fig. 10). Fig. 10 shows that dissolution of FeS is a first-order reaction with respect to [H\(^+\)] (slope of the regression line 1.03 ± 0.02). An apparent activation energy of 41.6 ± 10.4 kJ mol\(^{-1}\) was derived from the Arrhenius diagram presented in Fig. 10. The value of apparent activation energy suggests that a mix of surface reaction and diffusion controls the dissolution rate [29].

Because of different trends of \(n_{\text{Fe}}\) versus time (see Figs. 1C and 2B), our attempt to plot the total dissolved iron against square root of time gave a poor fit to many experimental data

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Table 1
Rate coefficients (\(k_{\text{H}}\)) for consumed H\(^+\) during FeS oxidative dissolution

<table>
<thead>
<tr>
<th>Initial pH</th>
<th>Temperature (°C)</th>
<th>Rate coefficient (k_{\text{H}}) (mmol m(^{-2}) h(^{-0.5}))</th>
<th>Error</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.75</td>
<td>25</td>
<td>0.439</td>
<td>0.018</td>
<td>0.952</td>
</tr>
<tr>
<td>3.00</td>
<td>25</td>
<td>0.250</td>
<td>0.007</td>
<td>0.974</td>
</tr>
<tr>
<td>3.45</td>
<td>25</td>
<td>0.084</td>
<td>0.003</td>
<td>0.970</td>
</tr>
<tr>
<td>3.00</td>
<td>35</td>
<td>0.542</td>
<td>0.019</td>
<td>0.968</td>
</tr>
<tr>
<td>3.00</td>
<td>45</td>
<td>0.657</td>
<td>0.025</td>
<td>0.954</td>
</tr>
</tbody>
</table>
and it was not possible to estimate meaningful rate coefficients of FeS dissolution, $k_{Fe}$, at studied pHs and temperatures.

### 3.7. $n_{H}^{+}:n_{Fe}$ ratio

From the presented results it is obvious that $n_{H}$ and $n_{Fe}$ differ in behavior, and that they show distinct trends as a function of time. Therefore we decided to use the $n_{H}$ to $n_{Fe}$ ratio ($n_{H}^{+}:n_{Fe}$) in order to interpret our experimental data. It must be noted that the ratios of Fe, S, and H dissolved concentrations were successfully used in different experimental studies to clarify the mechanisms of pyrite [22,30] and pyrrhotite [4] oxidation, or of troilite anoxic dissolution [31]. Therefore, $n_{H}^{+}:n_{Fe}$ ratios were calculated and plotted versus time (Figs. 11A–11C). At 25 °C $n_{H}^{+}:n_{Fe}$ shows distinct trends, over two time intervals. Over the first period of time (0–4 h), there are obvious changes in $n_{H}^{+}:n_{Fe}$ (Fig. 11A). All $n_{H}^{+}:n_{Fe}$ values are greater than 2 for $t \leq 4$ h, except for the value recorded after 4 h of dissolution at 25 °C and initial pH 3.45 ($n_{H}^{+}:n_{Fe} = 0.92$). The $n_{H}^{+}:n_{Fe}$ value decreases
from 7.97 (initial pH 3.00) down to 2.01 after 4 h of dissolution. At initial pH 2.75 and 3.45, \( n_{H^+}^{Fe} \) shows a different trend during the first 4 h of dissolution. Initially, it increases from 5.27 (initial pH 2.75) and 2.05 (pH 3.45) up to 6.44 and 4.02, respectively, over the first 3 h of dissolution. Then, it decreases down to 3.22 and 0.92, respectively. During the second time interval (4–72 h), \( n_{H^+}^{Fe} \) remains roughly constant (Fig. 11B).

The second time interval is characterized by \( n_{H^+}^{Fe} < 2 \). Nevertheless, \( n_{H^+}^{Fe} \) values at initial pH 3.45 (\( n_{H^+}^{Fe} \) average 0.97), 2.75 (\( n_{H^+}^{Fe} \) average 1.77), and 3.00 (\( n_{H^+}^{Fe} \) average 1.63) are clearly distinct.

At higher temperatures (35 and 45 °C) and pH 3.00, \( n_{H^+}^{Fe} < 2 \) and is quasi-invariant over the reaction time (Fig. 11C). The \( n_{H^+}^{Fe} \) ratios measured at 35°C (\( n_{H^+}^{Fe} \) ~ 1.4) and 45°C (\( n_{H^+}^{Fe} \) ~ 1.55) are close to \( n_{H^+}^{Fe} \) ratios recorded after 4 h of FeS dissolution at 25 °C and initial pH 3.00 (\( n_{H^+}^{Fe} \) average 1.59).

### 4. Discussion

Our experimental data indicate that FeS oxidation by oxygen-bearing acidic solutions is a complex process, characterized by different trends of \( n_{H^+}^{Fe} \) ratio and controlled by a mixed regime of surface reaction and diffusion. The observed high initial \( n_{H^+}^{Fe} \) ratios cannot be reasonably explained by the presence of minor amounts of FeS\(_2\) and \( \alpha\text{-S}_2 \) (the oxidation of both compounds is known as a proton-producing process), and \( \alpha\text{-Fe}\) (0) dissolution (a simple proton-consuming process) is expected to induce, at least at initial pH < 3.00, a \( n_{H^+}^{Fe} = 2 \) [32]. Therefore, our experimental data can be explained only by FeS (pyrrhotite and troilite) oxidative dissolution.

#### 4.1. Short-term reactions

Let us first assume that the large variations recorded for \( n_{H^+}^{Fe} \) ratios during the first 4 h of FeS dissolution be explained by simple overall reactions of solid dissolution yielding sulfoxanion release,

\[
\text{FeS} + \frac{1}{2} \left(1 + \frac{y}{x} - \frac{1}{3}\right) \text{O}_2 + 2 \left(1 - \frac{1}{x}\right) \text{H}^+ = \text{Fe}^{2+} + \frac{1}{x} \text{S}_x\text{O}_{y}^{2-} + \left(1 - \frac{1}{x}\right) \text{H}_2\text{O}.
\]

(5)

or simply leading to surface precipitation of elemental sulfur,

\[
\text{FeS} + \frac{1}{2} \text{O}_2 + 2\text{H}^+ = \text{Fe}^{2+} + \text{S} + \text{H}_2\text{O},
\]

(6)

where \( S_x\text{O}_{y}^{2-} \) is the sulfur-bearing species (polysulfide or sulfoxanion) resulting from FeS oxidative dissolution. As we can observe, the theoretical \( n_{H^+}^{Fe} \) ratio, \( 2(1 - 1/x) \), derived from Eq. (5) is lower than 2. Taking into account the iron deficiency (\( q \leq 0.125 \)) of pyrrhotite, \( n_{H^+}^{Fe} \) equals \( 2 - 2/x(1-q) \), still lower than 2. Equation (6) leads to a theoretical ratio \( n_{H^+}^{Fe} = 2 \) that also differs from most \( n_{H^+}^{Fe} \) ratios. It is thus clear that the initial process of FeS dissolution can be neither solid dissolution yielding formation of sulfoxanion nor elemental sulfur, but instead follows another reaction path. A first hypothesis is that the high \( n_{H^+}^{Fe} \) ratios observed at initial pH > 3 can be explained by ferrous iron oxidation into ferric iron and its removal from the system as ferric hydroxides or oxyhydroxides as shown by the evolution of \( E_h \) and the FTIR or XRD observations. In contrast, at pH < 3, \( n_{H^+}^{Fe} \) ratios cannot be reasonably explained by precipitation of any ferric or ferrous-bearing compounds. Hence, another explanation must be taken into consideration for the high \( n_{H^+}^{Fe} \) ratios recorded during the first time interval of FeS oxidative dissolution.

It is possible that preferential adsorption of iron occurs on the FeS surface during the first 4 h, or iron is obstructed to migrate from FeS surface into solution during this time interval. On the other hand, a preferential adsorption of ferrous iron at FeS surface at low pH seems difficult, and not been supported yet. On the other hand, there are various studies suggesting that the obstruction of iron migration from solid surface into solution is a consequence a SRL forming on FeS surface [3,4,8,14–18,31]. Keeping in mind this general observation, we propose a scenario for the initial stage of oxidative dissolution based on the model elaborated by Schippers and Sand [5] and Sand et al. [7]. The scenario states that the oxidative dissolution of FeS starts by proton attack to monosulfide groups followed by oxidation of protonated monosulfide groups into polysulfides and elemental sulfur. As a preliminary assumption, the surface is broken down in equal numbers of Fe and S sites, i.e., >Fe\(^{2+}\) and ∼S\(^{2-}\). Then, immediately after immersion, surface sulfide groups are rapidly protonated according to

\[
>\text{S}^{2-} + 2\text{H}^+ = >\text{SH}_2. \tag{7}
\]

A fraction (\( \alpha \)) of the surface >SH\(_2\) sites is transformed into ∼S\(_m^{2-}\) sites by oxidation with oxygen,

\[
\alpha >\text{SH}_2 + \frac{\alpha}{2} \left(1 - \frac{1}{m}\right) \text{O}_2 = \frac{\alpha}{m} >\text{S}_m^{2-} + \alpha \left(1 - \frac{1}{m}\right) \text{H}_2\text{O} + 2 \frac{\alpha}{m} \text{H}^+, \tag{8}
\]

and an equivalent fraction (\( \alpha \)) of iron (>Fe\(^{2+}\)) is released into solution:

\[
\alpha >\text{Fe}^{2+} = \alpha \text{Fe}_{(aq)}^{2+}. \tag{9}
\]

Reaction (8) is self-inhibiting, because the >S\(_m^{2-}\) polymers will hinder the oxidant (O\(_2\)) access to >SH\(_2\) groups and blocks a fraction (1 − \( \alpha \)) of >Fe\(^{2+}\) sites at the FeS surface. By combining Eqs. (7), (8), and (9) one obtains:

\[
>\text{FeS} + \frac{\alpha}{2} \left(1 - \frac{1}{m}\right) \text{O}_2 + 2 \left(1 - \frac{\alpha}{m}\right) \text{H}^+ = (1 - \alpha) >\text{Fe}^{2+} + (1 - \alpha) >\text{SH}_2 + \frac{\alpha}{m} >\text{S}_m^{2-} + \alpha \text{Fe}_{(aq)}^{2+} + \alpha \left(1 - \frac{1}{m}\right) \text{H}_2\text{O}. \tag{10}
\]

\( \alpha (0 \leq \alpha \leq 1) \) is the fraction of >SH\(_2\) groups being oxidized, and increases with reaction time. The \( n_{H^+}^{Fe} \) ratio correspond-
ing to reaction (10) is \(2(1/\alpha - 1/m)\). As \(\alpha\) is a function of time, \(n_{H2:n_{Fe}}\) ratio depends on time. Fig. 12 presents the plot of \(2(1/\alpha - 1/m)\) versus \(\alpha\) and \(m\). The \(2(1/\alpha - 1/m)\) parameter is computed for values of \(\alpha\) between 0.2 and 1 and for \(m\) between 2 and 8. As can be seen, the \(n_{H2:n_{Fe}}\) ratio decreases from 9.70 to 1.00 when \(\alpha\) increases from 0.2 to 1 and \(m\) decreases from 8 to 2. This is in good agreement with the observed variation of \(n_{H2:n_{Fe}}\) during an experimental run conducted at initial pH values 3.00. However, \(n_{H2:n_{Fe}}\) ratios observed during the first 3 h of experiments conducted at initial pH 2.75 and 3.45 seem not to be in good agreement with this proposed model. The observed variation of \(n_{H2:n_{Fe}}\) ratios during experiments conducted at initial pH 2.75 and 3.45 can be explained only by an additional process that occurs after >SH₂ oxidation to \(>S^{m-}\), namely the condensation of \(>S^{m-}\) to form \(>S^{n-}\) groups (\(n > m\)) according to

\[
\beta >S^{2-}_m + \frac{\beta}{2} \left(1 - \frac{m}{n}\right)O_2 + 2\beta \left(1 - \frac{m}{n}\right)H^+ = \beta \frac{m}{n} >S^{2-}_n + \beta \left(1 - \frac{m}{n}\right)H_2O. \tag{11}
\]

where \(\beta\) (0 \(\leq\) \(\beta\) \(\leq\) 1) is the degree of \(>S^{2-}_m\) transformation into \(>S^{2-}_n\), and \(m\) and \(n\) denote mean sizes of polysulfide groups. The reaction (11) is characteristic of the inhibition stage of FeS oxidative dissolution and depicts a SRL rearrangement process leading to a decrease in the mean number of sulfur atoms in chains. We can then propose that the obstructive effect of SRL depends on the length and relative position of S chains. The short S chains are thought to easily arrange into closely packed structures, while the long S chains awkwardly adopt such arrangements. Hence, iron migration among short S chains will be more difficult. After approximately 1 h of dissolution at initial pHs 2.75 and 3.45, the FeS surface must be covered by a SRL formed by short S chains. This SRL will inhibit the iron migration into solution. Gradually, this SRL undergoes a rearrangement process (according to Eq. (11)). As the length of S chains increases, the protons are consumed and \(n_{H2:n_{Fe}}\) will increase. When SRL becomes more permeable for iron (end of the inhibition period), iron starts to migrate into solution and \(n_{H2:n_{Fe}}\) then decreases.

Unfortunately details on the SRL structure, on the number of sulfur atoms in chains, and on their impact on Fe migration into solution are lacking. Only the study of Jones et al. [19] provides information regarding the structure of SRL formed during pyrrhotite dissolution in deoxygenated acidic solutions. According to these authors the formed SRL (Fe₂S₃) has a defective tetragonal symmetry. In the present study, the formation of a poorly ordered solid phase (SRL) is inferred from the broad XRD band centered near 9 Å (Fig. 6).

According to Pratt et al. [14], Pratt and Nesbitt [4], and Thomas et al. [3] the product (SRL) of oxidative dissolution of pyrrhotite consists of polysulfide (\(S^{2-}_n\)) and elemental sulfur. Hence, a possible >SH₂ oxidation to elemental sulfur should not be neglected according to

\[
>FeS + \frac{\alpha}{2}O_2 + 2H^+ = (1 - \alpha)>Fe^{2+} + (1 - \alpha)>SH_2 + \alpha>S^0 + \alpha Fe^{2+}_{(aq)} + \alpha H_2O, \tag{12}
\]

and the \(n_{H2:n_{Fe}}\) ratio is \(2/\alpha\). Notwithstanding, Mikhlin et al. [18] considered that the oxidation of >SH₂ groups unlikely proceeds directly into elemental sulfur. Hence, we assume that the elemental sulfur is formed during the rearrangement process of SRL described by

\[
\gamma >S^{2-}_m + \frac{\gamma}{2}O_2 + 2\gamma H^+ = \gamma \frac{m}{8} >S_{8(\alpha)} + \gamma H_2O, \tag{13}
\]

where \(\gamma\) (0 \(\leq\) \(\gamma\) \(\leq\) 1) is the degree of \(>S^{2-}_m\) transformation into \(>S_{8(\alpha)}\). In conclusion, although our results somewhat disagree with those of Jones et al. [19], they are in agreement with those of Mikhlin et al. [18]. Therefore the model developed in this latter paper may well describe the mechanism of FeS oxidative alteration in our system.

### 4.2. Long-term reactions

After approximately 4 h, the constant \(n_{H2:n_{Fe}}\) ratios point to a stable dissolution regime. To explain this stable regime, three overall chemical processes are suggested. First, during the first time subinterval (up to 20 h) the following net reaction

\[
>FeS + \frac{1}{2} \left(1 - \frac{1}{n}\right)O_2 + 2 \left(1 - \frac{1}{n}\right)H^+ = \frac{1}{n} >S^{2-}_n + Fe^{2+}_{(aq)} + \left(1 - \frac{1}{n}\right)H_2O \tag{14}
\]

would induce a \(n_{H2:n_{Fe}}\) ratio equal to 2(1 - 1/n) < 2, in good agreement with experimental observed ratios. After approximately 20 h of dissolution (the second time subinterval) the net reaction explaining oxidative dissolution may be
FeS + \frac{1}{4}(3 - \frac{2}{n})O_2 + \left(\frac{1}{2} + \frac{1}{n}\right)H_2O \\
= \alpha-FeOOH(\gamma-FeOOH) + \frac{1}{n}S^{2-}_n + \frac{2}{n}H^+.

(15)

Or, assuming the precipitation of solid sulfur,

FeS + \frac{3}{4}O_2 + \frac{1}{2}H_2O = \alpha-FeOOH(\gamma-FeOOH) + S_{(s)}.

(16)

For these reactions the theoretical \(n_H:n_{Fe}\) ratios cannot be estimated, as there is no net release of iron in the supernatant. Occurrence of these reactions is suggested, on one hand, by the evolution in dissolved iron and proton concentrations after approximately 20 h of dissolution, and, on the other hand, by the FTIR and XRD observation of goethite and lepidocrocite. Note that the presence of lepidocrocite in reacted samples may also be explained by aqueous Fe\(^{2+}\) oxidation [33]. The presence of lepidocrocite in leaching solutions was also reported by Pratt and Nesbitt [4].

Contrary to Eq. (14), Eq. (15) anticipates a release of \(2/n\) moles of protons per mole of oxidized FeS. This production is confirmed by the slight decrease of experimental \(n_H:n_{Fe}\) ratios toward the end of the experiments (Fig. 11B).

During the FeS oxidative dissolution, a fraction of surface sulfur may have oxidized to form \(S_x\) \(O_y\)\(^{2-}_{(aq)}\) species, such as sulfite, sulfate, thiosulfate, or tetrathionate [34]. The formation of these species is confirmed by characteristic FTIR signals of sulfoxyanions (for example, the lines at 1115, 982, and 667 cm\(^{-1}\)). These structural modifications may complicate the oxidation process [35]. Oxidation of sulfide to sulfate implies the transfer of eight electrons, while oxidation to polysulfide or elemental sulfur implies the transfer of a maximum of two electrons. Therefore, the oxidation of sulfur to sulfate likely involves several supplementary elementary reactions in comparison with oxidation into polysulfide or elemental sulfur.

4.3. The nature of the observed reaction order with respect to [H\(^+\)]

As stated bellow, the FeS sulfur oxidation into polysulfide species or elemental sulfur implies the transfer of one up to two electrons per sulfur atom and, mainly, various structural modifications. These structural modifications may complicate the sulfur oxidation process. Instead, the iron removal from solid FeS would be a simple process because its oxidation to iron(III) implies the transfer of only one electron and does not involve important structural modifications. In addition, Pratt and Nesbitt [4] and Chirita and Descostes [8,31] have postulated that protons (species with small dimensions that easily migrate through solution and SRL) promoted the ferrous iron diffusion from FeS bulk into solution. The oxidation of sulfur groups from the FeS surface by molecular oxygen induces proton release or consumption (see, for example, Eqs. (8), (11) or (13)). Instead, the iron dissolution does not result in any variation of proton concentration (except when ferric (oxy)hydroxide precipitate). Hence, the observed reaction order with respect to [H\(^+\)] could illustrate the oxidation and structural reorganization of FeS sulfur. The evaluated reaction order with respect to [H\(^+\)] (1.03 ± 0.02), the value of apparent activation energy \(E_a = 41.6 ± 10.7 \text{ kJ mol}^{-1}\), and the square-root dependence of \(n_H\) against time (Figs. 8A and 8B) suggest that the sulfur oxidation is controlled by the diffusion of oxidant species across SRL that undergoes evident chemical transformations (rearrangement processes) modifying its porosity and permeability [8].

The nature of oxidant species remains unclear. On one hand, ferric iron (the oxidation product of Fe\(^{2+}\) resulting from Eq. (1)) has a smaller size than molecular oxygen and it can easily permeate the SRL toward >SH\(_2\) groups, but, on the other hand, taking into account the low concentration of ferric iron (as a consequence of the slow oxidation rate of dissolved Fe\(^{2+}\) into Fe\(^{3+}\) by dissolved O\(_2\) in acidic media), the dissolved oxygen appears as a more likely oxidizer for >SH\(_2\) groups. Schippers and Sand [5] showed that both species (Fe\(^{3+}\) and O\(_2\)) can act as oxidizing agents of FeS, forming elemental sulfur and polysulfide polymers, but Fe\(^{3+}\) is much more efficient than O\(_2\) for extracting electrons from the FeS lattice. Studies of pyrite oxidation have also shown that ferric iron is a more aggressive oxidant than the dissolved oxygen [36,37]. At lower pH (<3.5) the rates of pyrite oxidation by Fe\(^{3+}\) are one order of magnitude higher than by O\(_2\) [38]. According to Luther [39] the efficiency of Fe\(^{3+}\) is due to its higher capacity to chemically bind to the pyrite surface than O\(_2\). In conclusion, Fe\(^{3+}\) likely acts as an oxidizer for >SH\(_2\) groups at lower pH (<3.5), and O\(_2\) as an oxidizer for >SH\(_2\) groups at higher pH (>3.5).
Future studies should be designed to take into account the surface protonation of FeS, and the sorption of Fe\(^{2+}\) and other metal cations on the FeS surface. Knowledge of the acid-base properties of the FeS/water interface will certainly help to improve our understanding of their dissolution kinetics and mechanisms.

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References