Anoxic dissolution of troilite in acidic media

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Received 24 May 2005; accepted 22 July 2005
Available online 9 September 2005

Abstract

The anoxic dissolution of troilite (FeS) in acidic medium has been investigated at 50 °C using batch dissolution experiments. Two different progress variables were followed during solid dissolution, i.e., the amounts of dissolved iron (nFe) and formed hydrogen sulfide (nH2S). The experimental studies performed at hydrogen ion concentrations ([H+] ) ranging from 0.04 to 0.2 mol L−1 showed that anoxic dissolution of troilite is dependent on [H+]. The cumulative release of both Fe and H2S could be described by a diffusion-like rate law, with rate constants for Fe (kpFe) always greater than for H2S (kpH2S). The surplus of dissolved iron over formed hydrogen sulfide was quantified by the nFe:nH2S ratio, and ranged from 1.21 to 1.46, higher than the specific nFe:nH2S ratio of troilite bulk, i.e., 1. Rate constants are linearly related to the pH with a slope of 0.66 ± 0.23 (kpFe) or 0.63 ± 0.13 (kpH2S). The obtained results suggest that troilite anoxic dissolution is a process controlled by the diffusion of the reaction products across an obstructive layer, sulfur-rich layer (SRL), having a thickness that increases during reaction progress. The accumulation of H2S between the surface and the SRL, eventually leads to the mechanical destruction of this outer layer, a process that results an increased flux of reaction products.

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Keywords: Troilite; Hydrogen sulfide; Dissolved iron; Anoxic dissolution; Reaction mechanism; Diffusion

1. Introduction

The dissolution reaction of iron sulfide is of high importance in various natural or industrial processes (acid mine drainage, remediation of mineral wastes, or metal extraction). There are two important categories of natural iron sulfide: iron disulfide (FeS2), such as pyrite and marcasite, and iron monosulfide (Fe1−xS), such as troilite, mackinawite and pyrrhotite. The second category encompasses a series of nonstoichiometric members (0 < x ≤ 0.125), on the whole called pyrrhotite, and a stoichiometric endmember called troilite (x = 0). However, a limited iron deficiency is allowed even for troilite [1]. Furthermore, an important characteristic of troilite and pyrrhotite consists in the presence of various imperfections on their surface, such as truncated Fe–S bonds, iron deficiency, or the presence of oxidized species of iron and sulfur [2–11].

In contrast to the high interest paid to the dissolution process of iron disulfide [12–18], little attention was given to the dissolution process of iron monosulfide. Only a few studies were dedicated to troilite [10,19] and pyrrhotite dissolution [8–10,19–22] and their results are not always in good agreement. Unlike iron disulfides, which dissolve only in presence of an oxidizing agent, troilite and pyrrhotite can undergo both oxidative and nonoxidative dissolution processes [23]. Both dissolution mechanisms proceed nonstoichiometrically, with a preferential release of iron [8–10,21,22]. Oxidative dissolution releases ferrous and ferric iron, and sulfate [22,24]. Additionally, a partial oxidation of FeS by ferric iron or oxygen may produce elemental sulfur [8,9,22] according to:

FeS(s) = S0 + Fe2+ + 2e− (1)
thermodynamically unstable in acidic medium (pH < 5). The sulfide surface of iron monosulfide can be simply written: 

\[ \text{FeS (s)} \] 

The overall mass balance for acidic dissolution of troilite dissolution in anoxic medium should be hydro- 

dissolution [8–10,19]: 

\[ \frac{1}{2} \text{O}_2(\text{aq}) + 2 \text{H}^+ + 2e^- = \text{H}_2\text{O}. \] 

It must be noted that during air oxidation, the iron monosulfide surface undergoes sulfur enrichment [2,5]. The sulfur-rich layer (SRL) forming on the iron monosulfide surface consists of elemental sulfur and various polysulfide ions [2,5,7]. 

The stability diagram of Fe–S system (calculated for \( \sum \text{[Fe]} = [\text{S}] = 10^{-3} \, \text{mol} \, \text{L}^{-1} \) [23]) predicts that troilite is thermodynamically unstable in acidic medium (pH < 5). This diagram also shows that the main sulfur-bearing product of troilite dissolution in anoxic medium should be hydrogen sulfide. The overall mass balance for acidic dissolution of iron monosulfide can be simply written:

\[ \text{FeS(s)} + 2\text{H}^+(\text{aq}) = \text{Fe}^{2+}(\text{aq}) + \text{H}_2\text{S(}\text{aq}). \] 

Laboratory investigations however showed that the dissolution mechanism is more complex than would be inferred from this simple mass balance relation. This complexity can be illustrated by the four stages reported during pyrrhotite dissolution [8–10,19]:

1. the dissolution of outermost layer consisting from oxidized species of iron and sulfur;
2. the inhibition of dissolution as a result of the formation/presence of a SRL;
3. the “reduction” of the SRL, concomitant with proton attack on \( S^{2-} \) groups resulting in a rapid release of iron and sulfur;
4. the “oxidative” dissolution, characterized by formation of a new sulfur-rich phase on the surface and a slow release of iron.

It is assumed that at temperatures \( \leq 40^\circ C \), the SRL strongly hinders the attack of protons on surface \( S^{2-} \) groups [8]. In such conditions the inhibition periods are long and the pyrrhotite dissolution is controlled by diffusion. However, when temperature exceeds 40 \( ^\circ C \), the SRL can be destroyed as a result of complex reactions that, on the whole, consist in sulfur reduction into hydrogen sulfide by the electrons accumulated on the pyrrhotite surface [8,9], according to:

\[ S_{n(s)}^{2-} + 2(n - 1)e^- = nS_{(aq)}^{2-}. \] 

Therefore, at high temperatures the solid dissolution is kinetically controlled by a surface reaction [19].

The proposed mechanism explains many features of FeS anoxic dissolution, but some aspects of this reaction are still unclear. Perhaps, the main remaining question is that the anoxic dissolution is depicted as a mixture of reductive, oxidative, and nonredox processes. 

In this work we examine the kinetics of the anoxic dissolution of synthetic troilite as a function of perchloric acid concentration [HClO\(_4\)] at 50 \( ^\circ C \) by monitoring dissolved Fe (\( n_{\text{Fe}} \)) and released H\(_2\)S (\( n_{\text{H}_2\text{S}} \)). The variation in concentration of both reaction products will be investigated to clarify the mechanism of troilite dissolution, and discuss the various different mechanisms for iron and sulfur release from iron monosulfide proposed in earlier studies.

2. Experimental

Synthetic troilite obtained from Rieden-De-Haen was used in this study. The troilite was prepared into a nitrogen-filled glove bag. The material was crushed under ethanol in a ceramic mortar. After crushing, the supernatant suspension was decanted and the solid material was rinsed with ethanol. The cleaning procedure was repeated until the supernatant was relatively clear. The troilite sample was transferred under vacuum, where it was dried. The particles below 63 \( \mu m \) were further separated by dry sieving under nitrogen atmosphere. These particles were transferred in an evacuated desiccator where they were stored until use. No crystalline impurities were detected by XRD analysis. An acid cleaning, like for pyrite [18], was not applied in this study because of such a pretreatment may cause an alteration of the troilite surface. It is well known that by etching in acidic solutions the pyrrhotite dramatically change its surface structure and composition [6,7].

Specific surface of the unreacted troilite grains was determined by Kr-BET using a MICROMERITICS ASAP 2010 analyzer. The surface area was 0.5053 ± 0.0031 m\(^2\) g\(^{-1}\).

The dissolution experiments were performed in an air-tight, round bottomed reactor (1 L) under an atmosphere of oxygen-free methane which had been passed through pyrogallol. No stirring system was used, as the suspensions were sufficiently homogenized only by methane bubbling. A constant temperature of 50 \( ^\circ C \) was maintained with a thermostated bath. All experiments were carried out with the same initial water to solid ratio (1:700 g:ml). The reactor has ports for troilite sample and methane inlet, methane and H\(_2\)S outlet, and suspension sampling (Fig. 1). The gas flowing out of the outlet was first flowed through a condenser, and then to a H\(_2\)S trapping system made of two parallel-mounted flasks containing copper acetate. The H\(_2\)S released by troilite anoxic dissolution was precipitated as CuS in these flasks by bubbling the evolved gas in 0.5 L copper acetate solution (0.02 mol L\(^{-1}\)) in a flush of methane at 3.3 L min\(^{-1}\) flow. In each experiment the onset of H\(_2\)S formation was immediately (up to 5 s) visualized by a dark precipitate forming into the copper acetate solution. The flasks were easily changed between each troilite dissolution stage, by the mean of two connectors.

Perchloric acid solutions (0.04, 0.06, 0.1 and 0.2 mol L\(^{-1}\)) were prepared by diluting 70–72% HClO\(_4\) solution (Merck, p.a.) into distilled deionised water. Prior to each experiment, these solutions were deaerated by bubbling methane for at least 1 h and equilibrated at 50 \( ^\circ C \).
The quantity of released H$_2$S during a given dissolution stage period of time was obtained by deviating the outflowing gas through the parallel flask, centrifuging the flask content, and determining by titration the copper remaining in the clear supernatant by EDTA [25].

For determination of the amounts of total dissolved iron (n$_{Fe}$), 20 ml aliquots of the suspension were withdrawn through a sample port fitted with a filter (5 µm pore-size). After a second filtration (0.22 µm pore-size) dissolved iron was fully oxidized and later analyzed by EDTA method [25]. The quantity of iron was corrected for volume modification and extracted iron. Additionally, the quantity of ferric iron in solution [Fe(III)], was monitored by immediate analysis of 5 ml supernatant aliquots withdrawn from the reactor using the ammonium thiocyanate method [26]. The detection limit of this method is 1 µm L$^{-1}$.

3. Results and interpretation

3.1. Effect of perchloric acid concentration on troilite anoxic dissolution

The temporal evolution of dissolved iron and formed hydrogen sulfide as a function of perchloric acid concentration ([HClO$_4$]) is illustrated in Figs. 2a and 2b. Both figures show that the rate of anoxic troilite dissolution increases with [HClO$_4$]. Practically, when the [HClO$_4$] increases from 0.04 to 0.2 mol L$^{-1}$, n$_{Fe}$ and the cumulative amount of released H$_2$S (n$_{H_2S}$) increase from 7 to 19 and from 5 to 15 mmol m$^{-2}$, respectively, over a time span of 1200 s.

Also visible in Fig. 2a is the decreasing rate of Fe(II) production as a function of time, as well as some small but significant deviations from this trend, especially at higher pH.
Fig. 3. Reproducibility of troilite dissolution experiments in 0.06 mol L\(^{-1}\) perchloric acid at 50° C. ([HClO\(_4\)] = 0.06 and 0.04 mol L\(^{-1}\)). The same observations can be made for \(n_{H_2S}\) as a function of time (e.g., Fig. 2b). In order to verify if the apparition of these deviations were fortuitous, duplicate experiments for troilite dissolution in 0.06 mol L\(^{-1}\) HClO\(_4\) were conducted. The results of the two sets of experiments (Fig. 3) confirm the existence of these deviations characteristic of troilite dissolution at low acid concentration.

3.2. Ferric iron concentration

Fig. 4 plots the evolution of [Fe(III)] during troilite dissolution in 0.06 mol L\(^{-1}\) HClO\(_4\). During the first 4000 s, [Fe(III)] was below the detection limit. After 4000 s a rapid increasing of [Fe(III)] to 23.3 µmol L\(^{-1}\), followed by a slight decrease is observed. The ferric iron apparition in acidic solutions clearly begins only when the rate of H\(_2\)S release decreases.

3.3. Kinetics analysis

The reaction which kinetically controls the whole process can be identified from the kinetics of Fe and H\(_2\)S release in solution [27]. The decreasing rate of Fe(II) and H\(_2\)S production as a function of time suggests that the troilite anoxic dissolution is controlled by a diffusion process. Indeed, when a process is controlled by diffusion, the quantity of reaction products is expected to linearly increases with square root of time [28], according to:

\[
\frac{n}{X} = \frac{n}{X}^0 + 2k_p^{X} t^{0.5},
\]

where \(n_X\) is the quantity of component X in the system at time \(t\), \(n_X^0\) is the quantity of component X in the system at time \(t = 0\), \(k_p^{X}\) are rate coefficients.

The equations fitting the experimental data for dissolved iron and formed H\(_2\)S are of the form:

\[
n_{Fe} = 2k_p^{Fe} t^{0.5}
\]

and

\[
n_{H_2S} = 2k_p^{H_2S} t^{0.5}.
\]

The experimental data from Figs. 2a and 2b were plotted against the square root of time (Figs. 5a and 5b). A linear trend vs \(t^{0.5}\) is clearly observed for \(n_{Fe}\) and for \(n_{H_2S}\) after a certain period of time. The absence of a linear trend for H\(_2\)S at short reaction periods likely results from the consumption of some H\(_2\)S as a result of side reactions with ferric iron present in system or a low initial concentration of sulfide groups on troilite surface [8]. Also, a particular slow initial diffusion of H\(_2\)S could be responsible for this low gas production. Additionally, the apparition of some H\(_2\)S surges was observed during dissolution experiments at low acid concentration. The H\(_2\)S surges can be easily noted in Fig. 6 where the average rate of H\(_2\)S formation over a period of time (rate(H\(_2\)S)) was plotted at the end of each time period. This observation points out to a similarity between the behavior of troilite and pyrrhotite dissolution in anoxic conditions.

The rate coefficients \((k_p^{Fe} and k_p^{H_2S})\) derived from the slope of regression lines are given respectively in Table 1. It must be stated that the initial quantity for both Fe and H\(_2\)S
equals is zero \( (n_X^0 = 0) \). From Table 1 it is clear that \( k_{Fe}^p \) is always greater than \( k_{H_2S}^p \), meaning that the Fe release rate is higher than that of \( H_2S \) release. Also, both rate coefficients increase with initial \([HClO_4]\). This trend is confirmed by plots of \(-\log(k_{Fe}^p \text{ or } k_{H_2S}^p)\) against pH (Fig. 7). Fig. 7 also shows that troilite anoxic dissolution is a fractional order reaction with respect to \([HClO_4]\). The obtained values of reaction order when the used progress variables were \( n_{Fe} \) or \( n_{H_2S} \) were 0.66±0.23 and 0.63±0.13, respectively is found. The obtained values of reaction order are identical (within uncertainties) and consistent with a kinetics controlled by a diffusion of both reaction products through an obstructive layer on troilite surface.

The integral form of rate law is:

\[
n_{Fe} = 0.85(\pm0.50)[H^+]^{0.66(\pm0.23)}t^{0.5} \quad \text{(9)}
\]

and

\[
n_{H_2S} = 0.58(\pm0.21)[H^+]^{0.63(\pm0.13)}t^{0.5} \quad \text{(10)}
\]

**Table 1**
Linear regression parameters for iron dissolution \( (n_{Fe} = 2k_{Fe}^p t^{0.5}) \) and hydrogen sulfide production \( (n_{H_2S} = 2k_{H_2S}^p t^{0.5}) \) during troilite dissolution in acidic medium.

<table>
<thead>
<tr>
<th>Medium (mol L(^{-1}))</th>
<th>( 2k_{Fe}^p ) (mmol m(^{-2}) s(^{-0.5}))</th>
<th>Error</th>
<th>( R^2 )</th>
<th>( 2k_{H_2S}^p ) (mmol m(^{-2}) s(^{-0.5}))</th>
<th>Error</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>([HClO_4]) = 0.04</td>
<td>0.194</td>
<td>0.009</td>
<td>0.992</td>
<td>0.154</td>
<td>0.007</td>
<td>0.989</td>
</tr>
<tr>
<td>([HClO_4]) = 0.06</td>
<td>0.277</td>
<td>0.021</td>
<td>0.981</td>
<td>0.194</td>
<td>0.030</td>
<td>0.942</td>
</tr>
<tr>
<td>([HClO_4]) = 0.06(^a)</td>
<td>0.275</td>
<td>0.024</td>
<td>0.966</td>
<td>0.186</td>
<td>0.028</td>
<td>0.931</td>
</tr>
<tr>
<td>([HClO_4]) = 0.1</td>
<td>0.426</td>
<td>0.041</td>
<td>0.981</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>([HClO_4]) = 0.2</td>
<td>0.557</td>
<td>0.020</td>
<td>0.997</td>
<td>0.418</td>
<td>0.040</td>
<td>0.969</td>
</tr>
</tbody>
</table>

\(^a\) The result of duplicate experiment.
Both ble 2. Calculated cause the formed H 2 S undergoes a series of side reactions (Table 1) can be mainly attributed to counter ion action of data. In order to evaluate this ratio, \( n \) and acidic solution. However, these experiments also point across an obstructive layer existing between troilite surface step of which is a diffusion process of reaction products.

4. Discussion

Our experiments clearly demonstrate that global troilite dissolution is an incongruent process, the rate controlling step of which is a diffusion process of reaction products across an obstructive layer existing between troilite surface and acidic solution. However, these experiments also point to distinct rate coefficients for Fe and H 2 S, presumably because the formed H 2 S undergoes a series of side reactions that modify \( n \). In the next sections one will discuss the manner by which the iron dissolution and hydrogen sulfide formation proceed. Two phenomena are here postulated to be of fundamental importance:

1. the easy diffusion of protons through solution and an obstructive layer existing on troilite surface;
2. the differences between diffusion rate of H 2 S and Fe 2+ through the obstructive layer.

4.1. Diffusion of reaction products through an obstructive layer

The enhanced release rate of Fe with increasing [HClO 4 ] (Table 1) can be mainly attributed to counter ion action of protons on ferrous iron existing on troilite surface [21]. Both chemical species have a positive charge, and between each other a repulsive Coulombic force appears. Therefore, as the concentration of protons near iron site increases the number of repulsive forces increases, and so the rate of iron diffusion through obstructive layer increases. This situation occurs because protons are chemical species with very low size, and can easily diffuse in the solution and through the obstructive layer existing on troilite surface. Hence, we may postulate that the surface concentration of protons is at equilibrium with the solution concentration. The iron and H 2 S removal from the troilite surface is regarded as a faster process than their diffusion across SRL. Accordingly, we can assume that in the first stages of dissolution will appear a gradient between the iron and H 2 S concentration in the boundary layer next to the surface and aqueous solution. The iron concentration gradient will progressively decrease as the results of metal accumulation into solution. Hence, the iron concentration gradient would be considered only an ephemeral enhancing factor of its diffusion. Instead, the H 2 S concentration gradient will permanently exist, because this reaction product was flushed from system via methane gas and was trapped into copper acetate solution. Therefore, it will be the main driving force of H 2 S diffusion.

We have observed that the experimental amounts of reaction products formed during anoxic troilite dissolution are well fitted by Eqs. (9) and (10). To improve our knowledge on nature of rate determining step of troilite dissolution, will be needed to examine these equations, and implicitly our experimental data, in the light of the Fick first law of diffusion (see for analogy with pyrite Jerz and Rimstidt [28]):

\[
J = \frac{D}{\delta} (C_{\text{surface}} - C_{\text{solution}}) = \frac{D}{\delta} \Delta C,
\]

where \( J \) is the flux of reaction products across the obstructive layer, \( D \) is the diffusion coefficient, \( \delta \) is the thickness of obstructive layer and \( C_{\text{surface}} \) and \( C_{\text{solution}} \) are respectively the concentration of Fe 2+ and H 2 S in the boundary layer next to the surface and in solution. This equation may help estimating the amount of diffused reaction products by a layer with thickness that is a function of reaction progress.

\[
J = \frac{dn}{dt} = \frac{D}{k_3 n} \Delta C,
\]

where \( k_3 \) is the thickness constant and \( n \) is the number of moles of dissolved iron or released H 2 S. Rearranging the terms of Eq. (12), integrating and solving for \( n \) we obtain the next relation:

\[
n = \sqrt{\frac{2D}{k_3}} \Delta C^{0.5} t^{0.5}.
\]

If we accept that the concentration of reaction products at the troilite surface \( C_{\text{solution}} \) is small relative to \( C_{\text{surface}} \), then Eq. (13) becomes:

\[
n = \sqrt{\frac{2D}{k_4}} (C_{\text{surface}})^{0.5} t^{0.5}.
\]
In order to relate the integral rate law to the total proton concentration, we can assume the following equilibrium between all chemical species involved in surface troilite nonstoichiometric dissolution:

\[ \text{FeS} + 2\text{H}^+ \rightleftharpoons y\text{SH}_2 + \text{Fe}^{2+} + (1 - y)\text{H}_2\text{S}. \quad (15) \]

The corresponding equilibrium constant is:

\[ K' = \frac{[\text{SH}_2]^y[\text{Fe}^{2+}][\text{H}_2\text{S}]^{1-y}}{[\text{FeS}][\text{H}^+]^y}. \quad (16) \]

or

\[ K = \frac{K'}{[\text{SH}_2]^y} = \frac{[\text{Fe}^{2+}][\text{H}_2\text{S}]^{1-y}}{[\text{H}^+]^2}, \quad (17) \]

where \{FeS\} and \{SH2\} are the troilite and SH2 surface concentration, and \{Fe2+\}, \{H2S\}, and \{H+\} are the concentrations of Fe2+, H2S, and H+ in the boundary layer next to the surface. >SH2 denotes a precursor site of SRL formation. We must to note that for a given y \{FeS\}:\{SH2\} ratio can be assumed constant and equal with \((1 - y):y\). Between the iron and H2S concentrations there is the following relation:

\[ \{\text{H}_2\text{S}\} = (1 - y)[\text{Fe}^{2+}]. \quad (18) \]

Inserting Eq. (18) into Eq. (17) yields:

\[ K = \frac{[\text{Fe}^{2+}](1 - y)^{1-y}[\text{Fe}^{2+}]^{1-y}}{[\text{H}^+]^2}. \quad (19) \]

The surface concentration of iron derives as

\[ [\text{Fe}^{2+}] = \frac{K}{(1 - y)^{1-y}}[\text{H}^+]^{2/(2-y)}. \quad (20) \]

If one combine Eqs. (14) and (20), keeping in mind our initial assumption that \{H+\} = \{H+\}, one obtain the integral form of iron diffusion rate law:

\[ n_{\text{Fe}} = k_{\text{Fe}}[\text{H}^+]^{1/(2-y)}t^{0.5}, \quad (21) \]

where

\[ k_{\text{Fe}} = \sqrt{2D} k_3 \left( \frac{K}{(1 - y)^{1-y}} \right)^{1/(2-y)}. \quad (22) \]

Similarly the integral form of H2S diffusion rate law can be obtained:

\[ n_{\text{H}_2\text{S}} = k_{\text{H}_2\text{S}}[\text{H}^+]^{1/(2-y)}t^{0.5}, \quad (23) \]

where

\[ k_{\text{H}_2\text{S}} = \sqrt{2D} k_3 \left( K(1 - y) \right)^{1/(2-y)}. \quad (24) \]

In first approximation, a value of 0.57 for reaction order with respect to hydrogen ion concentration, \(1/(2 - y)\) ratio, can be estimated from the average value of experimental \(n_{\text{Fe}}:n_{\text{H}_2\text{S}}\) ratios (see Table 2). Within the experimental uncertainty this value is equal with measured reaction orders. From Eqs. (22) and (24) we see that the kinetic constants \(k_{\text{Fe}}\) and \(k_{\text{H}_2\text{S}}\) are different functions of y. Moreover, we observe that for the same other terms of these equations the proposed model predicts a kinetic constant \(k_{\text{Fe}}\) higher than \(k_{\text{H}_2\text{S}}\). Also, our model predicts identical reaction order with respect to proton concentration both for dissolved iron and for formed H2S. These predictions are in good agreement with our experimental results.

The similarity between the theoretical and experimental integral rate laws demonstrates that the diffusion of reaction products through an obstructive layer (SRL) with an increasing thickness is the rate determining step of troilite anoxic dissolution. Nevertheless, the basic assumptions in deriving Eqs. (21) and (22) must be regarded carefully. We have already seen that during troilite dissolution there is an iron accumulation in solutions. Therefore our assumption that \(C_{\text{solution}}\) is small relative to \(C_{\text{surface}}\) is only true for initial moments of dissolution. Also, for reaction order estimation we assumed a constant value of y. As we can see from Table 2 this parameter can vary with initial experimental conditions and it can also vary during the same experimental run. Initial high values of \(n_{\text{Fe}}:n_{\text{H}_2\text{S}}\) ratio will bring the reaction order close to experimental values. For example, when we have computed (accordingly with procedure described in Section 3.4) the ratio of \(n_{\text{Fe}}:n_{\text{H}_2\text{S}}\) for 525 s of troilite anoxic dissolution in 0.04 mol L\(^{-1}\) HClO\(_4\) a value of 1.74 was found. The corresponding reaction order of 0.64 is placed between experimental values. A reaction order of 0.74, higher than experimental values, was found for 359 s of troilite dissolution in 0.06 mol L\(^{-1}\) HClO\(_4\). Taking into account the observed initial low production of H2S, these findings are not a surprise, and support the proposed model. Perhaps, the number of >SH2 sites is related to the surface amount of Fe(III). Therefore, high initial y values are found.

### 4.2. Reaction mechanism of anoxic troilite dissolution

The dissolution of the initial outermost layer, presumably formed by oxidized sulfur and iron species, in acidic solutions, can be described by reactions like:

\[ \text{Fe(OH)}_3(\text{s}) + 3\text{H}^+_{\text{(aq)}} = \text{Fe}^{3+}_{\text{(aq)}} + 3\text{H}_2\text{O}. \quad (25) \]

\[ \text{FeOOH}_{(s)} + 3\text{H}^+_{(aq)} = \text{Fe}^{3+}_{(aq)} + 2\text{H}_2\text{O}. \quad (26) \]

\[ \text{Fe}_2(\text{SO}_4)_{(s)} + 3\text{H}^+_{(aq)} = 2\text{Fe}^{3+}_{(aq)} + 3\text{HSO}_4^-_{(aq)} \quad (27) \]

Because during the time interval of 0–4000 s the ferric iron concentration was below detection limit of used analytical method denotes either its fast reduction by evolved H2S, or its adsorption on troilite surface. However the appearance of H2S in the first five second of each experiment may be explained by the presence of S\(^2-\) groups in outermost and defective troilite layers [10]. Another possible reason for this immediate formation of H2S can be given by assuming that SRL is not a perfect barrier to
protons and reactions products, leading to limited, but still significant, acidi
cing dissolution of troilite according to:
\[
S^{2-} + 2H^{+} = H_{2}S^{0}\quad (28)
\]
Also, in the first stages of dissolution it is possible that a part of
formed H_{2}S would be consumed by the ferric iron exist-
ing on troilite surface [10] or formed during the short time of
samples manipulation in air. The possible reactions are
summarized in Table 3 (see Refs. [29,30] for free enthalpies
of formation). Therefore, the experimentally measured n_{H_{2}S}
would be lower than the actual amount formed at the troilite
surface. The consumption of gas coupled with the slowed
diffusion of H_{2}S through SRL leads to the initial deficit in
n_{H_{2}S} against t^{0.5} observed in Fig. 5b. Finally, it is reason-
able to assume that H_{2}S and iron will diffuse through the
troilite SRL with distinct rates, a consequence of their dif-
ference in electrical charge (0 vs +2 or +3) and in radii (r(H_{2}S) = 1.33 Å and r(Fe^{2+}) = 0.74 Å). The diffusion of
H_{2}S is not promoted by a counter ion action of protons. The
solely enhancing factor of H_{2}S diffusion is the concentra-
tion between the surface boundary layer and the bulk super-
natant. Therefore, some H_{2}S may accumulate between the
troilite surface and the SRL. Such a gas accumulation can
break the SRL and lead to the apparition of reaction prod-
cuts surges, as observed in Figs. 6 and 8. Theses surges are
conspicuous in experiments at low perchloric acid concen-
trations. We believe that in the cases of experiments at high

5. Conclusions and implication for the anoxic
dissolution of pyrrhotite

Troilite anoxic dissolution is a process that can be de-
scribed by the diffusion of reaction products (i.e., iron and
hydrogen sulfide) across an obstructive layer with increas-
ing thickness. Diffusion through the forming layer causes the
apparent dissolution rate to show a factionary dependence
on hydrogen ions concentration. The accumulation of H_{2}S
between the surface and the SRL, eventually leads to the me-
chanical destruction of this outer layer, a process that results
an increased flux of reaction products (“surges”). Then ferric
iron, which exists on surface and inside of troilite lattice, can
react with sulfur and promote the formation of sulfur-rich phase,
as result of a set of oxidative processes. The proposed
mechanism suggests that the apparition of obstructive
layer is imminent during anoxic dissolution of iron monosul-
fides. This is in perfect agreement with previous studies ded-
icated to anoxic dissolution of iron monosulfides [8–10,19].
In these studies, it was observed that independently of its
type, stoichiometric or nonstoichiometric, iron monosulfide
dissolution conducts at the enrichment in sulfur of their sur-
face. Also, the proposed mechanism does not exclude in any
way the SRL “reduction” step encountered during nonox-
idative dissolution of pyrrhotite [8–10,19]. However, in our
opinion, this process is rather a mechanical process of SRL
destruction due to accumulation of H_{2}S between the layer
and the surface leading to H_{2}S overpressure, rather than a
reducing reaction. This mechanism can also explain the long
inhibition periods observed at low temperatures (the pres-
sure increases with temperature). Also, the proposed model
explains the high ratio of the rate of S release to the rate of Fe
release observed at approximately 1200 s in study of Thomas
et al. [8]. This ratio has an approximate value of 5.5, as extrapolated from Fig. 4a of Thomas et al. study [8], and it can reflect right the excess of accumulated $\text{H}_2\text{S}$ over $\text{Fe}^{2+}$ under SRL. It is known that on pyrrhotite surface there is a thick SRL [3], which will need a high pressure for its destruction. When SRL is not thinned (by polishing), its destroying is not observed and the whole dissolution process is governed only by reaction products diffusion through this layer.

Finally up to four stages are proposed to occur sequentially during the troilite or pyrrhotite anoxic dissolution in acidic medium:

1. Dissolution of oxidized species of iron and sulfur existing on solid surface;
2. Dissolution-inhibition (if the experimental conditions and mechanical resistance of formed SRL allow the accumulation of $\text{H}_2\text{S}$);
3. Apparition of one or several $\text{H}_2\text{S}$ and iron surges as a result of mechanical destruction of the SRL, the surge magnitude being conditioned by the mechanical resistance of SRL and temperature;
4. The reaction products diffusion across a SRL that continues to develop on troilite surface.

This model is constructed on the pattern of the mechanism proposed by Thomas et al. [8,9] and tries to unify the different observations about iron monosulfides behavior in anoxic acidic media.

Acknowledgments

We are grateful to Dr. Michel Schlegel (CEA) and an anonymous reviewer for valuable comments and suggestions of the manuscript.

References