Effect of inorganic anions on FeS oxidative dissolution
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Abstract
The oxidative dissolution of FeS at 30 °C in aerated aqueous solutions in the 5.5-6.0 pH range in the presence of inorganic anions (NO₃⁻ and Cl⁻) was investigated by a potentiodynamic polarization method. The corrosion current Icorr increased with increasing [NO₃⁻] and [Cl⁻], demonstrating the ionic nature of activated complex of FeS oxidative dissolution. The corrosion potentials (Ecorr) varied between -367.4 mV (in 0.25 M NaCl) and -277.5 (in 0.5 M NaNO₃). These results indicate that the FeS stability may be significantly affected by a change in the composition of natural water, and imply that any dissolution model at the FeS surface should also take into account the specific impact of these anions.

Keywords: FeS; anions; oxidative dissolution; potentiodynamic polarization

1. Introduction

Iron monosulfides (pyrrhotite, troilite and mackinawite) form in reductive conditions. When minerals are exposed to aqueous solutions containing dissolved oxygen they are oxidized and release ferrous/ferric iron, sulfur/polysulfide/sulfoxy species, and protons [1-3]. Protons and ferric iron (a strong oxidant) can in turn enhance dissolution of accompanying minerals, such as CuFeS₂, Fe₃S₄, CuS, HgS, CdS, thereby releasing toxic elements incorporated in these matrices. The incomplete oxidation of iron monosulfides (IMS) produces soluble sulfur-bearing anions with sulfur in low oxidation states [1, 2, 4, 5]. These anions can migrate and alter the redox potential of reached geologic media [2, 4].

The composition of aqueous fluids can influence the rate of mineral dissolution [6]. The anions that form complexes with Fe(II) and Fe(III) are expected to affect the oxidative dissolution of iron sulfides. For example, Sasaki et al. [7] found that the rate of pyrite oxidative dissolution decreased when the...
concentration of various anions increased. They surmised that these anions modified the activity of dissolved Fe(III) (i.e., oxidant activity). Also, the salt effect of anions on the oxidative dissolution rate cannot be neglected. The effect can be explained in terms of transition state theory and the Debye-Hückel theory [8].

In the present study the effect of NO$_3^-$ and Cl$^-$ on the oxidative dissolution of IMS in the presence of dissolved oxygen was investigated by potentiodynamic polarization method.

2. Experimental

Experiments were performed in a conventional three-electrode cell. The working electrode was synthetic troilite (FeS, Merk) embedded in epoxy resin and cut to expose a mineral surface of 1 cm$^2$. A rectangular Pt foil was used as counter electrode and a saturated calomel electrode (SCE) as reference electrode. The troilite electrode was polished with fine emery paper and carefully cleaned with acetone prior to use.

The electrolytes used in experiments were prepared with reagent grade salts (NaNO$_3$ and NaCl) and distilled water. The initial pH of aerated solutions was measured at 30°C with a combined electrode connected to a pH/millivoltmeter (Consort C538). The electrode response was calibrated against two commercial pH buffers.

The polarization curves were recorded using potentiodynamic technique with a constant scan rate of 1 mV s$^{-1}$. Electrochemical measurements and analysis were performed using an electrochemical workstation ZHANER Elektrik IM6e (Germany) with Thales software. Temperature was maintained at 30°C using a thermostated water bath.

3. Results and discussion

The potentiodynamic polarization behaviour of FeS electrode in aerated solutions without and with the addition of NO$_3^-$ and Cl$^-$ ions is shown in Figure 1. The presence of electrolytes shifts both anodic and cathodic curves towards higher currents, meaning higher rates of FeS oxidative dissolution. This effect is more important for the anodic curves.

The electrochemical parameters derived from data presented in Figure 1 are summarized in Table 1. These parameters are:
- corrosion currents ($I_{corr}$);
- cathodic and anodic Tafel slopes ($b_c$ and, respectively, $b_a$), and
- corrosion potential ($E_{corr}$).

Table 1. Electrochemical parameters for FeS in aqueous solutions at different concentrations of electrolytes (NaA), 30°C and pH between 5.5 and 6.0.

<table>
<thead>
<tr>
<th>Electrolyte (NaA)</th>
<th>[A$^-$]</th>
<th>$I_{corr}$ / µA</th>
<th>$b_c$ / mV dec$^{-1}$</th>
<th>$b_a$ / mV dec$^{-1}$</th>
<th>$E_{corr}$ / mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaNO$_3$</td>
<td>0.125</td>
<td>68.9</td>
<td>-138</td>
<td>122</td>
<td>-342.9</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>93.3</td>
<td>-225</td>
<td>117</td>
<td>-300</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>111</td>
<td>-222</td>
<td>84.2</td>
<td>-277.5</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.25</td>
<td>142</td>
<td>-185</td>
<td>148</td>
<td>-367.4</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>209</td>
<td>-220</td>
<td>94.6</td>
<td>-342</td>
</tr>
<tr>
<td>No electrolyte</td>
<td>0</td>
<td>6.09</td>
<td>-303</td>
<td>302</td>
<td>-340.5</td>
</tr>
</tbody>
</table>
From the Table 1 it is clear that the presence of electrolytes in the 0.125-0.5 M concentration range increases significantly $I_{corr}$ (i.e., the rate of oxidative dissolution of FeS). The impact of Cl$^-$ on $I_{corr}$ is greater than that of NO$_3^-$.

The corrosion potentials ($E_{corr}$) vary between -367.4 (in 0.25 M NaCl) and -277.5 (in 0.5 M NaNO$_3$) mV. The observed increase of oxidation rate of FeS in the presence of electrolytes suggests that FeS oxidative dissolution is driven by an activated complex of ionic nature [8], which most likely is closely related to the ionic character of FeS bonds from troilite.

![Polarization curves for FeS](image)

Fig. 1. Polarization curves for FeS in the absence (a) and in the presence of anions (NO$_3^-$ (b) and Cl$^-$ (c)). (SHE=Standard hydrogen electrode).
4. Conclusions

The addition of NaNO\textsubscript{3} and NaCl to aerated solutions increases the oxidative dissolution rate of FeS. The effect induced by Cl\textsuperscript{-} on oxidative dissolution rate is greater than the effect of NO\textsubscript{3}\textsuperscript{-}. The corrosion potentials (E\textsubscript{corr}) varied between -367.4 and -277.5 mV. The increase of I\textsubscript{corr} with [NO\textsubscript{3}\textsuperscript{-}] and [Cl\textsuperscript{-}] can be related to the ionic character of Fe-S bounds.

Our study shows the importance of inorganic anions, such as Cl\textsuperscript{-} and NO\textsubscript{3}\textsuperscript{-}, on FeS oxidative dissolution. Cl\textsuperscript{-} and NO\textsubscript{3}\textsuperscript{-} are involved in rate determining step of overall process and accelerate the environment contamination with toxic species resulted from oxidative dissolution of FeS.

Future electrochemical impedance spectroscopy (EIS) experiments will be performed in order to characterize the processes at electrode/solution interface. Also the effects of other inorganic anions on FeS oxidative dissolution in aerated solutions will be studied.

Acknowledgements

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References


**Nomenclature**

- \( b_a \) anodic Tafel slope
- \( b_c \) cathodic Tafel slope
- \( E_{corr} \) corrosion potential
- \( I_{corr} \) corrosion current