Phase Formation in Fe$^{0}$–H$_2$O–O$_2$ System in the Presence of Iron Cations: 2. Fe$^{0}$–H$_2$O–O$_2$–Fe$_2$(SO$_4$)$_3$ System

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Abstract—Formation mechanisms of ultradispersed (nanosized) iron–oxygen particles in a Fe$^{0}$–H$_2$O–O$_2$ system in the presence of trivalent iron cations are investigated. It is shown that, depending on the solution concentration and pH and the presence or absence of an oxidant on the surface of iron, nanosized nuclei, mainly ferrihydrite, are formed in the surface layer and in the solution. Further growth of these nuclei occurs via several mechanisms to yield ultradispersed phases of iron oxides and monohydrates with different crystalline modifications.

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INTRODUCTION

The study of new phase formation in the processes proceeding in natural systems and solutions in the presence of cations and aquahydroxocomplexes of trivalent iron showed that the necessary condition for the formation of iron–oxygen phases is the generation of a reaction protoproduct, particles of ferrihydrite 5Fe$_2$O$_3$·9H$_2$O [1]. This compound contains only Fe$^{3+}$ cations, a phenomenon that distinguishes it from protoproteodicroticites formed in the Fe$^{0}$–H$_2$O–O$_2$–FeSO$_4$ system containing both Fe$^{3+}$ and Fe$^{2+}$ cations. Thus, the modeling of the phase formation in the Fe$^{0}$–H$_2$O–O$_2$ system proceeding in a Fe$_2$(SO$_4$)$_3$ solution makes it possible to separate the stage of anodic dissolution of an iron disk to form Fe$^{3+}$ ions and the stage of nucleation of Fe$^{3+}$ cation–containing primary products on the disk surface. The analysis of further phase transformations involving ferrihydrite and proceeding on the disk surface, in the surface layer, and in the solution, enables us to disclose their mechanism, to draw an analogy with natural systems, and to specify the main regularities of nucleation and transformation of ultradispersed and nanosized iron–oxygen structures in the Fe$^{0}$–H$_2$O–O$_2$–Fe$_2$(SO$_4$)$_3$ system.

EXPERIMENTAL

Formation of Iron–Oxygen Particles on an Iron Surface

The mechanism of the initial stage of the phase formation occurring on the surface of iron disk in a Fe$_2$(SO$_4$)$_3$ solution is governed by the contact between the surface and the solution containing cations and aquahydroxocomplexes of trivalent iron prior to the onset of metal ionization yielding Fe$^{2+}$ cations. Under such conditions, the protoproduct of the phase formation is an unstable compound, ferrihydrite, 5Fe$_2$O$_3$·9H$_2$O (Fig. 1a), which was identified by the X-ray diffraction and DTA methods. After the onset of iron ionization, another protoproduct, ferriprotoproteodicroticite, containing both trivalent and bivalent iron is formed. This product was for the first time described in [2] and detected by us on the surface of iron disk in the Fe$^{0}$–H$_2$O–O$_2$–Fe$_2$(SO$_4$)$_3$ system (Fig. 1b). The final products of the phase formation on the iron surface are the phases of magnetite Fe$_3$O$_4$ and delta-iron monohydrate, δ-FeOOH (Table 1). As is seen from Table 1, when the initial solution concentration increases, the phase formation on the disk surface either proceeds until goethite (α-FeOOH) phase is formed or does not proceed at all. This may be explained by the adsorption of SO$_4^{2-}$ anions on the iron surface, which retard the iron ionization by blocking active sites on the electrode surface [3].

The optimal conditions for the formation of magnetite, Fe$_2$O$_3$, phase are neutral or alkaline media and the conservation of a certain ferrite ratio in the system.

### Table 1. The phase composition of ultradispersed particles formed on the surface of iron disk upon its contact with Fe$_2$(SO$_4$)$_3$ solutions

<table>
<thead>
<tr>
<th>Concentration of Fe$^{3+}$, mg/l</th>
<th>The pH value in the phase formation</th>
</tr>
</thead>
<tbody>
<tr>
<td>3–3.2</td>
<td>6.0–6.5</td>
</tr>
<tr>
<td>10</td>
<td>Fe$_3$O$_4$, δ-FeOOH</td>
</tr>
<tr>
<td>100</td>
<td>δ-FeOOH</td>
</tr>
<tr>
<td>1000</td>
<td>α-FeOOH</td>
</tr>
</tbody>
</table>
According to [4], the Fe$^{2+}$-to-Fe$^{3+}$ ratio should be within 1 : 2 limit that takes place at low initial Fe$_2$(SO$_4$)$_3$ concentrations. Figure 2 shows nanosized magnetite particles with a characteristic hexahedral shape prepared in the Fe$^0$–H$_2$O–O$_2$–Fe$_2$(SO$_4$)$_3$ system. The δ-FeOOH phase is formed in acidic media at initial Fe$^{3+}$ concentrations of 10 and 100 mg/l; in alkaline media, it is formed at the initial content of Fe$^{3+}$ of 100 mg/l and it is not observed in neutral media.

The phase transformations of iron–oxygen compounds formed on the surface of iron electrode upon its contact with a Fe$_2$(SO$_4$)$_3$ solution are schematically illustrated by Fig. 3. Figure 4 demonstrates the scheme of phase formation proceeding on the surface of iron electrode and including the stages of the contact between the iron surface and the dispersion medium containing hydrolyzed Fe$^{3+}$ cations (Fig. 4a), the formation of ferrihydrite (Fig. 4b), its transformation through goethite into magnetite (Fig. 4c), and possible decomposition of the latter to yield a maghemite phase (Fig. 4d).

Ferrihydrite [5Fe$_2$O$_3$·9H$_2$O], the protoproduct of the first chain of phase transformations (Fig. 1a), is formed at pH 3.0–9.5 in the presence of trivalent iron complexes, in particular, [Fe(OH)]$^{2+}$ and [Fe(OH)$_2$]$^+$. Further evolution of ferrihydrite involves its interaction with solution components and the formation of goethite α-FeOOH and hematite α-Fe$_2$O$_3$ by the reactions reported in [5, 6] (see reactions (1) and (2)). The transformation of ferrihydrite into goethite under the effect of Fe$^{2+}$ cations [4] is possible to proceed in moderately acidic solutions through the reactions

\[
[5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}] + 5[\text{Fe(OH)}]^2+ + \text{H}_2\text{O} = 15\alpha\text{-FeOOH} + 10\text{H}^+. \tag{1}
\]

and

\[
[5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}] + 5[\text{Fe(OH)}]_2^+ + 4\text{H}_2\text{O} + 5\text{H}^+. \tag{2}
\]

In this process, the part of Fe$^{2+}$ cations is not involved in the oxidation and remains in the goethite structure as phase inclusions of FeO:

\[
[5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}] + 5\text{Fe}^{2+} + \text{O}_2 + 3\text{H}_2\text{O} = 14\alpha\text{-FeOOH} + \text{FeO} + 10\text{H}^+. \tag{3}
\]

Fig. 1. Electron microscope images of the products of phase formation in the Fe$^0$–H$_2$O–O$_2$–Fe$_2$(SO$_4$)$_3$ system: (a) ferrihydrite 5Fe$_2$O$_3$·9H$_2$O and (b) ferrirhodocrocite.

Fig. 2. Electron microscope image of nanosized magnetite particles formed on the surface of iron disc in the Fe$^0$–H$_2$O–O$_2$–Fe$_2$(SO$_4$)$_3$ system.