Iron is the fourth most abundant element by weight in the earth's crust. The chemistry of aqueous iron primarily involves the ferrous (II) and ferric (III) oxidation states and is of interest in water supplies, wastewaters, limnology, and oceanography. Recent quantitative studies have included: iron removal mechanisms in estuarine and oceanic waters (1-3); adsorption of trace metals by hydrous ferric oxides or ferric oxyhydroxides (4-6); iron speciation and redox reactions in synthetic and real seawater (7-10).

Although the oxygenation kinetics of ferrous iron have been studied extensively there is a rather wide spread in the reported rate constant. The present work was undertaken to study the effect of ionic media, alkalinity, and temperature on the kinetics of ferrous iron oxygenation and to identify the product(s) of oxygenation.

**Methods**

**Iron Analysis.** Ferrous iron concentration was determined spectrophotometrically with 1,10-phenanthroline, using fluoride as a masking agent for ferric iron (17). Ten-milliliter samples were quenched in 1 mL of 3.8 M sulfuric acid; 2 mL of 2 M ammonium fluoride, 1 mL of 1% 1,10-phenanthroline,
The oxygenation kinetics of ferrous iron in aqueous media were studied experimentally. Solutions buffered by \( \text{HCO}_3^- \) and \( \text{CO}_2 \) with \( \text{NaClO}_4 \), \( \text{NaCl} \), and \( \text{Na}_2\text{SO}_4 \) were investigated. The general rate law was confirmed to be \(-d[\text{Fe(II)}]/dt = k[\text{OH}^-]P_{\text{O}_2}[\text{Fe(II)}] \) for solutions with pH less than 7. The variation of the reported values of \( k \) with different alkalinities can be explained by the variation in ionic strength and temperature. The presence of \( \text{NaCl} \) and \( \text{Na}_2\text{SO}_4 \) reduces the rate further and adequately explains the observed rate in seawater, which is usually a factor of 100 times slower compared to solutions of freshwater-like composition. Autocatalysis of ferrous iron oxygenation was observed for pH greater than 7; a mathematical treatment of the kinetic data for this regime is presented. The product of oxygenation in various solution compositions was shown to be lepidocrocite, \( \gamma-\text{FeOOH} \), by infrared spectroscopy and this was confirmed by X-ray diffraction.

Ozone. The water used for the experiments was doubly distilled and all chemicals used were analyzed reagent grade. The ferrous iron solutions were prepared by dissolving electrolyte grade iron powder in 0.1 M redistilled HC104. Bicarbonate–carbon dioxide buffers were prepared from solutions of sodium bicarbonate and bubbling through an air–CO2 mixture. The air–CO2 compressed gas mixture was prepared from solutions of sodium bicarbonate and bubbling through an air–CO2 mixture. The air–CO2 mixture was bubbled through the stirred solution. When sufficient time had elapsed for the pH and temperature to reach equilibrium, the ferrous iron solution was added and a stopwatch started. Aliquots of the test solution were withdrawn at appropriate time intervals and analyzed for ferrous iron.

Standard Ferric Oxhydroxide Preparation. Burns and Burns (12) reported five synthetic allotropes of the ferric oxhydroxides, \( \alpha-, \beta-, \gamma-, \delta-, \) and \( \epsilon-\text{FeOOH} \), and an additional amorphous ferric hydroxide. \( \epsilon-\text{FeOOH} \) is a high-pressure polymorph and is not considered here. \( \delta-\text{FeOOH} \) also was not considered since its natural occurrence is debatable.

Goethite, \( \alpha-\text{FeOOH} \), was obtained by hydrolyzing ferric nitrate in KOH (Fe/OH ratio = 0.25, final pH near 12) at 60 °C for 48 h. (See ref 13.) At higher temperatures \( \alpha-\text{FeO}_2 \), hematite, forms. (Standard \( \alpha-\text{FeOOH} \) was also obtained from Dr. G. R. Rossman of the Department of Geology, California Institute of Technology.) \( \beta-\text{FeOOH} \), akaganeite, was obtained by hydrolyzing ferric chloride in HCl (Fe/H ratio = 9, final pH near 2) at 100 °C for 24 h. (See ref 14.) \( \gamma-\text{FeOOH} \), lepidocrocite, was obtained by oxidizing ferric chloride in the presence of a slight excess of pyridine (final pH about 6) with air at room temperature for about 1 h. (Standard \( \gamma-\text{FeOOH} \) was also obtained from Dr. D. L. Janes of the 3M Co.)

The synthetic products were centrifuged, washed with distilled water three to four times, and dried at 45 °C in an oven.

Amorphous ferric hydroxide was obtained by hydrolyzing ferric nitrate in NaOH (Fe/OH ratio = 0.33, final pH near 8) at room temperature for 2 h. The product was filtered through a 0.22-µm Millipore filter and dried in a desiccator under slight vacuum. (A sample of amorphous iron oxyhydroxide was obtained from K. Hayes of Stanford University.)

Infrared Spectroscopy. At the conclusion of an oxygenation kinetics experiment, the solution was filtered through a 0.22-µm Millipore filter and the filter dried under slight vacuum in a desiccator. Appropriate amounts were scraped off with a spatula, dispersed in KBr powder, and pressed into a pellet (usually 1 mg sample in 200 mg of KBr). Infrared spectra were obtained for the 1400–2000 cm–1 region with a Perkin-Elmer Model 180 spectrophotometer.

X-ray Diffraction. Oxygenation products were also placed in 0.3-mm glass capillary tubes and powder patterns obtained with a 114.6-mm Debye–Scherrer camera with Co radiation and Fe filter. Typical exposure settings were 35 kV, 9 mA, and 16-h exposure time.

Results

Homogeneous Oxidation. The kinetics of ferrous iron oxygenation in laboratory systems have been previously studied (10, 15–19), and the general rate law was found to be:

\[-d[\text{Fe(II)}]/dt = k[\text{OH}^-]P_{\text{O}_2}[\text{Fe(II)}] \]  

where \( k \) is the rate constant with units \( M^{-2} \text{ atm}^{-1} \text{ min}^{-1} \), \([\text{OH}^-]\) denotes the concentration of hydroxyl ions, and \([\text{Fe(II)}]\) denotes the concentration of total ferrous iron. At constant pH and \( P_{\text{O}_2} \), Equation 1 reduces to a first-order equation:

\[-d[\text{Fe(II)}]/dt = k_1[\text{Fe(II)}] \]

where \( k_1 = k[\text{OH}^-]P_{\text{O}_2} \) and has units of inverse time. Equation 2 integrates to:

\[ [\text{Fe(II)}] = [\text{Fe(II)}]_0 \exp(-k_1t) \]  

Pseudo-first-order kinetics with respect to ferrous iron were also observed in treatment plants or seawater (3, 7, 20, 21). Table I summarizes the reported values for \( k \).

Since the rate is strongly dependent on pH, one of the major uncertainties in the numerical value for the rate constant arises from the variation of pH within an experiment. Reported variations range from ±0.02 to ±0.05 pH unit. Figure 1 shows the typical variation in pH during the course of an oxygenation experiment. The initial drop in pH coincides with the addition of the stock ferrous iron solution, which is also a source of strong-acid protons. The subsequent increase in pH can be adequately explained by the diffusion of aqueous \( \text{CO}_2 \) from the solution. Substantial error can be introduced if the oxygenation kinetics are studied on the same time scale of about 20 min. The variation of ferrous iron was plotted arithmetically vs. time and slopes were constructed to obtain instantaneous rates which were then normalized with respect to the instantaneous \([\text{OH}^-] \), \( P_{\text{O}_2} \), and \([\text{Fe(II)}]\) at that time. Rate constants obtained this way have about 20% variability (2σ) and compare well with the rate constants obtained by linear regression from first-order plots.
Table I. Summary of Previous Results on Oxygenation Kinetics of Ferrous Iron

<table>
<thead>
<tr>
<th>Investigators</th>
<th>solution composition</th>
<th>reported rate Information</th>
<th>remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stumm and Lee (15)</td>
<td>29 to 39 mequiv/L of alk as NaHCO₃, PO₂ varies, T = 20.5 °C</td>
<td>( k = 8.0 \pm 2.5 \times 10^{13} \text{ M}^{-2} \text{ atm}^{-1} \text{ min}^{-1} )</td>
<td>assume ionic strength = 34 ( \times 10^{-3} ) M ( \gamma_{OH} \approx 0.64 ) ( k_{O_{2}} \text{ oxygen at } 20.5^\circ \text{C} = 0.00138 \text{ M atm}^{-1} )</td>
</tr>
<tr>
<td>Morgan and Birkner (16)</td>
<td>( P_{O_{2}} = 0.6 \text{ atm, } T = 25 \text{ °C}, \text{ alk } = 32 \text{ mequiv/L} )</td>
<td>( \tau_{1/2} \approx 16 \text{ min at pH 6.70 } \rightarrow ) ( k = 2.0 \times 10^{13} \text{ M}^{-2} \text{ atm}^{-1} \text{ min}^{-1} ) ( \tau_{1/2} \approx 47 \text{ min at pH 6.52 } \rightarrow ) ( k = 1.7 \times 10^{13} \text{ M}^{-2} \text{ atm}^{-1} \text{ min}^{-1} )</td>
<td></td>
</tr>
<tr>
<td>Schenck and Weber (17)</td>
<td>( P_{O_{2}} = 0.21 \text{ atm, } T = 25 \text{ °C}, \text{ alk } = 30–50 \text{ mequiv/L} )</td>
<td>( k = 2.1 \pm 0.5 \times 10^{13} \text{ M}^{-2} \text{ atm}^{-1} \text{ min}^{-1} )</td>
<td>assume ionic strength = 40 ( \times 10^{-3} ) M</td>
</tr>
<tr>
<td>Theis (18)</td>
<td>( P_{O_{2}} = 0.5 \text{ atm, } T = 25 \text{ °C}, \text{ alk } = 0.0158 \text{ M as NaOH initially} )</td>
<td>( \tau_{1/2} = 25.4 \text{ min at pH 6.3 } \rightarrow ) ( k = 1.36 \times 10^{14} \text{ M}^{-2} \text{ atm}^{-1} \text{ min}^{-1} )</td>
<td></td>
</tr>
<tr>
<td>Kester et al. (7)</td>
<td>( T = ? , P_{O_{2}} = 0.21 \text{ atm, Naragansett seawater Sargasso seawater } )</td>
<td>( \tau_{1/2} = 5.5 \text{ min at pH 8.0 } \rightarrow ) ( k = 6 \times 10^{11} \text{ M}^{-2} \text{ atm}^{-1} \text{ min}^{-1} ) ( \tau_{1/2} = 3.3 \text{ min at pH 8.0 } \rightarrow ) ( k = 1 \times 10^{12} \text{ M}^{-2} \text{ atm}^{-1} \text{ min}^{-1} )</td>
<td>kinetics were followed by ferric iron absorbance in the UV region</td>
</tr>
<tr>
<td>Tamura et al. (19)</td>
<td>( T = 25 \text{ °C, } P_{O_{2}} \text{ varies, alk } = 10^{-2} \text{ M NaHCO}_{3} \text{ total } \text{ionic strength } = 0.11 \text{ M} )</td>
<td>( 0.1 \text{ M ClO}<em>{4}^{−} : k = 2.38 \times 10^{14} \text{ M}^{-3} \text{ s}^{-1} = 1.6 \times 10^{13} \text{ M}^{-2} \text{ atm}^{-1} \text{ min}^{-1} ) ( 0.1 \text{ M NO}</em>{3}^{−} : k = 3 \times 10^{14} \text{ M}^{-3} \text{ s}^{-1} = 1.6 \times 10^{13} \text{ M}^{-2} \text{ atm}^{-1} \text{ min}^{-1} )</td>
<td>( 0.1 \text{ M Cl}^{−} : k = 1.83 \times 10^{14} \text{ M}^{-3} \text{ s}^{-1} ) ( 2 \times 10^{13} \text{ M}^{-2} \text{ atm}^{-1} \text{ min}^{-1} ) ( 0.1 \text{ M Br}^{−} , 0.1 \text{ M I}^{−}, 0.033 \text{ M SO}_{4}^{2−} ): ( k = 1.36 \times 10^{14} \text{ M}^{-3} \text{ s}^{-1} = 1.0 \times 10^{13} \text{ M}^{-2} \text{ atm}^{-1} \text{ min}^{-1} )</td>
</tr>
<tr>
<td>Murray and Gill (3)</td>
<td>( T = ? , Puget Sound seawater )</td>
<td>( \tau_{1/2} = 3.9 \text{ min at pH 8.0 } \rightarrow ) ( k = 8.9 \times 10^{11} \text{ M}^{-2} \text{ atm}^{-1} \text{ min}^{-1} )</td>
<td>first 5 min linear on first-order plot</td>
</tr>
</tbody>
</table>

Table II. Variation of \( k \) with Ionic Strength (Adjusted by NaClO₄) *

<table>
<thead>
<tr>
<th>Ionic strength, M</th>
<th>( \tau_{1/2} ) min (least squares)</th>
<th>( k ), M⁻² atm⁻¹ min⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.009</td>
<td>18.0</td>
<td>4.0 ( \pm 0.6 \times 10^{13} )</td>
</tr>
<tr>
<td>0.012</td>
<td>18.8</td>
<td>5.1 ( \pm 0.7 \times 10^{13} )</td>
</tr>
<tr>
<td>0.020</td>
<td>18.5</td>
<td>2.9 ( \pm 0.6 \times 10^{13} )</td>
</tr>
<tr>
<td>0.040</td>
<td>21.5</td>
<td>2.2 ( \pm 0.5 \times 10^{13} )</td>
</tr>
<tr>
<td>0.060</td>
<td>26.8</td>
<td>1.8 ( \pm 0.3 \times 10^{13} )</td>
</tr>
<tr>
<td>0.110</td>
<td>37.9</td>
<td>1.2 ( \pm 0.2 \times 10^{13} )</td>
</tr>
</tbody>
</table>

\* \( T = 25 \text{ °C}; \text{ alkalinity } = 9 \times 10^{-2} \text{ M NaHCO}_{3} \); [Fe(II)]₀ = 34.7 \text{ M } \mu \text{M}; P_{O_{2}} = 0.2 \text{ atm; pH } = 6.84.

Figures, the rate constants of ref 16, 17, and 19 are in reasonable agreement with those found in this study. Better agreement with the data of ref 19 can be obtained if further normalization with respect to the activity coefficient of the OH⁻ ion is carried out. The value of Theis (18) is at variance with results in this study and no satisfactory explanation is evident.

Another series of experiments was initiated with temperature ranging from 5 to 30 °C. Figure 3 shows first-order plots for these experiments. The temperature effect appears to be large, but when normalization with respect to changes in \( K_w \) and \( O_{2} \) solubility with temperature was carried out, as in Table III, the rate constant was seen to vary slightly with temperature. When proper attention was given to ionic strength, it was found that this study's results compare well with those of ref 15. The error bars are sufficiently large to make meaningful calculations of activation energy impossible.

Tamura et al. (19) studied the effects of anions on the oxygenation kinetics of ferrous iron and found the rate constant to decrease in the order ClO₄⁻, NO₃⁻, Cl⁻, Br⁻, I⁻, SO₄²⁻. The present study confirms the order of ClO₄⁻, Cl⁻, and SO₄²⁻.

Figure 4 shows first-order plots of ferrous iron oxygenation in chloride media.

The role of alkalinity in the oxygenation kinetics is unclear, apart from its buffering capacity for acidity and its contribution to the ionic strength. Data from this study show that effects of variation in alkalinity from 9 to 50 mM can be adequately explained by ionic strength effects. Tamura et al. (19) reported that the rate constant did not change with variations of bicarbonate from 2 to 10 mM. The scatter in data is large for low alkalinites (less than 5 mM) and may result in spuriously high rate constants.

Tamura et al. (19) proposed the following reaction as the rate-limiting step: Fe(OH)²⁺ + O₂ + H₂O −→ Fe(OH)₃ + O₂⁻. If this is correct, transition-state theory predicts a slope of −1 in a plot of log \( k \) vs. \( \sqrt{T} \). Instead, the present study shows a slope of −2, which indicates that the product of the charges of the species involved in the rate-limiting step is −2.

Kester et al. (7) and Murray and Gill (3) reported \( \tau_{1/2} \) of ferrous iron oxidation in seawater to be in the range of 3–6 min. Tamura et al. (19) studied the effects of anions on ferrous iron oxidation and proposed that complexation of ferrous iron by anions can account for retardation of oxygenation. From the data in Table IV (discussed under Heterogeneous Oxidation), it can be shown that, at pH 8, the \( \tau_{1/2} \) of ferrous iron oxidation in 0.50 M NaCl or 0.165 M Na₂SO₄ is on the order of 1 min. This work confirms that of Liang and Kester (10).
that the presence of Cl\(^-\) and SO\(_4^{2-}\) anions can effectively reduce the oxygenation rate to that of its counterpart in seawater.

**Heterogeneous Oxidation.** Takai (22) studied the catalytic oxidation removal of Fe(II) by α-FeOOH and γ-FeOOH experimentally and found the latter to be effective. Tamura et al. (23) studied the effect of ferric hydroxide on the oxygenation of ferrous iron in neutral solutions and found that at constant pH and O\(_2\) concentration the rate is:

\[
-k_1 \frac{d[Fe(II)]}{dt} = (k_1 + k_2[Fe(III)])[Fe(II)]
\]  
(4)

where \(k_1\) is the homogeneous rate constant with inverse time units and \(k_2\) is the heterogeneous rate constant with inverse concentration and time units (M\(^{-1}\) min\(^{-1}\)). They also showed that:

\[
k_2 = k_3[O_2]K/[H^+]
\]  
(5)

where \(k_3\) is the surface rate in M\(^{-1}\) min\(^{-1}\), [O\(_2\)] is the concentration of oxygen in solution, and \(K\) is the adsorption constant of ferrous iron on ferric hydroxide, whose numerical value was determined to be 10\(^{-9.6}\) mol mg\(^{-1}\) for amorphous iron hydroxide, which converts to the dimensionless value of 10\(^{-4.85}\).

For a system with ferric iron initially absent, we can write the mass balance for any time:

\[
[Fe(III)] + [Fe(II)] \approx [Fe(II)]_0
\]  
(6)

Substituting Equation 6 into 4, we obtain the autocatalytic rate law:

\[
-k_1 \frac{d[Fe(II)]}{dt} = [k_1 + k_2][Fe(II)]_0[Fe(II)] - k_2[Fe(II)]^2
\]  
(7)

This equation can be readily integrated for the condition at \(t = 0\):

\[
[Fe(II)] = [Fe(II)]_0
\]

to give:

\[
[Fe(II)] = \frac{[Fe(II)]_0(k_1 + k_2[Fe(II)]_0)}{k_2[Fe(II)]_0 + k_1 \exp([k_1 + k_2[Fe(II)]_0]t)}
\]  
(8)

If \(k_1 \gg k_2[Fe(II)]_0\), Equation 8 reduces to Equation 3:

\[
[Fe(II)] \approx \frac{[Fe(II)]_0k_1}{k_1 \exp([k_1]t)}
\]

Using the reported values of Tamura et al. (23), \(k_2\) (at pH 7, 25 °C, and a \(P_{O_2}\) of 0.21 atm) is 133.6 M\(^{-1}\) min\(^{-1}\) and \(k_2[Fe(II)]_0 = 6.88 \times 10^{-5}\) min\(^{-1}\) for [Fe(II)]\(_0\) = 50 \(\mu\)M. For the same conditions, \(k_1\) is \(-7.5 \times 10^{-2}\) min\(^{-1}\) for 0.01 M ionic strength, so \(k_1/k_2[Fe(II)]_0 \approx 1\). The ratio \(k_1/k_2[Fe(II)]_0\) ac-
Table III. Variation of \( k \) with Temperature

<table>
<thead>
<tr>
<th>( T, ^\circ C )</th>
<th>( t/2, \text{min} )</th>
<th>( \text{pH} )</th>
<th>( K_W \times 10^{14} )</th>
<th>( \text{O}_2 ) saturation ( \times 10^4 ) M</th>
<th>( k, \text{M}^{-3} \text{min}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>315.6</td>
<td>6.76</td>
<td>0.1846</td>
<td>3.81</td>
<td>2.7 ± 0.5 ( \times 10^{16} )</td>
</tr>
<tr>
<td>15</td>
<td>63.1</td>
<td>6.80</td>
<td>0.4505</td>
<td>3.06</td>
<td>2.2 ± 0.3 ( \times 10^{16} )</td>
</tr>
<tr>
<td>20.5 ( ^\circ C )</td>
<td>0.70</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>37.9</td>
<td>6.84</td>
<td>1.008</td>
<td>2.50</td>
<td>9.4 ± 1.7 ( \times 10^{15} )</td>
</tr>
</tbody>
</table>

* Alkalinity = 9 \( \times 10^{-3} \) M NaHCO\(_3\); ionic strength = 0.11 M adjusted by NaCl; \( [\text{Fe(II)}_0] = 3.47 \) \( \mu \text{M} \). \( ^{23} \) Stumm and Lee (15). \( k = 6.0 \pm 2.5 \times 10^{17} \text{M}^{-2} \text{min}^{-1} \); \( k = 5.8 \pm 1.8 \times 10^{16} \text{M}^{-2} \text{min}^{-1} \) at 34 mM ionic strength, \( k = 2.9 \pm 0.9 \times 10^{16} \text{M}^{-2} \text{min}^{-1} \) at 0.11 M ionic strength using the \(-2\) slope dependence of \( \log k \) on \( 1/\sqrt{T} \).

Table IV. Values of \( k_1 \) and \( k_2 \) in Autocatalytic Rate Expression

<table>
<thead>
<tr>
<th>solution composition</th>
<th>( \text{pH} )</th>
<th>( t/2, \text{min} )</th>
<th>( K_W \times 10^{14} )</th>
<th>( k_1, \text{min}^{-1} )</th>
<th>( k_2, \text{M}^{-2} \text{atm}^{-1} \text{min}^{-1} )</th>
<th>( k_2, \text{M}^{-1} \text{min}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 M NaCl</td>
<td>6.5</td>
<td>3.108 h</td>
<td>13.803</td>
<td>0.037 717</td>
<td>8.8 ( \times 10^{12} )</td>
<td></td>
</tr>
<tr>
<td>0.25 M NaCl</td>
<td>6.5</td>
<td>13.577 h</td>
<td>13.82</td>
<td>0.000 8509</td>
<td>1.9 ( \times 10^{12} )</td>
<td></td>
</tr>
<tr>
<td>0.50 M NaCl</td>
<td>6.5</td>
<td>22.8 44h</td>
<td>13.864</td>
<td>0.000 5057</td>
<td>1.6 ( \times 10^{12} )</td>
<td></td>
</tr>
<tr>
<td>0.50 M NaClO(_4)</td>
<td>7.2</td>
<td>12 min</td>
<td>13.86</td>
<td>0.056</td>
<td>5.6 ( \times 10^{12} )</td>
<td></td>
</tr>
<tr>
<td>0.50 M NaCl</td>
<td>7.2</td>
<td>21 min</td>
<td>13.86</td>
<td>0.018</td>
<td>1.8 ( \times 10^{12} )</td>
<td></td>
</tr>
<tr>
<td>0.165 M Na(_2)SO(_4)</td>
<td>7.2</td>
<td>36 min</td>
<td>13.86</td>
<td>0.016</td>
<td>7.8 ( \times 10^{12} )</td>
<td></td>
</tr>
<tr>
<td>0.70 M NaCl, alk</td>
<td>2.5 ( \times 10^{-3} ) M</td>
<td>7.05</td>
<td>13.926</td>
<td>0.0079</td>
<td>2.1 ( \times 10^{12} )</td>
<td></td>
</tr>
</tbody>
</table>

\( k_2 \) is obtained in a few trials. Pertinent data are summarized in Table IV. The agreement between Tamura et al. \((23)\) and this study is surprisingly good, since their adsorption constant \( K \) was obtained for amorphous iron hydroxide formed by hydrolysis and not oxygenation.

Product Identification. Initial attempts to obtain X-ray diffraction patterns for the oxygenation products were unsuccessful. They were amorphous to X-rays. Misawa et al. \((24)\) claimed that \( \gamma\text{-FeOOH} \) was formed in cases of the rapid aerial oxidation of ferrous iron and Fe(II)-Fe(II\(_3\)) green intermediates in neutral and slightly acidic solutions. In order to gain information about the nature of the products, additional experimental techniques were needed. Infrared spectroscopy proved to be most useful in this case. Standard infrared spectra for various ferric oxyhydroxides have been reported \((22,25-27)\), of which the y-FeOOH pattern was the one that best matched the experimental patterns (tabulated in Table V) confirming that y-FeOOH is the product.

Table V. X-ray Diffraction Pattern of Fe(II) Oxygenation Product

<table>
<thead>
<tr>
<th>( d, \AA )</th>
<th>Intensity</th>
<th>( d, \AA )</th>
<th>Intensity</th>
<th>( d, \AA )</th>
<th>Intensity</th>
<th>( l/\theta ^{a} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.36</td>
<td>s, br</td>
<td>2.380</td>
<td>v( \beta )</td>
<td>6.26</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>3.27</td>
<td>s</td>
<td>1.996</td>
<td>m, sh</td>
<td>3.29</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>2.821</td>
<td>ms, sh</td>
<td>1.8385</td>
<td>s</td>
<td>2.47</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>2.479</td>
<td>br, s</td>
<td>1.5297</td>
<td>w, br</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* The three strongest lines of lepidocrocite from ASTM card file 6-98.
Figure 7. Infrared spectra of standard ferric oxyhydroxides: (1) α-FeOOH, synthetic; obtained from G. Rossman, California Institute of Technology, 0.8-mg sample in 2.00 mg of KBr. (2) β-FeOOH, synthetic; 1-mg sample in 200 mg of KBr. (3) γ-FeOOH, synthetic; 0.6-mg sample in 200 mg of KBr. (4) Amorphous FeOOH, synthetic; 1-mg sample in 200 mg of KBr.

requires a time scale much longer than hours at such pH values. The hydrolyzed ferric oxide at pH values close to 12 exhibits goethite peaks, although X-ray diffraction shows it to be amorphous. It is of interest to note that, although it is known that anions are important in determining the nature of the product in ferric salt hydrolysis, in oxygenation experiments it is γ-FeOOH that invariably forms first, whether ClO₄⁻, Cl⁻, or SO₄²⁻ media. The γ-FeOOH so formed is unstable, as γ-FeOOH is unstable with respect to α-FeOOH.

Summary and Conclusions

This work presents new experimental data on the oxygenation kinetics of ferrous iron in aqueous systems and on the identity of the solid phase formed in the reaction. We have attempted to place these results and earlier observations for the oxygenation process in a consistent framework to help account for the behavior of iron in different aquatic environments.

The general rate law, consistent with earlier work, is:

\[
-d[\text{Fe(II)}]/dt = k[\text{OH}^-]^2P_{O_2}[\text{Fe(II)}] = k'[\text{OH}^-]^2[O_2][\text{Fe(II)}]
\]

where \(k'\) is related to \(k\) by the Henry's law constant for oxygen and the activity coefficient of oxygen. For solutions of sufficiently low pH, ca. 7, the rate constant \(k\) is dependent on ionic strength, concentration of individual anions, and temperature. At 25 °C, pH 6.84, and \(P_{O_2} = 0.20\) atm, an increase of ionic strength (with NaClO₄) from 9 to 110 mM increases the half-time for oxidation from 18 to 38 min. A change in temperature from 5 to 30 °C (\(P_{O_2} = 0.20\) atm, pH 6.84, ionic strength = 110 mM, alkalinity = 9 mequiv/L) causes a decrease in oxidation half-time from 316 to 4 min, which is mainly caused by the change in \(\text{OH}^-\) concentration due to the temperature dependence of the ionization constant of water.

Chloride and sulfate ions have a significant retarding influence on the oxygenation rate in the pH range from 6.5 to 7.2. The oxygenation half-times are in the sequence \(\text{SO}_4^{2-} > \text{Cl}^- > \text{ClO}_4^-\) for constant ionic strength in agreement with the results of Tamura et al. (19).

For pH greater than ~7, the kinetic data indicate catalysis of aqueous Fe(II) disappearance by the reaction product. An autocatalytic rate expression with first- and second-order rate constants \(k_1\) and \(k_2\), where \(k_1\) is the apparent homogeneous rate constant and \(k_2\) the apparent catalytic constant, adequately describes the experimental data.

Comparison of the infrared (IR) spectra of products of our oxygenation experiments under various solution conditions with IR spectra of ferric oxyhydroxide standards showed that the product was invariably closest to γ-FeOOH, lepidocrocite. This observation was confirmed by comparison of the X-ray diffraction patterns of the Fe(II) oxygenation product with that of standard lepidocrocite.

The results of this study may have implications for understanding the short-term dynamics of iron transformations in freshwater and marine systems. It is suggested that an autocatalytic rate expression is needed at higher pH, and that the influence of simple media ions (Cl⁻, SO₄²⁻) in retarding oxygenation–removal helps to explain reported differences in behavior for freshwater, estuarine, and marine waters. An Fe(II) oxygenation half-time on the order of minutes, rather than seconds, for marine waters may help to provide an explanation for biological availabilities of Fe(II) and Fe(III) in

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Figure 8. Infrared spectra of ferrous iron oxygenation product. All spectra run with 1-mg sample in 200 mg of KBr. Spectra 1, 2, and 3 are run at experimental conditions of pH 7.2, \( T = 25^\circ C \), ionic strength = 0.5 M, HCO\(_3^-\) /CO\(_2\) buffers, [Fe(II)] = 50 \( \mu \)M: (1) 0.5 M NaCl; (2) 0.165 M Na\(_2\)SO\(_4\); (3) 0.5 M NaClO\(_4\); (4) experimental conditions—pH 8.3, \( T = 25^\circ C \), 0.7 M NaCl, HCO\(_3^-\) /CO\(_2\) buffers, [Fe(II)] = 10\(^{-3}\) M; (5) experimental conditions—pH 9.0, \( T = 25^\circ C \), 0.1 M NaClO\(_4\), NH\(_4^+\) /NH\(_3\) buffers.

Figure 9. Infrared spectra of some ferric iron hydrolysis products. All spectra run with 1-mg sample in 200 mg of KBr: (1) \( 10^{-3}\) M Fe(ClO\(_4\)) in 0.7 M NaCl; pH 8.3 by HCO\(_3^-\) /CO\(_2\) buffer; 4-h equilibration time. (2) Fe(NO\(_3\)) in 0.1 M NaN\(_2\)O; pH 8 by addition of CO\(_3^2-\) free NaOH; from K. Hayes, Stanford University. (3) FeCl\(_3\) in 0.01 M NaOH; from D. Wilson, Waterways Experimental Station, Vicksburg, Miss.

Surface waters containing both reducing agents and dissolved oxygen. The observation that \( \gamma \)-FeOOH is the oxygenation product under the solution conditions studied suggests that this ferric oxyhydroxide adsorbent merits study in work on adsorption directed to natural waters. In the long run, \( \gamma \)-FeOOH is unstable with respect to \( \alpha \)-FeOOH, but short-term sorption and catalytic behavior will be governed by the nature of the immediate oxygenation products.
Literature Cited


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