Lecture #35

Precipitation and Dissolution: Iron Hydroxides

(Stumm & Morgan, Chapt. 7)

Benjamin; Chapter 8.7-8.15

CEE 680: Water Chemistry

Updated: 11 April 2018
Topics

- Exam #2 Review
  - Alkalinity, Carbonates and pH
- Hydrolysis
  - Aquo metal ion gives rise to hydroxo complexes
- Iron Hydroxide solubility
Concentration of inorganics in fresh water

From: Stumm & Morgan, 1996; Benjamin, 2002; fig 1.1

Figure 15.1. Cumulative curves showing the frequency distribution of various constituents in terrestrial water. Data are mostly from the United States from various sources. (Adapted from Davies and DeWiest, 1966.)
Charge Balance & Alk

- Major Cation Charge = Major Anion Charge

\[
C_B \left\{ \begin{array}{c} Na^+ + K^+ + 2Ca^{+2} + 2Mg^{+2} \\ + H^+ \end{array} \right\} = C_A \left\{ \begin{array}{c} Cl^- + NO_3^- + 2SO_4^{2-} \\ + HCO_3^- + 2CO_3^{-2} + OH^- \end{array} \right\}
\]

- And simplifying:

\[
C_B - C_A = HCO_3^- + 2CO_3^{-2} + OH^- - H^+
\]

≡ Alkalinity

- Now combining with equilibria

\[
C_B - C_A \equiv Alk \equiv (\alpha_1 + 2\alpha_2)C_T + K_w/[H^+] - H^+
\]
Closed & Open

**Closed system**
- Most common, especially in treatment systems

- $C_T$ is fixed (from mass balance)
- Alkalinity is fixed or “conservative” (from mass balance)
- Calculate pH (and other carbonate species)

**Open System**
- Requires full equilibrium with bulk atmosphere or large volume of headspace

- $H_2CO_3$ is fixed (from fixed pCO2)

$Alk_{blend} = \frac{\sum Q_i Alk_i}{\sum Q_i}$
Ferrous Hydroxide I

- **Thermodynamics**
  - \( \text{Fe(OH)}_2 (s) = \text{Fe}^{+2} + 2\text{OH}^- \) \( K_{so} = 10^{-15.1} \)
  - \( \text{Fe}^{+2} + \text{OH}^- = \text{FeOH}^+ \) \( K_1 = 10^{4.5} \)
  - \( \text{Fe}^{+2} + 3\text{OH}^- = \text{Fe(OH)}_3^- \) \( K_2 = 10^{11.0} \)

- **Mass Balance**
  - \( \text{Fe}_T = [\text{Fe}^{+2}] + [\text{FeOH}^+] + [\text{Fe(OH)}_3^-] \)

Constants from Stumm & Morgan, 1996; identical to those from Morel & Hering, 1993
Ferrous Hydroxide II

- Log C vs pH relationships
  - Log \([Fe^{+2}]\) = 12.9 - 2pH
  - Log \([FeOH^+]\) = 3.4 - pH
  - Log \([Fe(OH)_3^-]\) = -18 + pH

Based on: Constants from Stumm & Morgan, 1996; identical to those from Morel & Hering, 1993
<table>
<thead>
<tr>
<th>Species</th>
<th>Fe(OH)₂ (s)</th>
<th>H⁺</th>
<th>Log K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe+2</td>
<td>1</td>
<td>2</td>
<td>13.3</td>
</tr>
<tr>
<td>FeOH⁺</td>
<td>1</td>
<td>1</td>
<td>4.6</td>
</tr>
<tr>
<td>Fe(OH)₃⁻</td>
<td>1</td>
<td>-1</td>
<td>-19.08</td>
</tr>
<tr>
<td>H⁺</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>OH⁻</td>
<td>0</td>
<td>-1</td>
<td>-14</td>
</tr>
<tr>
<td>Log(conc.)</td>
<td>0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[
\log[\text{Fe}^{2+}] = 13.3 - 2\text{pH} \\
\log[\text{FeOH}^+] = 4.6 - 1\text{pH} \\
\log[\text{Fe(OH)}_3^-] = -19.08 + 1\text{pH}
\]
The graph shows a pH scale ranging from 0 to 14 on the x-axis and Log C values ranging from -14 to 0 on the y-axis. The pH scale is labeled with intervals of 1, and the log scale is marked with intervals of 1, starting from -14 up to 0.
Based on:
Constants from Stumm & Morgan, 1996; identical to those from Morel & Hering, 1993.
Based on:
Constants from Snoeyink & Jenkins, 1980

- Log \([\text{Fe}^{+2}]\) = 13.5 – 2pH
- Log \([\text{FeOH}^+]\) = 4.6 – pH
- Log \([\text{Fe(OH)}_3^-]\) = -19.1 + pH
Trivalent Metal Hydrolysis

- Case for iron

\[ \text{Fe(H}_2\text{O)}_6^{+3} \leftrightarrow \text{FeOH(H}_2\text{O)}_5^{+2} \leftrightarrow \text{Fe(OH)}_2(\text{H}_2\text{O)}_4^{+} \]

\[ + \text{H}^+ \]

\[ + 2\text{H}^+ \]

\[ + 3\text{H}^+ \]

\[ + 4\text{H}^+ \]

\[ \text{Fe(OH)}_3(\text{H}_2\text{O)}_3 \leftrightarrow \text{Fe(OH)}_4(\text{H}_2\text{O)}_2^- \]

\[ \downarrow \]

\[ \text{Fe(OH)}_3 (s) \]
Ferric Hydroxide I

**Thermodynamics**
- \(\text{Fe(OH)}_3 (s) = \text{Fe}^{+3} + 3\text{OH}^-\) \(K_{so} = 10^{-38.8}\)
- \(\text{FeOH}^{+2} = \text{Fe}^{+3} + \text{OH}^-\) \(K_1 = 10^{-11.8}\)
- \(\text{Fe(OH)}_2^{+} = \text{FeOH}^{+2} + \text{OH}^-\) \(K_2 = 10^{-10.5}\)
- \(\text{Fe(OH)}_4^- = \text{Fe(OH)}_2^{+} + 2\text{OH}^-\) \(K_3 = 10^{-12.1}\)
- \(\text{Fe}_2(\text{OH})_2^{+4} = 2\text{Fe}^{+3} + 2\text{OH}^-\) \(K_{22} = 10^{-25.05}\)

**Mass Balance**
- \(\text{Fe}_T = [\text{Fe}^{+3}] + [\text{FeOH}^{+2}] + [\text{Fe(OH)}_2^{+}] + [\text{Fe(OH)}_4^-] + [\text{Fe}_2(\text{OH})_2^{+4}]\)
Ferric Hydroxide II

Log C vs pH relationships

- \( \log [\text{Fe}^{+3}] = 3.2 - 3\text{pH} \)
- \( \log [\text{FeOH}^{+2}] = 1.0 - 2\text{pH} \)
- \( \log [\text{Fe(OH)}_2^{+}] = -2.5 - \text{pH} \)
- \( \log [\text{Fe(OH)}_4^{-}] = -18.4 + \text{pH} \)
- \( \log [\text{Fe}_2(\text{OH})_2^{+4}] = 3.45 - 4\text{pH} \)
Ferric Hydroxide IV

\[
\begin{align*}
\text{Fe}^3 & \rightarrow \text{Fe}^2 (\text{OH})_2^{+4} \\
\text{Fe}^2 (\text{OH})_2^{+4} & \rightarrow \text{Fe}^+ (\text{OH})_2^{+2} \\
\text{Fe}^+ (\text{OH})_2^{+2} & \rightarrow \text{Fe}^+ (\text{OH})^+ \\
\text{Fe}^+ (\text{OH})^+ & \rightarrow \text{Fe}^{2+} (\text{OH})_2^{+4}
\end{align*}
\]
Magnesium

Divalent Alkaline Earth

[Graph showing the relationship between pH and log C, with lines for Mg²⁺, Mg(OH)⁻, H⁺, and OH⁻.]
• Divalent Transition Metal

Based on:
Constants from Snoeyink & Jenkins, 1980
Ferric-Fe

- Trivalent Transition Metal
Hemoglobin

- Electron transfer in the heme, forming superoxide ion that binds with the ferric
- \[ \text{Fe(II)} + \text{O}_2 \rightleftharpoons \text{Fe(III)}-\text{O}_2^- \]
Siderophores

- Mining Iron

Saha et al., 2016
Siderophores

- Fighting for Iron

Wilson et al., 2016

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Siderophores

- Ligand Atoms and immediate environment

Wilson et al., 2016
Siderophores

- Full Molecules

Wilson et al., 2016

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• To next lecture