Enhanced Reductive Dechlorination through Biological Interactions with Zero-Valent Iron

Brian A. Wrenn
Environmental Engineering Science Program
Civil Engineering Department
Washington University
St. Louis, MO
Biological Reductive Dechlorination Pathway

- sequential dechlorination mechanism
  - reaction rate is proportional to chlorine content
    - PCE > TCE > cis-1,2-DCE > vinyl chloride
Biological Reductive Dechlorination Pathway

- sequential dechlorination mechanism
  - reaction rate is proportional to chlorine content
    - PCE > TCE > cis-1,2-DCE > vinyl chloride
      - accumulation of intermediates is a concern
    - vinyl chloride is known human carcinogen
  - electron donor substrate is required as coreactant
Biological Reductive Dechlorination Pathway

- Hydrogen ($H_2$) is the preferred electron donor for biological reductive dechlorination.
- Competition for hydrogen from methanogens, sulfate reducers, and Fe(III) reducers.
  - Rapid turnover of hydrogen in subsurface.
  - Limited transport away from site of production.

∴ Hydrogen must be produced close to its site of consumption.
## Competition for Hydrogen

<table>
<thead>
<tr>
<th>TEAP</th>
<th>$\Delta G^\circ'$ (kJ/mol H₂)</th>
<th>$[H₂]_{ss}$ (nM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>denitrification</td>
<td>224</td>
<td>&lt;0.05 – 0.4</td>
</tr>
<tr>
<td>Fe(III) reduction</td>
<td>50</td>
<td>0.1 – 0.5</td>
</tr>
<tr>
<td>sulfate reduction</td>
<td>38</td>
<td>1 – 4.5</td>
</tr>
<tr>
<td>methanogenesis</td>
<td>34</td>
<td>2.5 – 24</td>
</tr>
<tr>
<td>PCE $\rightarrow$ TCE</td>
<td>112</td>
<td>0.6 – 0.9</td>
</tr>
<tr>
<td>TCE $\rightarrow$ DCE</td>
<td>102</td>
<td>0.6 – 0.9</td>
</tr>
<tr>
<td>DCE $\rightarrow$ VC</td>
<td>78</td>
<td>0.1 – 2.5</td>
</tr>
<tr>
<td>VC $\rightarrow$ ethene</td>
<td>93</td>
<td>2 – 24</td>
</tr>
</tbody>
</table>
# Competition for Hydrogen

<table>
<thead>
<tr>
<th>TEAP</th>
<th>$\Delta G^o'$ (kJ/mol H$_2$)</th>
<th>$[H_2]_{ss}$ (nM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>denitrification</td>
<td>224</td>
<td>$&lt;0.05 – 0.4$</td>
</tr>
<tr>
<td>Fe(III) reduction</td>
<td>50</td>
<td>0.1 – 0.5</td>
</tr>
<tr>
<td>sulfate reduction</td>
<td>38</td>
<td>1 – 4.5</td>
</tr>
<tr>
<td>methanogenesis</td>
<td>34</td>
<td>2.5 – 24</td>
</tr>
<tr>
<td>PCE $\rightarrow$ TCE</td>
<td>112</td>
<td>0.6 – 0.9</td>
</tr>
<tr>
<td>TCE $\rightarrow$ DCE</td>
<td>102</td>
<td>0.6 – 0.9</td>
</tr>
<tr>
<td>DCE $\rightarrow$ VC</td>
<td>78</td>
<td>0.1 – 2.5</td>
</tr>
<tr>
<td>VC $\rightarrow$ ethene</td>
<td>93</td>
<td>2 – 24</td>
</tr>
</tbody>
</table>
## Competition for Hydrogen

<table>
<thead>
<tr>
<th>TEAP</th>
<th>$\Delta G^o'$ (kJ/mol H$_2$)</th>
<th>$[H_2]_{ss}$ (nM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>denitrification</td>
<td>224</td>
<td>$&lt;0.05 – 0.4$</td>
</tr>
<tr>
<td>Fe(III) reduction</td>
<td>50</td>
<td>0.1 – 0.5</td>
</tr>
<tr>
<td>sulfate reduction</td>
<td>38</td>
<td>1 – 4.5</td>
</tr>
<tr>
<td>methanogenesis</td>
<td>34</td>
<td>2.5 – 24</td>
</tr>
<tr>
<td>PCE $\rightarrow$ TCE</td>
<td>112</td>
<td>0.6 – 0.9</td>
</tr>
<tr>
<td>TCE $\rightarrow$ DCE</td>
<td>102</td>
<td>0.6 – 0.9</td>
</tr>
<tr>
<td>DCE $\rightarrow$ VC</td>
<td>78</td>
<td>0.1 – 2.5</td>
</tr>
<tr>
<td>VC $\rightarrow$ ethene</td>
<td>93</td>
<td>2 – 24</td>
</tr>
</tbody>
</table>
## Competition for Hydrogen

<table>
<thead>
<tr>
<th>TEAP</th>
<th>$\Delta G^\circ$ (kJ/mol H$_2$)</th>
<th>$[H_2]_{ss}$ (nM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>denitrification</td>
<td>224</td>
<td>&lt;0.05 – 0.4</td>
</tr>
<tr>
<td>Fe(III) reduction</td>
<td>50</td>
<td>0.1 – 0.5</td>
</tr>
<tr>
<td>sulfate reduction</td>
<td>38</td>
<td>1 – 4.5</td>
</tr>
<tr>
<td>methanogenesis</td>
<td>34</td>
<td>2.5 – 24</td>
</tr>
<tr>
<td>PCE $\rightarrow$ TCE</td>
<td>112</td>
<td>0.6 – 0.9</td>
</tr>
<tr>
<td>TCE $\rightarrow$ DCE</td>
<td>102</td>
<td>0.6 – 0.9</td>
</tr>
<tr>
<td>DCE $\rightarrow$ VC</td>
<td>78</td>
<td>0.1 – 2.5</td>
</tr>
<tr>
<td>VC $\rightarrow$ ethene</td>
<td>93</td>
<td>2 – 24</td>
</tr>
</tbody>
</table>
## Competition for Hydrogen

<table>
<thead>
<tr>
<th>TEAP</th>
<th>$\Delta G^\circ$ (kJ/mol H$_2$)</th>
<th>$[H_2]_{ss}$ (nM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>denitrification</td>
<td>224</td>
<td>$&lt;0.05 – 0.4$</td>
</tr>
<tr>
<td>Fe(III) reduction</td>
<td>50</td>
<td>$0.1 – 0.5$</td>
</tr>
<tr>
<td>sulfate reduction</td>
<td>38</td>
<td>$1 – 4.5$</td>
</tr>
<tr>
<td>methanogenesis</td>
<td>34</td>
<td>$2.5 – 24$</td>
</tr>
<tr>
<td>PCE $\rightarrow$ TCE</td>
<td>112</td>
<td>$0.6 – 0.9$</td>
</tr>
<tr>
<td>TCE $\rightarrow$ DCE</td>
<td>102</td>
<td>$0.6 – 0.9$</td>
</tr>
<tr>
<td>DCE $\rightarrow$ VC</td>
<td>78</td>
<td>$0.1 – 2.5$</td>
</tr>
<tr>
<td>VC $\rightarrow$ ethene</td>
<td>93</td>
<td>$2 – 24$</td>
</tr>
</tbody>
</table>
## Competition for Hydrogen

<table>
<thead>
<tr>
<th>TEAP</th>
<th>$\Delta G^o'$ (kJ/mol H₂)</th>
<th>$[H_2]_{ss}$ (nM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>denitrification</td>
<td>224</td>
<td>&lt;0.05 – 0.4</td>
</tr>
<tr>
<td>Fe(III) reduction</td>
<td>50</td>
<td>0.1 – 0.5</td>
</tr>
<tr>
<td>sulfate reduction</td>
<td>38</td>
<td>1 – 4.5</td>
</tr>
<tr>
<td>methanogenesis</td>
<td>34</td>
<td>2.5 – 24</td>
</tr>
<tr>
<td>PCE $\rightarrow$ TCE</td>
<td>112</td>
<td>0.6 – 0.9</td>
</tr>
<tr>
<td>TCE $\rightarrow$ DCE</td>
<td>102</td>
<td>0.6 – 0.9</td>
</tr>
<tr>
<td>DCE $\rightarrow$ VC</td>
<td>78</td>
<td>0.1 – 2.5</td>
</tr>
<tr>
<td>VC $\rightarrow$ ethene</td>
<td>93</td>
<td>2 – 24</td>
</tr>
</tbody>
</table>
Reductive Dechlorination by Zero-Valent Iron

Potential Reaction Mechanisms:
- direct reaction with Fe⁰ at metal surface
- surface-mediated reaction with sorbed Fe(II)

Competing Reactions:
- corrosion of Fe⁰ surface by reaction with water
- passivation of reactive surfaces by accumulation of crystalline metal oxides (e.g., maghematite, magnetite)
Zero-Valent Iron Reaction Mechanisms

Reductive Dechlorination: Direct Reaction with Fe°

\[
\text{Fe}^0 \rightarrow \text{Fe}^{2+} + \text{Cl}^- + \text{Cl}^- + \text{PCE} \rightarrow \text{Cl} \equiv \text{C} \equiv \text{C} \equiv \text{Cl} + 2 \text{Cl}^-
\]

dichloroacetylene
Zero-Valent Iron Reaction Mechanisms

Corrosion: Reaction with Fe⁰ with Water

\[
\begin{align*}
\text{Fe}^0 & \rightarrow \text{Fe}^{2+} \\
2 \text{H}_2\text{O} & \rightarrow 2 \text{OH}^- + \text{H}_2 \\
\text{H}^+ + \text{Cl}^- & \rightarrow \text{HCl}
\end{align*}
\]

Cathodic Hydrogen-Supported Biological Reductive Dechlorination

PCE

\[
\begin{align*}
\text{Cl} & \equiv \text{Cl} \\
\text{Cl} & \equiv \text{Cl} \\
\text{Cl} & \equiv \text{Cl}
\end{align*}
\]

TCE

\[
\begin{align*}
\text{Cl} & \equiv \text{Cl} \\
\text{H} & \equiv \text{Cl}
\end{align*}
\]
Zero-Valent Iron Reaction Mechanisms

Reductive Dechlorination: Reaction with Sorbed Fe$^{2+}$

\[
\begin{align*}
\text{Fe}^{3+} + \text{Cl}^- &\rightarrow \frac{1}{2} \text{Cl} - \text{C} \equiv \text{C} - \text{Cl} + 2 \text{Cl}^- \\
\text{dichloroacetylene} &
\end{align*}
\]
Zero-Valent Iron Reaction Mechanisms

Biological Regeneration of Sorbed Fe$^{2+}$

Fe(III)-reducing bacteria

$\frac{1}{2} \text{H}_2$  \rightarrow  abiotic

$\text{Fe}^0$  \rightarrow  $\text{Fe}^{2+}$
Biological Interactions with Emulsified Zero-Valent Iron
Biological Interactions with Emulsified Zero-Valent Iron

\[ \text{PCE}_{(aq)} + \text{H}_2 \rightarrow \text{H}_2 \text{C}_2 \text{H}_4 + \text{H}_2 \text{O} \]

\[ \text{PCE}_{(aq)} + \text{H}_2 \text{O} \rightarrow \text{H}_2 \text{C}_2 \text{H}_4 + \text{H}_2 \]

\[ \text{TCE}_{(aq)} + \text{H}_2 \rightarrow \text{H}_2 \text{C}_2 \text{H}_4 + \text{H}^+ + \text{Cl}^- \]

\[ \text{PCE}_{(oil)} \rightarrow \text{ethene} \]

\[ \text{PCE}_{(aq)} \rightarrow \text{ethene} \]
Biological Interactions with Emulsified Zero-Valent Iron

GW transport

PCE\textsubscript{(aq)}

TCE\textsubscript{(aq)}

H\textsuperscript{+} + Cl\textsuperscript{-}

biodegradation of vegetable oil shell

hydrogen

\textit{hydrogen: }

\begin{itemize}
  \item 32% of e\textsuperscript{-} equivalents
  \item local production and consumption
\end{itemize}

Glycerol:

\begin{itemize}
  \item 4% of e\textsuperscript{-} equivalents
  \item potential distant source of H\textsubscript{2}
\end{itemize}

Acetate:

\begin{itemize}
  \item 64% of e\textsuperscript{-} equivalents
  \item poor anaerobic electron donor
\end{itemize}
Anaerobic Biodegradation of Vegetable Oil

triglyceride

enzymatic hydrolysis

glycerol

fermentative bacteria

H$_2$O

propionate

acetogens

CO$_2$ + H$_2$

hydrogenotrophic methanogens

acetate

aceticlastic methanogens

acetogens

H$_2$

CH$_4$

CH$_4$ + CO$_2$
Anaerobic Biodegradation of Vegetable Oil

Cumulative gas volume (ml)

- Methanogenic enrichment
- Fe(III)-reducing enrichment

Fatty acid resistant

Inhibition by fatty acids

Time (days)
Anaerobic Biodegradation of Vegetable Oil

- **Triglyceride**
  - Enzymatic hydrolysis

- **Glycerol**
  - Fermentative bacteria
  - Hydrolysis

- **Fatty Acids**
  - Acetogens (acetoclastic methanogens)
  - Aceticlastic methanogens
  - Syntrophic acetate oxidizers

- **Acetate**
  - H₂
  - CO₂ + H₂

- **CH₄**
  - Hydrogenotrophic methanogens

- **Propionate**

- **CO₂ + CH₄**
Fe(III) Effects on Fatty Acid Sensitivity

**Known:** Aceticlastic methanogens are very sensitive to inhibition by fatty acids.

\[ ^*\text{CH}_3\text{COOH} \rightarrow ^*\text{CH}_4 + \text{CO}_2 \]

**Hypothesis:** Acetate oxidizing Fe(III) reducers may be less sensitive to fatty acids. In the absence of bioavailable Fe(III), these organisms may grow as syntrophic acetate oxidizers with hydrogenotrophic methanogens.

\[ ^*\text{CH}_3\text{COOH} + 2 \text{H}_2\text{O} \rightarrow 2 \text{^*CO}_2/\text{CO}_2 + 4 \text{H}_2 \]

\[ ^*\text{CO}_2/\text{CO}_2 + 4 \text{H}_2 \rightarrow ^*\text{CH}_4/\text{CH}_4 + 2 \text{H}_2\text{O} \]

\[ ^*\text{CH}_3\text{COOH} \rightarrow ^*\text{CH}_4/\text{CH}_4 + ^*\text{CO}_2/\text{CO}_2 \]
Anaerobic Oxidation of $^{13}\text{C}_{\text{methyl}}$-Acetate

![Graph showing the oxidation of $^{13}\text{C}_{\text{methyl}}$-Acetate over time](image)
Summary: Biological Interactions with Zero-Valent Iron

- Microbial activity can interact synergistically with zero-valent iron to enhance degradation rates of chlorinated aliphatic hydrocarbons (CAHs) in groundwater
  - Hydrogen produced by anaerobic corrosion of Fe$^0$ can support microbial reductive dechlorination
  - Fe(III)-reducing bacteria can reduce surface ferric oxides to generate sorbed Fe(II), which can reductively dechlorinate CAHs
Summary: Biological Interactions with Emulsified Zero-Valent Iron

• Microbial metabolism of vegetable-oil coat of emulsified zero-valent iron can support reductive dechlorination of chlorinated solvents in groundwater
  ➢ The vegetable-oil shell prevents direct interactions of microorganisms with zero-valent iron particles
  ➢ Anaerobic biodegradation of vegetable-oil fatty acids results in localized production of hydrogen, which can support biological reductive dechlorination of CAHs
  ➢ Acetate may serve as a distant hydrogen source if syntrophic-acetate oxidizing (iron-reducing) bacteria are present