Role of Iron and Vitamin B12 Amendments in Stimulating Reductive Dechlorination of TCE in High Sulfate Groundwater

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OUTLINE
Iron and Sulfate Geochemistry
Previous Microcosm Work
Column Study Set-up and Design
Column Operation
Role of Nutrients in Supporting Complete Biodegradation
Conclusions
Problems with High Sulfate Groundwater

“General” Organics

Simple Organics

Fermenters

Acetogens

Hydrogen

Methane

Methanogens

TCE

Ethene

HCl

Dehalorespirers

Sulfate Reducers

SO_4^{2-}

HS^{-}

CO_2

HCl

Ethene
Problems with High Sulfate Groundwater

Biological degradation of TCE: 
TCE $\rightarrow$ cDCE $\rightarrow$ VC $\rightarrow$ ethene

Complete biodegradation of TCE to ethene inhibited by high sulfide concentrations
Potential Solution – Add Iron

Iron-reducing Bacteria

Lactate-fermenting Bacteria

Sulfate-reducing Bacteria

Iron(III) Oxide

Iron(II) Sulfide

Fe$^{3+}$

Fe$^{2+}$

$\text{Lactate} \rightarrow \text{Lactate-fermenting Bacteria} \rightarrow \text{Acetate} \rightarrow \text{Acetate} \rightarrow \text{CO}_2 \rightarrow \text{CO}_2 \rightarrow \text{Sulfate-reducing Bacteria} \rightarrow \text{SO}_4^{2-} \rightarrow \text{Iron(II) Sulfide}

\text{Iron-reducing Bacteria} \rightarrow \text{Propionate} \rightarrow \text{Carbon dioxide} \rightarrow \text{Carbon dioxide} \rightarrow \text{HS}^-$

Image Source: http://www.bio.anl.gov/images/environtbio/subsurface/reduction_iron.gif
Microcosm Study Design

Study performed in serum bottles (125 mL groundwater, 25 g crushed gypsum-rich bedrock, 5 g sediment), in duplicate

Treatments:

- Killed controls
- Unamended
- Magnetite (Fe3O4) (Rockwood)
- Magnetite (Fe3O4) (Alfa Aesar)
- Ferric citrate
- Ferric sulfate
- Ferrous chloride
- Ferrous lactate
- Ferrous sulfate
Complete reductive dechlorination of TCE to ethene observed with EVO and magnetite.
Site Description

- Former plant site
- Electrical components manufactured from 1951-1990
- 55 acre site
- Waste solvents (TCE, acetone, methanol) disposed into evaporation pit(s)
Site Description – Gypsum-Rich Bedrock Layer

Primary GW flow in gypsum-rich D3 unit located ~ 46 meters bgs

Gypsum: CaSO$_4$·2H$_2$O
Column Set-Up

Tedlar bag in nitrogen blanket containing site groundwater with ~200 mg/L TCE

Glass soil column (5.0 cm ID x 60 cm length) with sampling ports and Teflon-lined septa

Teflon tubing

FMI metering pump

Pressure gauge

Flow = 2 mL/hr

Teflon tubing

Effluent sample collection vessel
## Experimental Design

<table>
<thead>
<tr>
<th>Column</th>
<th>Type</th>
<th>Rock Added (g)</th>
<th>Magnetite Added (g)</th>
<th>Oil Retained (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Control</td>
<td>1553</td>
<td>None</td>
<td>N/A</td>
</tr>
<tr>
<td>2</td>
<td>Active</td>
<td>1573</td>
<td>12.2</td>
<td>15.9</td>
</tr>
<tr>
<td>3</td>
<td>Active</td>
<td>1582</td>
<td>48.8</td>
<td>15.8</td>
</tr>
</tbody>
</table>
Bromide Tracer Testing Results

Mean residence time matched theoretical, but breakthrough was early and long tail was present

<table>
<thead>
<tr>
<th>Column</th>
<th>Bedrock mass (grams)</th>
<th>Pore volume (mL)</th>
<th>Total porosity</th>
<th>Calculated MRT (days)</th>
<th>Total bromide feed (mL)</th>
<th>Measured MRT (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (control)</td>
<td>1553</td>
<td>550</td>
<td>0.475</td>
<td>11.5</td>
<td>261</td>
<td>11.6</td>
</tr>
<tr>
<td>2</td>
<td>1573</td>
<td>542</td>
<td>0.466</td>
<td>11.2</td>
<td>259</td>
<td>11.6</td>
</tr>
<tr>
<td>3</td>
<td>1582</td>
<td>539</td>
<td>0.456</td>
<td>11.0</td>
<td>277</td>
<td>12</td>
</tr>
</tbody>
</table>
Control Column – VOC Results

Influent mostly TCE with lower amounts of cisDCE

Effluent mostly cisDCE with lower amounts of TCE and minor VC
\[ \text{Cl \#} = \frac{(\text{mol TCE \times 3}) + (\text{mol cDCE \times 2}) + (\text{mol VC})}{(\text{total mol chlorinated ethenes + ethene})} \]
Active Columns – Early VOC Results

Why is dechlorination stopping at cDCE and VC?

Why is dechlorination not progressing throughout the column?
Periodic nutrient amendment (N/P, YE, vitamin B12) beginning on Day 77 improved dechlorination performance.
Microbial Characterization Results

Dhc counts increasing in active columns, while vcr-A results are mixed.
Active Columns – Post-Bioaugs Degradation Results

Dechlorination progress slowed after 200 days

Bioaugsmentation with SDG-9™ on Day 238 did not improve performance
Active Columns – Degradation Results

4X increase in amount of vitamin B12 on Day 295 resulted in improved dechlorination performance

Column 2 – 90% conversion of TCE to ethene

Column 3 – Complete conversion of TCE to ethene
Chemical Structure of Vitamin B12

Figure Source: www.chemicalbook.com
Role of Cobalt in Reductive Dechlorination

Cobalt is critical for VCR enzyme function

Multiple strains within a single group (*Dehalococcoides*)

Vinyl Chloride Reductase Enzyme

Figure Source: SABRE training class
Potential Cobalt Removal Mechanisms

\[
\begin{align*}
\text{Co}^{2+} + \text{H}_2\text{S} & \rightarrow \text{Cobalt sulfide (CoS)} \\
\text{Fe}^{2+} + \text{H}_2\text{S} & \rightarrow \text{Iron sulfide (Fe}_x\text{S}_x\text{Co)} \\
\end{align*}
\]

Adsorption and Co-precipitation

Image Source: http://www.bio.anl.gov/images/environbio/subsurface/reduction_iron.gif
Final Microbial Characterization Results

Positive response to nutrient addition (incl. vitamin B12)

Addition of nutrients (N/P, YE) increased Dhc

Addition of vitamin B12 increased vcr-A
Why did Column 2 have 90% conversion of TCE to ethene, when Column 3 had complete conversion?

Sulfide levels in Column 2 consistently higher during last 50 days of study – suggests Fe limitation
Conclusions

Complete reductive dechlorination of TCE to ethene was achieved in active columns containing EVO and magnetite.

The periodic addition of supplemental nutrients was critical to process.

Vitamin B12 (cobalt) was particularly important.

Availability of cobalt potentially affected by co-precipitation with iron-sulfide minerals.

Moving forward with a pilot test in the deep bedrock to demonstrate process in-situ and collect data for full-scale design.
Thank you!
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