Sustained Remediation of Chlorinated Solvents Using In Situ Formation and Regeneration of Ferrous Sulfide

Lee Hovey
October 4th, 2017
• Case Study – Site A
  • Tetrachloroethene (PCE) contamination.
  • Initial remedy: Enhanced In Situ Bioremediation (EISB).
  • Sustained degradation by iron sulfide minerals.

• Additional Case Study Example
  • Carbon Tetrachloride (CT) contamination.

• Looking Forward
  • In situ formation of ferrous sulfide minerals as an engineered remedial approach.
Case Study – Site A

• Tetrachloroethylene (PCE) contamination in groundwater.

• Enhanced in situ bioremediation (EISB) remedy resulted in the in situ formation of iron sulfide minerals.

• PCE degradation sustained by iron sulfide minerals.
Dissolved Phase PCE – Q3 2013

10 µg/L
100 µg/L
1,000 µg/L
2,000 µg/L

Site Detail: EISB Treatment Area - November 2013

100 µg/L
1,000 µg/L
2,000 µg/L
Site A – Remedial Strategy

- **Bio-Trap® Study (2011)**
  - Deployed in wells GW-6 (in future EISB Area) and GW-7 (downgradient of future EISB Area).
  - Low-to-moderate level of biomass reported.
  - Moderate levels of *Dehalococcoides* Sp., the only known microorganism capable of facilitating complete degradation of PCE to ethene.
Site A – Remedial Strategy

- Bio-Trap® Study (2011).
- Dry Cheese Whey Injection (Nov. 2013).
  - Delivery via 7 injection wells.
  - ~2,250 gallons of a dry cheese whey and water mixture injected into each well.
Site A – Remedial Strategy

- Bio-Trap® Study (2011).
- Dry Cheese Whey Injection (Nov. 2013).
- Groundwater monitoring to evaluate treatment zone performance (ongoing).
  - = EISB performance monitoring well network
  - Monitoring well GW-6 was the only well located within the injection radius of influence (ROI).
Well GW-6 – PCE and Daughter Products

Hypothesized Biotic Pathway

- PCE
- TCE
- Cis 1,2-DCE
- Trans 1,2-DCE
- VC
- Ethene
- Ethane

Concentration (µg/L):

- Ethane
- Ethene
- Vinyl Chloride
- trans-1,2-DCE
- cis-1,2-DCE
- TCE
- PCE

November 2013
Dry Whey Injection
Site A – Remedial Strategy

- Bio-Trap® Study (2011).
- Dry Cheese Whey Injection (Nov. 2013).
- Groundwater monitoring to evaluate treatment zone performance (ongoing).
- Additional Bio-Trap® Study (July 2014).
  - Moderate level of biomass reported in GW-6 and PW-2 (in EISB Area).
  - *Dehalococcoides* Sp., counts were below reporting limits in GW-6 and PW-2.
Site A – Remedial Strategy

- Bio-Trap® Study (2011).
- Dry Cheese Whey Injection (Nov. 2013).
- Groundwater monitoring to evaluate treatment zone performance (ongoing).
- Additional Bio-Trap® Study (July 2014).
- Dry Cheese Whey Injection (June 2015).
  - Delivery via 8 injection wells.
  - ~2,100 gallons of a dry cheese whey and water mixture injected into each well.
Site A – Remedial Strategy

• Bio-Trap® Study (2011).
• Dry Cheese Whey Injection (November 2013).
• Additional Bio-Trap® Study (July 2014).
• Dry Cheese Whey Injection (June 2015).
• SDC-9™ Inoculation Injection (July 2015).
  • Culture contains Dehalococcoides Sp.
  • Nitrogen gas bubbled through chase water to attain dissolved oxygen (DO) concentration of <1 mg/L.
Well GW-6 – Constituents of Concern (COCs)

*Constituents below reporting limits in samples from GW-6.
Geochemical Observations

Sulfate Concentrations (mg/L) – Well GW-6

Baseline Concentration Range - Nov. 2013

<p>| | |</p>
<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>Sulfate</td>
<td>280-430 mg/L</td>
</tr>
</tbody>
</table>

Sulfate is reduced to sulfide

$\text{(H}_2\text{S, HS, S}^{2-}\text{)}$

Biotic Pathway

SO$_4^{2-}$

Sulfide
Geochemical Observations

Ferric iron ($\text{Fe}^{3+}$) is reduced to ferrous iron ($\text{Fe}^{2+}$)

<table>
<thead>
<tr>
<th>Baseline Concentration Range - Nov. 2013</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferrous Iron ($\text{Fe}^{2+}$)</td>
</tr>
</tbody>
</table>

Ferrous Iron Concentrations (mg/L) – Well GW-6
Ferrous Sulfide Generation

Ferric iron (Fe$^{3+}$) is reduced to ferrous iron (Fe$^{2+}$)

Biotic Pathway

Sulfate is reduced to sulfide (H$_2$S, HS, S$^{2-}$)

Biotic Pathway

Ferrous iron and sulfide combine to form iron sulfide minerals (FeS, FeS$_2$)
# Laboratory Testing of Sediment Samples

<table>
<thead>
<tr>
<th>Sediment Samples Collected on April 22, 2016</th>
<th>GW-6</th>
<th>GW-8</th>
<th>IW-3</th>
<th>IW-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rich Black</td>
<td>Reddish Brown</td>
<td>Blackish Grey</td>
<td>Very Light Grey</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>GW-6</th>
<th>GW-8</th>
<th>IW-3</th>
<th>IW-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sediment sample appearance dissimilar from boring log?</td>
<td>✓</td>
<td>×</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td>Iron and sulfur concentrations elevated &amp; correlated?</td>
<td>✓</td>
<td>×</td>
<td>✓</td>
<td>×</td>
</tr>
<tr>
<td>(\text{H}_2\text{S}) Odor observed when acid was added to sample?</td>
<td>✓</td>
<td>×</td>
<td>✓</td>
<td>×</td>
</tr>
</tbody>
</table>
Dissolved Phase PCE – Q4 2016

Site Detail: EISB Treatment Area - December 2016

100 µg/L
10 µg/L
100 µg/L
100 µg/L
100 µg/L
100 µg/L
PCE Trends

- PCE concentrations in the EISB Area decreased by an order of magnitude.
Site A - Conclusions

• Iron sulfide minerals facilitated degradation of PCE and daughter products.

• Under the right geochemical conditions, iron sulfide minerals can form as a result of carbon substrate injections.

• Cost savings realized due to the formation of iron sulfide minerals
  • Extended treatment longevity relative to EISB-only approach and the need for less frequent injections.

• Site is currently undergoing monitoring activities in support of site closure.
Thank you

Questions?

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