Hydraulic Fracturing with ZVI Emplacement for Treatment of Chlorinated Solvents in a Low Permeability Aquifer

April 11, 2012

Tamzen Macbeth, Ph.D., P.E., Co-Authors: Hamide Kayaci, Kent Sorenson, Ryan Wymore, Andy Greazel, Gord Bures, Gord Guest, Melanie Kito, Keith Forman, Adam Locke, Gorm Heron

CDM Smith
Background

- Hunters Point Naval Shipyard (HPNS), Building 134
- Chlorinated benzenes and ethenes in the subsurface as dense non aqueous phase liquid (DNAPL)
- Treatability study evaluated a multi-component treatment strategy including:
  - Hydraulic fracturing
  - EHC® injection
  - Thermal treatment
HPNS Treatability Study Area

Building 134

Former degreaser/sump
Problem: Complex Mix of Contaminants in Groundwater and Low-Permeability Soils

Volatile Organic Contaminants (VOCs):
- 1,2-Dichlorobenzene (DCB)
- 1,3-DCB
- 1,4-DCB
- Chlorobenzene (CB)
- Trichloroethene (TCE)
- Tetrachloroethene (PCE)
- cis-Dichloroethene (DCE)
- Vinyl chloride (VC)
Complex Geology/Hydrology

- **A-Aquifer**
  - Bay Mud
  - Bedrock
  - \( k = 0.014 - 0.078 \) ft/d

- **B-Aquifer**
  - \( k = 0.8 - 4.2 \) ft/d

- **Bedrock**
  - \( k = 0.36 - 1.04 \) ft/d
Treatability Study Objectives

**Groundwater Technology: Hydraulic Fracturing/EHC®**
- 80% reduction of chlorinated VOCs
- Polish remaining VOCs post-TCH to meet very stringent cleanup criteria (generally less than 5 ppb).

**Soil/DNAPL Technology: Thermal Conduction Heating (TCH)**
- 90% reduction in chlorinated VOCs
- Thermally-Enhanced Extraction of DNAPL

18-month Cleanup Timeframe
Pre-Remediation: DNAPL/Soil Mass Estimate

Estimate ~300 lb of VOCs present in the source area.

### Mixture Composition, %

- **Tetrachloroethene**: 41%
- **Trichloroethene**: <1%
- **1,2 Dichlorobenzene**: 43%
- **1,3 Dichlorobenzene**: 12%
- **1,4 Dichlorobenzene**: 12%
- **1,2 Dichloroethane**: 3%

<table>
<thead>
<tr>
<th>Total (lbs)</th>
<th>1,2-DCB</th>
<th>1,2-DCA</th>
<th>1,3-DCB</th>
<th>1,4-DCB</th>
<th>PCE</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before Remediation:</td>
<td>136</td>
<td>2.8</td>
<td>2.8</td>
<td>48</td>
<td>101</td>
<td>291</td>
</tr>
</tbody>
</table>
Pre-Remediation: Groundwater Contaminant Plume

<table>
<thead>
<tr>
<th>Parent Compounds</th>
<th>Reductive Daughter Products</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1,2-DCB</td>
</tr>
<tr>
<td>Total (lbs)</td>
<td></td>
</tr>
<tr>
<td>Before Remediation:</td>
<td>4.7</td>
</tr>
</tbody>
</table>

**Total Mass in Groundwater: 10.6 lbs**
In Situ Degradation Pathways

Chloroethene Degradation Pathway

Tetrachloroethene (PCE)
  reductive dechlorination

Trichloroethene (TCE)
  reductive B-elimination
  reductive dechlorination

Dichloroethene (trans-1,2-DCE) (1,1-DCE)
  reductive dechlorination
  manganese-reducing conditions
  anaerobic oxidation
  CO₂

Vinyl Chloride (VC)
  sulfate-reducing/iron reducing conditions’/anaerobic oxidation
  CO₂
  CH₄

Ethene

Ethane

Chloroacetylene

Acetylene

Chlorobenzene Degradation pathway

1,2,4-trichlorobenzene (1,2,4-TCB)

Dichlorobenzene (1,2-DCB, 1,4-DCB)

Chlorobenzene

Benzene

CO₂

biological reaction

abiotic reaction
Hydraulic Fracturing

- Oil and gas industry developed in the 1940s
- At HPS: viscous fluid (guar, crosslinkers, breaker, water) carried EHC® and in some cases sand to create fractures containing treatment amendment
Technology 1 Implementation: Hydraulic Fracturing/EHC® Emplacement

- 6 source fracture wells and 6 plume fracture wells
- 15- to 20-ft radius of amendment distribution
- Emplaced 13,419 lbs in source and 17,126 lbs of amendment EHC® in plume
### Hydraulic Fracturing and EHC™ Emplacement

<table>
<thead>
<tr>
<th>Frac Boreholes</th>
<th>Depth interval for fractures, fracs initiated ~3 ft</th>
<th>Mass EHC (lb)</th>
<th>Target Loading % EHC Met?</th>
<th>Sand (lb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFW1</td>
<td>10-43</td>
<td>3700</td>
<td>✓</td>
<td>1100</td>
</tr>
<tr>
<td>PFW2</td>
<td>10-33</td>
<td>3150</td>
<td>✓</td>
<td>3300</td>
</tr>
<tr>
<td>PFW3</td>
<td>10-33</td>
<td>3150</td>
<td>✓</td>
<td>3300</td>
</tr>
<tr>
<td>PFW4</td>
<td>10-33</td>
<td>3150</td>
<td>✓</td>
<td>4400</td>
</tr>
<tr>
<td>PFW5</td>
<td>13-43</td>
<td>3540</td>
<td>✓</td>
<td>0</td>
</tr>
<tr>
<td>PFW6</td>
<td>13-28</td>
<td>2300</td>
<td>✓</td>
<td>2200</td>
</tr>
<tr>
<td>SFW-1, -1A, and -1B</td>
<td>14-36</td>
<td>5801</td>
<td>✓</td>
<td>0</td>
</tr>
<tr>
<td>SFW2</td>
<td>13-23</td>
<td>1900</td>
<td>✓</td>
<td>0</td>
</tr>
<tr>
<td>SFW3</td>
<td>13-40</td>
<td>7450</td>
<td>✓</td>
<td>0</td>
</tr>
</tbody>
</table>

- Target EHC concentration 0.1% and 0.5% wEHC/wsoil in plume and source
- Range EHC dose for PF wells 0.09-0.11% wEHC/wsoil
- Range EHC dose for SF wells 0.36-0.63 % wEHC/wsoil
Evaluate Fracture Propagation: Tiltmeter Geophysics

- Analyzed tiltmeter data for 60 of 87 fracs
- Modeled fracs for every borehole except PFW6 (near IR26MW16A).

Tiltmeters estimate:
1) Fracture extent
2) Fracture orientation
3) Fracture “center”
Results of Fracking: Amendment Distribution

- Estimated 18 to 23-ft treatment radius
- Geochemical conditions conducive to reductive dechlorination
- Heterogeneous distribution of amendments.
- Evaluated technology for 4 months.
Technology 2 Implementation: Thermal Conduction Heating

- 18 heater wells
- Soil vapor extraction system
- Above ground treatment
- 4 month operations
Contaminant Removal During TCH
Contaminant Removal During TCH

VOC (ppbv)

Temperature (F)

1,2-DICHLOROBENZENE
1,3-DICHLOROBENZENE
1,4-DICHLOROBENZENE
BENZENE
CHLOROBENZENE
TETRACHLOROETHENE
TRICHLOROETHENE
1,2-DICHLOROETHANE
CIS-1,2-DICHLOROETHENE
VINYL CLORIDE (CHLOROETHENE)

Temperature
## Contaminant Mass Before and After-Treatment in Soil

<table>
<thead>
<tr>
<th></th>
<th>12DCB</th>
<th>12DCA</th>
<th>13DCB</th>
<th>14DCB</th>
<th>PCE</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Total (lbs)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Before Remediation:</strong></td>
<td>136</td>
<td>2.80</td>
<td>2.80</td>
<td>48.00</td>
<td>101.00</td>
<td>291</td>
</tr>
<tr>
<td><strong>After Remediation:</strong></td>
<td>19.1</td>
<td>0.01</td>
<td>0.08</td>
<td>2.60</td>
<td>0.01</td>
<td>22</td>
</tr>
<tr>
<td><strong>% Reduction</strong></td>
<td>86%</td>
<td>99.8%</td>
<td>97.2%</td>
<td>94.6%</td>
<td>99.9%</td>
<td>92.5%</td>
</tr>
</tbody>
</table>
Contaminant Mass Before and After Treatment in Groundwater

<table>
<thead>
<tr>
<th>Total (lbs)</th>
<th>Parent Compounds</th>
<th>Reductive Daughter Products</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1,2-DCB</td>
<td>1,2-DCA</td>
</tr>
<tr>
<td>Before Remediation:</td>
<td>4.7</td>
<td>0.7</td>
</tr>
<tr>
<td>After Remediation:</td>
<td>2.7</td>
<td>0.0</td>
</tr>
<tr>
<td>% Reduction</td>
<td>44%</td>
<td>100%</td>
</tr>
</tbody>
</table>

Total CoC Mass In Groundwater Pre-Treatment- 10.6 lbs
Total CoC Mass In Groundwater Post-Treatment- 4.1 lbs
Chlorinated Benzenes: IR25MW63A

Fracturing

TCH

1,3-DCB, 1,4-DCB, CB and Benzene (ug/L)

1,2-DCB (ug/L)

1,3-DICHLOROBENZENE
1,4-DICHLOROBENZENE
CHLOROBENZENE
BENZENE
1,2-DICHLOROBENZENE
Fracturing and Injection

1,2-DCB PAL = 600 ug/L
1,3-DCB PAL = 183 ug/L
CB PAL = 70 ug/L
Benzene PAL = 0.5 ug/L
1,4-DCB PAL = 2.1 ug/L
Chlorinated Ethenes: IR25MW63A

FRACTURING TCH

VOCs (ug/L)


TETRACHLOROETHENE
TRICHLOROETHENE
1,2-DICHLOROETHANE
CIS-1,2-DICHLOROETHENE
VINYL CHLORIDE
ETHENE
ETHANE
Fracturing and Injection
Chlorinated Benzenes: IR25MW65B

Graph showing the concentration of 1,3-DCB, 1,4-DCB, CB, and Benzene (ug/L) over time from 01/2010 to 07/2011. The graph indicates a peak concentration of 1,2-DCB at 600 ug/L and 1,3-DCB at 183 ug/L, with other concentrations below these levels. The data is marked with different colors representing various compounds and events such as Fracturing and Injection.
Chlorinated Ethenes: IR25MW64A

- Fracturing
- TCH

![Graph showing VOC levels and fraccing and injection dates for chlorinated ethenes.]

- TETRACHLOROETHENE
- TRICHLOROETHENE
- 1,2-DICHLOROETHANE
- CIS-1,2-DICHLOROETHANE
- VINYL CHLORIDE
- ETHENE
- ETHANE
- Fracturing and Injection

cis-1,2-DCEPAL = 6 ug/L
TCF PAL = 2.9 ug/L
PCE, 1,2-DCA, and VC PAL = 0.5 ug/L
Conclusions: HPNS Treatability Study

- Fracture extents: 2.5 to 89 ft
  - Averaged 18-23 feet in the source area
  - Averaged 13-24 feet in the plume
- Treatment radius of influence > 20 ft
  - EHC® emplaced as discrete “sheets”
  - Diffusion of amendments created reducing conditions
- Fracturing/EHC®: 24-99.9% reduction in PCE and 1,2-DCA and 5-57% reduction in 1,2-, 1,3- and 1,4-DCB within four months.
- Biological degradation pathways predominated
Conclusions: Impact of Thermal Treatment

- Insignificant biological degradation at temperatures >70°C.
- Removed >90% of total VOC mass in soil
  - Lowest removal for 1,2-DCB (86%)
  - Highest removal for PCE (99.9%) 
- Parent compound groundwater concentrations reduced:
  - 50-93% for 1,2-DCB, 1,3-DCB, 1,4-DCB, except in IR25MW63A
  - >94-100% for PCE and 1,2-DCA
- Degradation product concentrations reduced 61-99% for chlorobenzene/benzene except IR25MW62A and IR25MW63A, which increased (due to post-TCH attenuation of DCBs).
- Post-treatment polish from emplaced carbon and EHC ® will be evaluated over the next year.
## Summary of Technology Performance

<table>
<thead>
<tr>
<th>Groundwater</th>
<th>Treatment Component</th>
<th>Total lbs removed</th>
</tr>
</thead>
<tbody>
<tr>
<td>TC1</td>
<td>TC2</td>
<td>TC3</td>
</tr>
<tr>
<td>Cost ($) per cubic yard</td>
<td>$50</td>
<td>$1,950</td>
</tr>
<tr>
<td>Reduction (%) of PCE and 1,2-DCA</td>
<td>45.0%</td>
<td>99.0%</td>
</tr>
<tr>
<td>Reduction (%) of 1,2-DCB, 1,3-DCB and 1,4-DCB</td>
<td>33.9%</td>
<td>1.34%</td>
</tr>
<tr>
<td>Reduction (%) of total PCE, TCE, 1,2-DCA, 1,2-cis-DCE, VC</td>
<td>33.0%</td>
<td>97.6%</td>
</tr>
<tr>
<td>Reduction (%) of total 1,2-DCB, 1,3-DCB, 1,4-DCB, chlorobenzene, benzene</td>
<td>15.9%</td>
<td>25.5%</td>
</tr>
<tr>
<td>Total DCB mass removed (lbs)</td>
<td>1.7</td>
<td>1.1</td>
</tr>
<tr>
<td>Total PCE, 1,2-DCA mass removed (lbs)</td>
<td>5.25</td>
<td>6.36</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Soil</th>
<th>Treatment Component</th>
<th>Total lbs removed</th>
</tr>
</thead>
<tbody>
<tr>
<td>TC1</td>
<td>TC2</td>
<td>TC3</td>
</tr>
<tr>
<td>Reduction (%) of PCE and 1,2-DCA mass</td>
<td>NA</td>
<td>99.98%</td>
</tr>
<tr>
<td>Reduction (%) of 1,2-DCB, 1,4-DCB, 1,3-DCB mass</td>
<td>NA</td>
<td>88.3%</td>
</tr>
<tr>
<td>Reduction (%) total VOC mass</td>
<td>NA</td>
<td>92.4%</td>
</tr>
<tr>
<td>Total VOC mass removed (lbs)</td>
<td>NA</td>
<td>269</td>
</tr>
<tr>
<td>Total 1,2-DCB, 1,4-DCB, 1,3-DCB mass removed (lbs)</td>
<td>NA</td>
<td>165</td>
</tr>
<tr>
<td>Total PCE and 1,2-DCA mass removed (lbs)</td>
<td>NA</td>
<td>104</td>
</tr>
</tbody>
</table>
THANK YOU!

Questions?