Field Evaluation of the Treatment of DNAPL Using Emulsified Zero-Valent Iron (EZVI)

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May 2009
Outline

• EZVI Technology Background
• EZVI Applications
• ESTCP Project Objectives
• Overview of Lab Study
• Field Demonstration – Parris Island
ZVI Chemistry

- ZVI is a strong reducing agent
- ZVI is an accepted technology for degradation of dissolved CVOCs such as PCE and TCE
- Basic chemistry the same for granular, micro- or nano-scale ZVI (mZVI or nZVI)
• ZVI Permeable Reactive Barriers (PRBs) with granular iron are effective in treating dissolved CVOCs but:
  - are dependent on dissolution and transport of CVOCs
  - do little to reduce the clean up time and long-term monitoring costs
• ZVI needs to be in the presence of water to promote reductive dehalogenation
• Injection of ZVI into a DNAPL source zone will only treat the dissolved phase at the edges of the DNAPL
Properties of EZVI

- Emulsion droplets contain iron particles in water surrounded by an oil-liquid membrane
- Oil layer of emulsion is miscible with the DNAPL
- CVOCs diffuse through the oil membrane and are degraded by the ZVI
- EZVI enhances contact between the DNAPL and the ZVI particles
- Vegetable oil act as electron donor and promotes anaerobic biodegradation
Image of EZVI and DNAPL Contact

DNAPL dyed red

DNAPL with nano-scale ZVI

DNAPL with EZVI
EZVI Technical Capabilities

- Combines capabilities of three remediation technologies:
  - Zero-valent iron (ZVI) – abiotic degradation
  - Biodegradation - biodegradation
  - Oil sequestration – mobility reduction

- Enhances contact between ZVI and DNAPL
EZVI Application Methods

- Injection
  - Direct injection
  - Pneumatic injection
  - Pressure pulse injection
  - Hydraulic fracturing

- Large diameter auger mixing

- Viscous fluid can be difficult to emplace in the target treatment interval
• NASA holds the patent for EZVI
• Technology has been successfully commercialized by NASA and has been licensed to six companies
• EZVI awarded Invention of The Year and Commercial Invention of The Year by NASA and the Federal Government, and was inducted into the Space Technology Hall of Fame
• 16 Sites from 2002 - 2008
ESTCP Project Objectives

• **Laboratory Study:**
  - Evaluate degradation mechanisms - Completed 2005

• **Field Demonstration Testing:**
  - Inject EZVI into two pilot test areas within a DNAPL source zone using: Direct Injection, Pneumatic Injection
  - Evaluate ability of EZVI to reduce mass flux of CVOCs from a DNAPL source zone and reduce the DNAPL mass
Treatability Testing

- Lab tests conducted to evaluate treatment of near saturation dissolved phase concentrations (1000 ppm) and DNAPL (10 x saturation) using:
  - Controls (active and sterile)
  - Vegetable oil & surfactant (Emulsion)
  - nZVI
  - nZVI in EZVI

- Monitor VOCs, DHG and chloride in the water phase of each reactor
**Active Control**

- TCE at saturation concentration
- No degradation by-products observed (no DHG or chloride)

**Oil Emulsion Treatment**

- TCE stable at ~30% of saturation concentration
- No degradation by-products observed (no DHG or chloride)
- DNAPL sequestered in oil phase – equilibrium concentrations lower than for pure phase DNAPL
nZVI Treatment

- TCE stable at saturation concentration
- Degradation by-products observed (ethane and ethene)
- Chloride production indicates degradation of ~73% of TCE

EZVI Treatment

- TCE ~10% of saturation concentration and dropping
- Degradation by-products observed (ethane and ethene)
- Chloride production indicates degradation of ~71% of TCE
EZVI Lab Testing – Chloride Production

70% conversion of TCE to ethene
Conclusions – Lab Testing

- EZVI benefits from sequestration due to oil plus degradation due to nZVI
  - Significant decrease in aqueous concentrations (drop in mass flux) greater than with just the oil; and
  - Reduction in mass of TCE
- Impacts of biodegradation not significant in these tests which utilized synthetic groundwater and no soil (expect to see biodegradation with emulsion and EZVI)
Case Study - Parris Island

- Environmental Securities Technology Certification Program (ESTCP) project ER-0431
- Site 45, Parris Island MCRD, SC
- Former dry cleaning facility
- Buildings have been torn down
- Source areas located around former above and below ground storage tanks
Demonstration Site

Fully screened and multilevel wells

Direct Injection Plot

- 0 ft
- 5 ft
- 10 ft
- 15 ft
- 20 ft

- sand
- silty sand
- sand
- sand/clay
- peat

Pneumatic Injection Plot

- 0 ft
- 5 ft
- 10 ft
- 15 ft
- 20 ft

- sand
- silty clay
- sand
- peat
Demonstration Site

Multilevel Well Construction

Direct and Pneumatic Injection Plots

Direct Injection Plot

Pneumatic Injection Plot

General Direction of Groundwater Flow
EZVI Preparation

- EZVI prepared on-site by mixing nano-scale iron (Toda), corn oil, surfactant and water in drums using top mounted industrial mixer

- EZVI pumped from mixing drums into injection tanks
EZVI Injections

Pneumatic Injection Plot

- 575 gal EZVI injected into 8 locations between 7 and 19 ft bgs (2 locations using Direct Injection)
- During injections, monitored injection pressure, pressure distribution in subsurface, ground heave, and looked for EZVI at ground surface (daylighting)
Pneumatic Injection Plot

- Monitoring Well
- Multilevel Well
- EZVI Direct Injection Point
- EZVI Pneumatic Injection Point
EZVI Injections

- EZVI daylighted in both Pneumatic and Direct Injection test plots

Pneumatic Injection plot (daylighting around ML-3 pad, downgradient of plot)  
Direct Injection plot (daylighting possibly from old soil core location)
Soil Cores – Distribution

- Cores collected to evaluate ability of injection technologies to distribute EZVI evenly over target treatment intervals

- EZVI in all cores but one (ESC-06)
VOC Trends: Downgradient Well

[Graph showing VOC trend data over time with various concentrations and injection points marked on the map.]
VOC Trends: Downgradient wells in Pneumatic Injection Plot
Summary of Case Study

• Downgradient wells show decrease in PCE/TCE with increase in degradation products including significant increases in ethene

• Upgradient wells and PMW-5 show continued presence of DNAPL although significant production of ethene in PMW-5 indicates that degradation is ongoing in the area

• DNAPL now being pumped from some wells where DNAPL was previously absent, indicating that some of the DNAPL is mobile

• Difficulty distributing EZVI due to shallow application and short-circuiting up existing investigation boreholes
Modified EZVI Applications

- mZVI versus nZVI to make EZVI
- Co-injection of ZVI and vegetable oil
- Bioaugmentation to enhance biodegradation
- Applications for co-mingled plumes or sources where either ZVI or bioremediation on its own wouldn’t work
Acknowledgements

• Project funding provided by ESTCP (ER-0431)

• USEPA (GWERD, National Risk Management Research Laboratory) provided drill rig for soil cores and well installations. Also providing field sampling support, equipment and analytical support

• Pneumatic injections performed by Pneumatic Fracturing, Inc. (Alpha, NJ)

• Direct injections performed by Vironex, Inc. (Golden, CO)

• Tim Harrington, Parris Island MCRD
Supplemental Slides
Cost of EZVI

- Cost of nZVI and to lesser extent mZVI drives cost of EZVI
- Cost of other ingredients are minimal (up to $6/gal)
- Small volumes can be prepared on-site; larger volumes prepared and shipped to the site
- Costs for EZVI with nZVI significantly more than with mZVI:
  - ~$10/gallon with BASF mZVI
  - ~$28/gallon with Toda nZVI

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<tr>
<th>Iron Product</th>
<th>Supplier</th>
<th>Cost</th>
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<tbody>
<tr>
<td>Nano-scale ZVI</td>
<td>Toda America</td>
<td>$26-$34 / lb</td>
</tr>
<tr>
<td>Micro-scale ZVI (40,000 nm)</td>
<td>Hepure (ARS)</td>
<td>$1.00 to $1.70/lb</td>
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<tr>
<td>Micro-scale ZVI (up to 3,000 nm)</td>
<td>BASF</td>
<td>$4.00 / lb</td>
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<tr>
<td>Granular Iron (comparison only, can’t use to make EZVI)</td>
<td>Peerless Metal Products, Master Builders, QMP, Connelly</td>
<td>$0.40 / lb</td>
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