In Situ DNAPL Destruction with the EZVI Technology: Lessons Learned and Recent Advancements

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Presentation Outline

- Background and History
- Technology Description
- Implementation
- Case Studies – 2
- Lessons Learned
- Technology Update – Product Optimizations
- Summary

Presentation GOAL:
For you to gain a good understanding of what the EZVI technology is, when it is an appropriate remedial alternative and what are the most recent advancements to the technology.
Background – The Nature of the Problem

History – DNAPL Remediation Issues

- Physical Chemistry
  - Hydrophobic
  - Density & Viscosity
  - Low Water Solubility

- Location
  - Precision

- Treatment
  - Contact

[Diagram showing DNAPL challenge, groundwater flow direction, DNAPL pool, residual DNAPL, and plume. EPA SITE Report, 2004.]
DEVELOPMENTS TO DATE
1997 – 1998: Conceptualization/Development
1999 – 2001: Proof of Concept R&D at UCF/KSC
2005 – 1st FULL SCALE implementation – PAFB
2005 – Present: Various Applications across USA, Canada, EU
Technology Description – What is EZVI?

- Surfactant stabilized, water-in-oil emulsification with small micron ($< 5 \mu m$) ZVI particles suspended in the water drops.

- EZVI is a DNAPL (hydrophobic, sinker).
Technology Description – How Does it Work?

- EZVI Processes
  - Sequestration
  - Dissolution
  - Reductive dehalogenation
    (abiotic & biotic processes)
- Emulsion **Structure** is KEY

![Image of EZVI Processes and Emulsion](image_url)
Technology Description – How Does it Work?

- **Reductive Dechlorination**
  - **Abiotic Processes:**
    - Interior of emulsion
    - Targeted use of ZVI
  - **Biotic Processes:**
    - Exterior of emulsion
    - Downgradient
Technology Description – What is the Innovation?

- **Miscibility** with DNAPLs
- **Combination Technology** utilizing abiotic & biotic processes AND physical chemistry
- Emulsion *structure* is key

**Miscible with DNAPL**
Ref: Brooks et al., 2000
Technology Description – How is it Unique?

Utilizes Contaminant Physical Chemistry

- Due to sequestration EZVI provides **reduced mass flux**
- Emulsion **structure** is key

Ref: O’Hara et al., 2005
- Engineered as an *in situ* source area destruction technology
- Implemented directly into source area soils
- Effective in **VADOSE** and **SATURATED** soils
- EZVI delivered via:
  - Pneumatic Enhanced IDS
  - Hydraulic & Pneumatic Emplacement
  - Soil Mixing
Implementation – FAQ’s

- **When is EZVI an option?**
  - DNAPL is present
  - Parent compound(s) ≥ 10% of water solubility
  - We have access to DNAPL area
  - We have time

- **How much do I need?**
  - Dosing driven by distribution/subsurface contact vs stoichiometry
  - Target ~ 8 - 15% of effective pore space

- **Can EZVI be injected through well screens?**
  - Not recommended
  - Minimizes efficacy
Case Study Examples

- Federal Site #1 – EZVI source destruction (TCE) with ERD in plume
- Federal Site #2 – EZVI source destruction (TCE) with ERD in plume
Case Studies – Federal Site #1

- Source Area - 75 ft x 150 ft x 40 ft (vertical)
  - Targeted GW TCE conc’s > 100 ppm
- Dissolved Plume - 20 acres
  - Targeted GW TCE conc’s between 10 – 100 ppm
- Source Zone Treatment - 62,000 gallons of 10% EZVI
  - Targeted 25% of effective pore volume
- Plume Treatment – Electron Donor & Bioaugmentation
- Injection Method – Pneumatic Fracture with injection
Case Study – Federal Site #1

- Baseline GW samples TCE up to 350 ppm
  - 1 YR = 89% destruction of source area TCE
  - 4 YRs = 94% destruction of source area TCE
  - 7 YRs = 99% destruction of source area TCE

- One EZVI injection event

- Prior to EZVI injection-
  - Estimated to take ~ 280 yrs. to remediate site via MNA

- Post EZVI injection-
  - Estimated to attain remediation goals < 60 yrs.
Case Study – Federal Site #2

- DNAPL Area “A” – 50 ft. x 100 ft. x 40 ft. (vert)
  - Targeted GW TCE conc’s > 200 ppm
- DNAPL Area “B” – 20 ft. x 60 ft. x 40 ft. (vert)
  - Targeted GW TCE conc’s > 200 ppm
- Source Zone Treatment – 37,500 USG 10% EZVI
  - Area A – Dosed at 6% of effective pore volume
  - Area B – Dosed at 10% of effective pore volume
- Plume Treatment – Electron Donor & Dhc
- Injection Method – Hybrid DPT system (Badger)
Case Study – Federal Site #2

Source Area A

Baseline

1 YR

Source Area B

Baseline

1 YR

1 yr post EZVI Injection

1 ppm TCE

10 ppm TCE

100 ppm TCE

200 ppm TCE

100 ppm TCE
Implementation – Lessons Learned

- **Dosage:**
  - Early projects targeted **25%** of effective soil pore space
  - Recent projects target **10%** of effective soil pore space (typically)
  - Conditions to adjust dosage
    - soil type and implementation method
    - free phase DNAPL and Vadose soils (~ 15%)

- **Formulation:**
  - Original formula included ZVI at 17% (w/w)
  - Current typical formulation contains ZVI at 10% (w/w)
  - Original formula used for high concentration and low permeability sites

- **ZVI:**
  - Original formulation used nano ZVI
  - Current typically use small micron ZVI (< 5 µm)

**Handling & Storage:**
- Early projects utilized large tanks for on site storage (6,000 USG tanks)
- Recent projects utilize IBC totes or tanker trucks with recirculation pumping for large projects (> 20,000 USG)
Recent Advancements to the EZVI Technology

- **Optimization of Biotic Processes**
  - Controlled methanogenesis

- **Optimization of Abiotic Processes**
  - Catalyzed ZVI
Recent Advancements
Optimization of Biotic Processes

- Methanogens dominate anaerobic ecosystems and they can hinder dechlorination by competing with dechlorinating bacteria for available $H_2$ (Yang and McCarty, 1998).
Recent Advancements
Optimization of Biotic Processes

What is the problem with methanogens?
- Even in a highly oxidized setting with relatively high total concentrations of PCE and TCE, generating just 20 mg/L of methane constitutes greater than 33% of the total amendment consumption based on moles of H₂.

<table>
<thead>
<tr>
<th>Microbe</th>
<th>Doubling Times</th>
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<tbody>
<tr>
<td>Dehalococcoides spp.</td>
<td>24 to 48 hours</td>
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<tr>
<td>Methanogens with cytochromes</td>
<td>10 hours</td>
</tr>
<tr>
<td>Methanogens without cytochromes</td>
<td>1 hour</td>
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</table>

Idealized Eh pH Ranges for Microbial Growth

<table>
<thead>
<tr>
<th>Const constituent</th>
<th>Groundwater Concentration (mg/L)</th>
<th>Molecular Weight (g/mol)</th>
<th>Moles of H₂ to Reduce Mole Analyte</th>
<th>Moles of H₂ acceptor in treatment area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetrachloroethene (PCE)</td>
<td>10.0</td>
<td>185.0</td>
<td>4</td>
<td>1,393</td>
</tr>
<tr>
<td>Trichloroethene (TCE)</td>
<td>7.0</td>
<td>131.1</td>
<td>3</td>
<td>364</td>
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<tr>
<td>cis-1,2-Dichloroethene (cDCE)</td>
<td>0.0</td>
<td>90.9</td>
<td>2</td>
<td>0</td>
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<tr>
<td>Vinyl Chloride (VC)</td>
<td>0.0</td>
<td>82.5</td>
<td>1</td>
<td>0</td>
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<tr>
<td>Complete Dechlorination (Soil+Groundwater) Subtotal</td>
<td>1,757</td>
<td></td>
<td></td>
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<tr>
<td>Native Electron Acceptors</td>
<td></td>
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<tr>
<td>Dissolved Oxygen</td>
<td>8.9</td>
<td>36</td>
<td>3</td>
<td>100</td>
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<tr>
<td>Nitrate (as nitrogen)</td>
<td>9.0</td>
<td>62</td>
<td>3</td>
<td>302</td>
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<tr>
<td>Sulfide</td>
<td>50.0</td>
<td>36.1</td>
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<td>Fe²⁺ Formation from Fe³⁺</td>
<td>27.0</td>
<td>58.9</td>
<td>0.5</td>
<td>63</td>
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<tr>
<td>Mn⁴⁺ Formation from Mn⁴⁺</td>
<td>10.3</td>
<td>54.9</td>
<td>1</td>
<td>64</td>
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<tr>
<td>Baseline Geochemistry Subtotal</td>
<td>1,745</td>
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<tr>
<td>Hydrogen waste for Methane Formation</td>
<td>20.0</td>
<td>100</td>
<td>4</td>
<td>1,769</td>
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Initial Treatment Area Hydrogen Usage: 5,271
Recent Advancements – Controlled Methane

How can methanogens be controlled?

- Genetically unique – *Archaea*
- Target Methanogens - using naturally occurring statins (RYR Extract) and select essential oils/saponins to disrupt enzyme and coenzyme processes unique to methanogens

<table>
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<tr>
<th></th>
<th>CH4</th>
<th>EVO</th>
<th>PV600</th>
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<tbody>
<tr>
<td>mg/L</td>
<td>2.75</td>
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<td>0.09</td>
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<td>umol</td>
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<td>15</td>
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<tr>
<td>ppmv</td>
<td>1,450</td>
<td>150</td>
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<tr>
<td>mcrA</td>
<td>2E6</td>
<td>1E2</td>
<td></td>
</tr>
<tr>
<td>DHC</td>
<td>5E6</td>
<td>3E6</td>
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<tr>
<td>dco</td>
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<td></td>
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</tr>
<tr>
<td>DHB</td>
<td>1E3</td>
<td>6E3</td>
<td></td>
</tr>
<tr>
<td>deha</td>
<td>Day 142</td>
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</tr>
</tbody>
</table>

Figure 5-7: qPCR results for the microcosms EVO with and without Provect-CH4™ (limit of detection (LOD) = 10 copies/mL)

qPCR data from Provectus
Recent Advancements – Controlled Methane

**Benefit:** in situ DNAPL destruction with controlled methanogenesis
Recent Advancements
Optimization of Abiotic Processes

Optimizing abiotic processes within the interior of the emulsion

- Reactivity:
  - Catalyzing ZVI electron transfer processes

Vitamin B12 (cobalamin)
- Naturally occurring organometallic compound
- Naturally occurring electron mediator
- Water soluble & non toxic
- Contains Co in center of corrin ring structure
- B12 must be in a reduced state to transfer electrons
Recent Advancements – Catalyzed ZVI

Optimizing abiotic processes

- **Reactivity:**
  - Electron transfer processes
  - 1,2 – Dichloroethane (1,2 – DCA)
Recent Advancements
Catalyzed ZVI

Optimizing abiotic processes within the
interior of the emulsion

Compounds Tested
- 1,2,3 – Trichloropropane (1,2,3 – TCP)
- 1,2 – Dichloropropane (1,2 – DCP)
- 1,3 – Dichloropropane (1,3 – DCP)
- 1 – Chloropropane (1 – CP)

Benefit: Expanded Range of Catalysis
Recent Advancements
Catalyzed EZVI

Optimizing abiotic processes within the interior of the EZVI emulsion

**Compounds Tested**
- 1,2,3 – Trichloropropane (1,2,3 – TCP)

**Benefit:** Expanded Range of Catalysis
Summary – DNAPL destruction with EZVI

- **Contaminant Reduction & EZVI Longevity**
  - Typical source area parent VOC concentration reduction of ~ 90% within < 1 year
  - EZVI has been shown to be effective in the subsurface for >5 years

- **Source Area Effects**
  - Directly destroys source material
  - Significantly reduces mass flux

- **Plume Effects**
  - Adjacent to source area: Fermentation reactions provide hydrogen for biotic transformations or “polishing” adjacent to injection area
  - Downgradient: Eliminates on-going source for downgradient areas

- **Recent Advancements**
  - Provide optimized abiotic and biotic capabilities and expand the scope of treatable contaminants

- **Estimated Costs**
  - For product and DPT injections approximately $121.66 - $155.08/yd³ of DNAPL impacted soil
Thank You!

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Managing Excessive Methanogenesis During ERD/ISCR Remedial Action

Jim Mueller

J. Greg Booth
Recent Advancements
Catalyzed ZVI

Optimizing Abiotic Processes within the interior of the emulsion

Research Article
Remediation of Chlorinated Alkanes by Vitamin B_{12} and Zero-Valent Iron

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