EMULSIFIED ZERO-VALENT IRON
Laboratory and Field Testing

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Research Participants

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Technology Rationale

- **ZVI PRBs are effective in treating dissolved CVOCs but:**
  - are dependent on dissolution and transport of CVOCs; and
  - 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.**
- **EZVI can be used to enhance degradation of DNAPLs by enhancing contact between the DNAPL and the ZVI particles.**
Properties of EZVI

- Emulsion droplets contain iron particles in water surrounded by an oil-liquid membrane.
- EZVI composed of food-grade surfactant, biodegradable vegetable oil, water, and ZVI (nano- or micro-scale iron).

![Diagram of EZVI](image)

**Properties of EZVI**

- Water
- Oil
- Surfactant
- Iron

**Diagram:**

- Water: Light blue
- Oil: Yellow
- Surfactant: Arrow
- Iron: Black dots

**Label:**

- 12.3 μm
EZVI In Contact with DNAPL

- **DNAPL** dyed red
- **DNAPL** with micro-scale ZVI
- **DNAPL** with EZVI
EZVI Technology Evaluation
Demonstration at LC34

- Demonstration conducted at NASA’s LC34.
- Performance evaluation based on GW mass flux and TCE mass in pre- and post-treatment soil cores.
- Monitored changes in CVOCs in:
  - GW (5 depth intervals, 2 upgradient and 2 downgradient wells); and
  - soil cores (8 depth intervals, 6 locations)
- EPA SITE Program independently evaluated technology demonstration.
Battelle conducted an independent evaluation of the EZVI demonstration at LC 34.
Field Demo Paper in ES&T

- ES&T published special issue on nanotechnology

- NASA and GeoSyntec co-authored paper in this issue on the EZVI Field Demonstration

Results of Demo at LC34

**Soil Core Samples:**

- Stated objective of 50% removal of total TCE
- EZVI migrated to shallow intervals with PPT injection
- Significant reduction of TCE in four months (>80%) where EZVI was present
- Average reduction of 58%

EZVI in 1- to 3-inch thick stringer
Results of Demo at LC34

- **Groundwater Samples:**
  - Significant reduction (60 to 100%) of TCE in target depths.
  - Reduction of 56% in the Mass Flux.
  - Elevated cis-1,2-DCE, VC suggest biodegradation due to oil as an electron donor may also be significant.
Recommendations From LC34 Demonstration

- Promising results at LC34 but needed to further evaluate:
  - how to control placement of EZVI in subsurface
  - the contribution of the abiotic and biological components of the degradation

- ESTCP funding acquired to address these questions
ESTCP-funded 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)
  - Nano-scale zero-valent iron (nZVI)
  - Emulsified zero-valent iron (EZVI)

- Monitor VOCs, DHG and Chloride

- Treatability tests done in triplicate and each test set up is done in both sterile and non-sterilized set ups
Dissolved Phase Treatments

- Near saturation concentrations of TCE
- TCE of 1,000 mg/L (0.8 mmoles per bottle)
- nZVI added to achieve 5 times theoretical ZVI requirement to degrade TCE
Dissolved Phase Testing (1)

**Active Control**
- No losses of TCE or production of degradation byproducts observed in control treatments

**Oil Emulsion Treatment**
- TCE concentration drops to 0.1 mmols - sequestered in oil
- No degradation by-products observed until ~day 50 when pH buffered and re-bioaugment with KB-1
- Impacts of biodegradation not significant in these tests which utilized DI water and no soil
**nZVI Treatment**

- TCE concentrations drop very rapidly
- Undergoes rapid and complete degradation
- TCE is non-detect by day 71

**EZVI Treatment**

- TCE concentration drops very rapidly
- EZVI treatment undergoes slightly slower degradation but also complete degradation
- TCE is non-detect by day 77
Chloride Production with Dissolved TCE

100% conversion of TCE to ethene
Conclusions - Dissolved Phase Testing

- Lab tests show that EZVI degradation, especially at early times, is mainly due to ZVI (abiotic)
- Abiotic degradation of the ZVI in the EZVI is not adversely impacted by the oil

So why use the EZVI if the nZVI promotes rapid and complete degradation?

In the presence of dissolved phase the ZVI may be slightly faster but in the presence of DNAPL the advantages of the EZVI become apparent
DNAPL Phase Treatments

• 10x saturation concentrations of TCE
• TCE of 10,000 mg/L (16.7 mmoles per bottle)
• nZVI added to achieve 2 times theoretical ZVI requirement to degrade TCE
**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
Chloride Production with DNAPL

70% conversion of TCE to ethene
Conclusions of DNAPL Testing

- Veg Oil Emulsion decreases TCE concentration due to sequestration (no degradation)
- nZVI reduces mass of TCE due to treatment but no decrease in aqueous concentration of TCE (no effect on mass flux)
- EZVI benefits from sequestration due to oil plus degradation due to nZVI
  - Significant decrease in aqueous concentrations (drop in mass flux) greater then with just the oil; and
  - Reduction in mass of TCE
Demonstration Site
Parris Island MCRD, SC

- Former dry cleaner site
- Buildings have been torn down
- Source areas located around former above and below ground storage tanks
- Evaluate two injection methods and performance assessment of EZVI’s ability to degrade VOCs
Technical Progress
DNAPL Distribution and Well Installation

- 9 soil cores and groundwater samples collected in 2005 and 2006 to evaluate contaminant distribution
- Wells installed in July 2006 to target the source areas identified through cores
- EPA (GWERD, National Risk Management Research Laboratory) provided drill rig for coring and well installation
Technical Progress
DNAPL Distribution and Well Installation

Multilevel Well Construction

Direct & Pneumatic Injection Plots

Direct Injection Plot

Pneumatic Injection Plot
Technical Progress
DNAPL Distribution and Well Installation

Fully screened and multilevel wells

Direct Injection Plot

Pneumatic Injection Plot

sand
silty sand
sand
sand/clay
peat

sand
silty clay
sand
peat
Baseline Characterization

Groundwater Sampling

- Groundwater sampling and analysis support provided by EPA
  - EPA personnel participate in all groundwater sampling events and some groundwater samples analyzed at Kerr Laboratories, Ada, OK

- Baseline samples collected from over 50 sample locations (including multilevel wells) during June, August and October 2006 sampling events (2-week sampling events)

- Sample parameters include field parameters (DO, ORP, pH, temperature, conductivity, turbidity) VOCs, DHGs, VFAs, anions, alkalinity, TOC/TIC, metals (dissolved, total), and isotopes (O, H, Cl)
Baseline Characterization

Groundwater Sampling

• DNAPL pumped out of ML-2-5 up-gradient of plot

• Multilevel wells: changes in groundwater mass flux downgradient of plot and evaluate incoming flux to plot (located within a larger plume)

• Fully screened wells: integrated samples within plot for performance evaluation and external to plot to evaluate changes during injection of EZVI
EZVI Preparation

- EZVI made on-site by combining:
  - Nano-scale iron (Toda)
  - Corn oil
  - Surfactant
  - Water

- Ingredients added to drum and mixed using a top mounted industrial mixer

- EZVI pumped from mixing drums into injection tanks
EZVI Injection

Pneumatic Injection Plot
- Total of 575 gal EZVI injected into 8 locations within the Pneumatic Injection Plot 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
EZVI Injection

Pneumatic Injection Plot

- Total of 575 gal EZVI injected into 8 locations within plot 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 (shown as grey areas on figure)
EZVI Injection

Direct Injection Plot
- Total of 150 gal EZVI injected into 4 locations within plot between 6 and 12 ft bgs
- During injections, monitored injection pressure and looked for EZVI at ground surface
Direct Injection

• Total of 150 gal EZVI injected into 4 locations within plot between 6 and 12 ft bgs

• During injections, monitored injection pressure and looked for EZVI at ground surface
EZVI Injection

- EZVI observed at ground surface in both Pneumatic Injection and Direct Injection Plots

Pneumatic Injection plot
(daylighting around ML-3 pad, down-gradient of plot)

Direct Injection plot
(daylighting possibly from old soil core location)
EZVI Injection

EZVI Soil Cores

- Collected cores to evaluate ability of injection technologies to distribute EZVI evenly over the target treatment intervals

Mineralized sand cores, saturated with EZVI

- Possible EZVI in all soil cores except ESC-06
## Performance Monitoring

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<th>Performance Monitoring Samples</th>
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**Sample numbers do not include additional 10% QA/QC samples**
Performance Monitoring
Groundwater Sampling Summary

• In general, 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

• Significant increases in VFAs (primarily acetic and propionic acids) and TOC

• Small decrease in pH, and increases in iron (dissolved and total)

• DNAPL now being pumped from ML-2-7 and PMW-5 (inside Pneumatic Injection plot) and from PMW-4 (south [transgradient] of Pneumatic Injection plot) as well as from ML-2-5 where DNAPL was present pre-injection
Performance Monitoring

Graphs showing concentration trends over different dates for various substances, including PCE, TCE, oDCE, VC, Ethene, and Chlorine.
Performance Monitoring
Pneumatic Injection

Interior Wells

Downgradient Well
Next Steps

- Continued monitoring at Parris Island proposed through Oct 09
- Continued use throughout US
- One licensee getting ready for European deployment
- EZVI has taken one private client’s site off the NPL
Questions?

EZVI team being inducted into the Space Technology Hall of Fame