STATE OF SERDP/ESTCP FUNDED ZERO-VALENT IRON (ZVI) RESEARCH AND TECHNOLOGY

Presented by
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Overview

- Scope of SERDP/ESTCP funded research on zero valent iron (ZVI) with particular focus on nanoscale Fe
- Individual Project Descriptions and Status
- Outstanding Issues and Concerns
Current ZVI Projects

• Two projects related to the application of nanoscale ZVI for treatment of CVOC DNAPL source zones
  – Application of bimetallic nanoscale ZVI (200 – 600 nm)
  – Application of emulsified nanoscale ZVI (10 – 100 nm)

• One project exploring the application of ZVI reactive barrier for treatment of dissolved TNT and RDX downgradient of the source zone
Bimetallic Nanoscale ZVI Project

Objectives:

– Test the efficacy of ball-milled nanoscale bimetallic ZVI to treat CVOC source zones
– Investigate colloid longevity issues in batch tests
– Evaluate transport properties in one dimensional column tests
Bimetallic Nanoscale ZVI Project

• Production Method
  – Use of conventional ball milling technology to create nanoscale colloids (200 nm – 600 nm size range) and sp. surface area of 2 m²/g
  – Palladization of nanoscale iron is performed by mixing the iron colloid with Pd salt (0.03%) whereby, Pd is rapidly reduced to form isolated packets of Pd metal at the iron colloid surface

• Surface area normalized reaction rates

<table>
<thead>
<tr>
<th>Nanoscale Forms</th>
<th>( K_{sa}, \text{L/(m}^2\cdot\text{hr)} )</th>
<th>Surface Area, m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Precipitated Forms</td>
<td>0.01-0.12</td>
<td>32</td>
</tr>
<tr>
<td>Ball-Milled Forms (original size particles)</td>
<td>0.01-0.08</td>
<td>2</td>
</tr>
<tr>
<td>Ball-Milled Forms (agglomerated particles)</td>
<td>0.05-0.35</td>
<td>0.2</td>
</tr>
</tbody>
</table>
Bimetallic Nanoscale Injectable (BNI) Iron Properties

Nanoscale Bimetallic Colloid For Treatment of Chlorinated Solvents via Direct Fe Reduction and Reduction by Hydrogen/Catalysis

\[ \text{Fe}^0 \text{ Reductant} \quad \text{RH}_n + n\text{Cl}^- \quad \text{RCI}_n \quad \text{H}_2 \quad \text{OH}^- \]

\[ \text{200} \text{ – 600 nm} \]

Catalyst (Pd or Pt)
BNI Fe Colloid Longevity Testing

- Effect of high TDS water (sulfates and soluble carbonates)
- Effect of trace catalyst (0.03% Pd), boron or other solute(s)
- Effect of water dissociation reaction on iron consumption (evaluate optimum formation of passivation layer for minimizing water dissociation but promote CVOC reactions)
- Evaluate the effect of CVOC concentration on iron passivation
- Both ball-milled and aqueous precipitated forms of BNI will be evaluated for colloid longevity
DNAPL Column Studies with BNI Fe

- Simulate residual and adsorbed DNAPL distribution in one dimensional treatment and control columns
- Inject BNI particles in the treatment column and compare effluent CAH concentrations between treatment and control column
- Evaluate CAH mass transfer rates from the DNAPL source zones in treatment and control columns
Current Status and Future of BNI Fe Colloid Technology

- Bench scale batch and column studies are in progress
- Good reactivity achieved with the ball-milled Fe colloid in the right size range (100 – 600 nm) for CVOC treatment ($t_{1/2} = 0.3-2\ \text{hr}$)
- 95% TCE removal in batch and column studies
- Technology looks promising (injectible slurry, high reactivity) although not mature enough to warrant a field demonstration at this point
- Current cost of ball-milled BNI particles is higher than Toda Fe powders but comparable to boron precipitated Fe
Emulsified Nanoscale ZVI Project

Objectives:

– Improve EZVI delivery process
  • Hydraulic Fracturing
  • Pneumatic Fracturing
  • Pressure Pulse Technology (PPT)
  • Direct Injection

– Evaluate contributions of the abiotic (ZVI mediated) and biotic (oil and surfactant mediated) processes on CVOC degradation

– Demonstrate and validate technology for widespread use in DNAPL source zones at DOD sites
Emulsified Nanoscale ZVI Production Method

- Nanoscale ZVI (10-100 nm) produced first by milling followed by hydrogen reduction of iron oxides (Toda Process)
- Following the generation of nanoscale ZVI, emulsification is performed with food grade surfactant, biodegradable vegetable oil, water and nanoscale ZVI
Emulsified Nanoscale ZVI (EZVI) Properties

- Since exterior oil membrane of emulsion droplets have hydrophobic properties similar to DNAPL, the emulsion is miscible with the DNAPL.
- CVOCs in DNAPL diffuse through the oil membrane and undergo reductive dechlorination in the presence of the ZVI in the interior aqueous phase.
- In addition to abiotic degradation due to ZVI, EZVI contains vegetable oil and surfactant which will act as long-term electron donors and promotes anaerobic biodegradation.
Previous Testing of the EZVI Technology

• Tested at NASA LC34 Site
• 15 ft by 10 ft test cell with PPT adopted to inject EZVI at two depth intervals
• Significant reduction in TCE (>80%) in soils
• Significant reduction in dissolved contaminants in groundwater (60 to 100%)
Current Status and Future of EZVI Technology

- ESTCP field demo will be underway in September of 2004
- The future of this technology looks promising
  - Creates reducing conditions suitable for natural attenuation or enhance bioremediation for “polishing”
  - Removal / Reduction of source areas allows natural attenuation or enhance bioremediation to provide a complete remedy
- Optimum reagent delivery at the source zone and the unit cost of EZVI will control the cost and performance of this technology
ZVI Permeable Reactive Barrier Project

Objectives:

– Demonstrate ZVI reactive barrier performance for in-situ treatment of TNT and RDX
– Assess long term performance
– Evaluate reactive barrier diagnostic parameters (e.g., core data, water quality indicators)
– Provide cost/performance metrics

Site Location: Cornhusker Army Ammunition Plant, Grand Island, NE
Technical Performance of the ZVI Barrier

• ZVI PRB is in-place and is performing well
• Explosives concentrations are all below detection limits
• Unanticipated Issue
  – High sulfate concentration upgradient of the barrier
  – Reduction of sulfate to sulfide and then to FeS resulting in long-term impact on barrier reactivity and permeability
General Issues and Concerns with Nanoscale ZVI Technologies

• Longevity Issues
  – Oxidation of Fe by water dissociation
  – Other fouling leading to Fe passivation
  – Extremely high reaction rates
  – Manufacturing Quality Control
  – Catalyst Poisoning

• Transport Issues in the Subsurface
  – High settling rates (function of size ranges)
  – Limited radius of influence from the injection zone
  – Impact on groundwater hydraulics (e.g., displacement of contaminants)
General Issues and Concerns with Nanoscale ZVI Technologies

• Reagent Delivery Techniques
  – Direct Injection
  – Pressure Pulse Technology
  – Hydraulic Fracturing
  – Pneumatic Fracturing

• Cost of Production
  – Need to be below $5/lb from economic standpoint
Current Research Addressing Key Performance Issues

- Colloid Longevity
  - Presence of boron in chemical precipitated forms offer superior control over water dissociation rates, thereby extending its longevity
  - Introduction of solute chemicals and iron impurities during ball milling process may help control less desirable reactivity with respect to water dissociation (slow hydrogen release)
  - Considerable amount of defects, triple junctions, grain boundaries introduced by high energy ball milling process creates kinetic barrier to further corrosion (incomplete passivation)
Current Research Addressing Key Performance Issues

• Longevity Issues
  – Presence of high chlorides (CVOC remediation zones) can prevent passivation

• Transport Issues
  – Controlling colloidal size is critical to minimize gravitational settling and attractive forces between the mineral matrix and iron (ideal size range: 100-600 nm)
Comparative Costs Between Different ZVI Materials

<table>
<thead>
<tr>
<th>Source</th>
<th>UNH ZVI</th>
<th>RNIP Toda America</th>
<th>RNIP/Pd Toda America</th>
<th>Cerac Milwaukee, WI</th>
<th>Mallinkrodt St. Louis, MO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cost</td>
<td>$N/A</td>
<td>$9/lb</td>
<td>$9/lb</td>
<td>$4.3/lb</td>
<td>$2.39/lb</td>
</tr>
<tr>
<td>Size</td>
<td>1-100 nm</td>
<td>30 nm</td>
<td>30 nm</td>
<td>50 μm</td>
<td>50 μm</td>
</tr>
<tr>
<td>Water Content</td>
<td>79.9% water</td>
<td>52.5% water</td>
<td>52.5% water</td>
<td>25.0% water</td>
<td>25.5% water</td>
</tr>
<tr>
<td>Surface Area</td>
<td>33.5 m²/g</td>
<td>23.6 m²/g</td>
<td>23.6 m²/g</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Characteristic</td>
<td>suspension</td>
<td>suspension</td>
<td>suspension</td>
<td>dry powder</td>
<td>dry powder</td>
</tr>
</tbody>
</table>

Nanoscale

Micron size 21