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

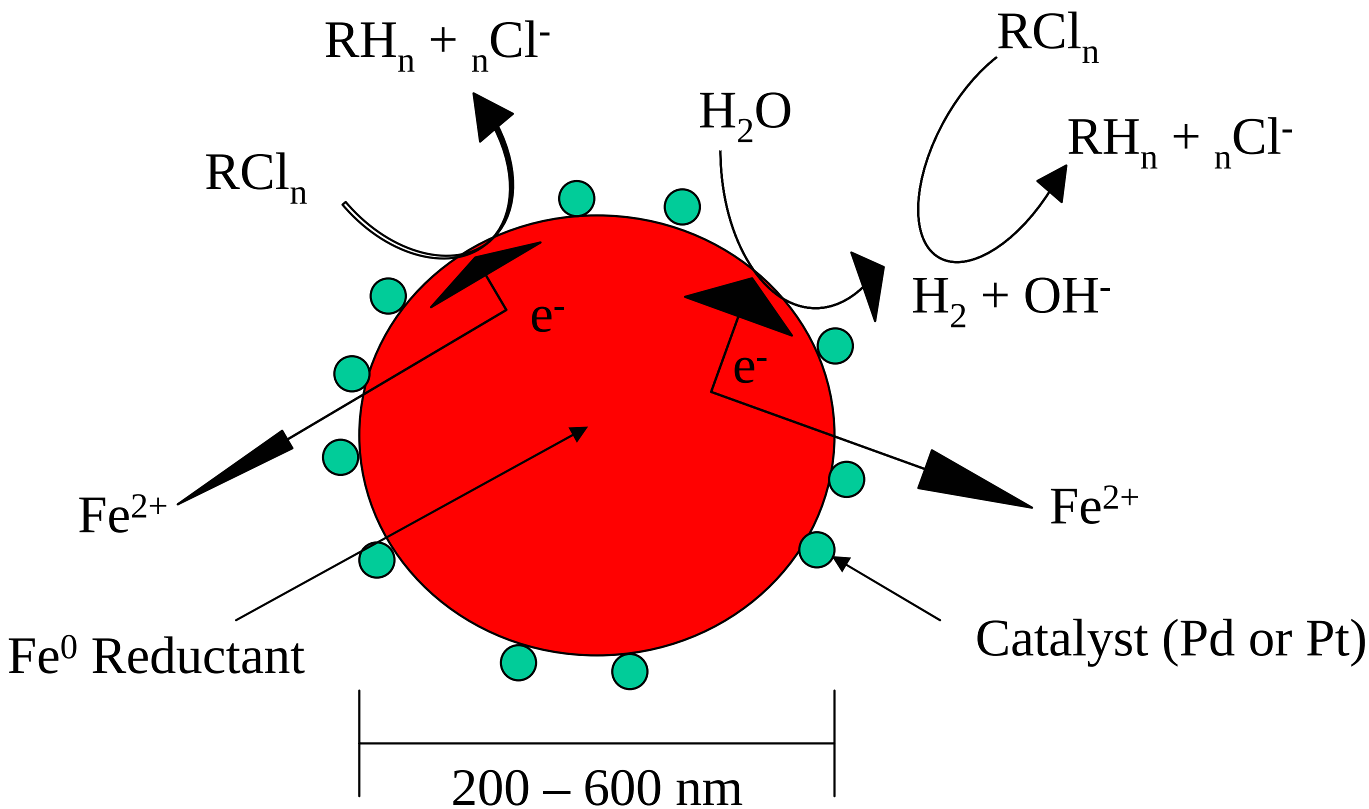
Bimetallic Nanoscale ZVI Project

- Production Method
  - Use of conventional ball milling technology to create nanoscale colloids (200 nm – 600 nm size range) and sp. surface area of 2 m^2/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

Nanoscale Forms	**K_{sa}, L/(m^2.hr)**	**Surface Area, m^2/g**
Chemical Precipitated Forms	0.01-0.12	32
Ball-Milled Forms (original size particles)	0.01-0.08	2
Ball-Milled Forms (agglomerated particles)	0.05-0.35	0.2

Bimetallic Nanoscale Injectible (BNI) Iron Properties

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



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 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

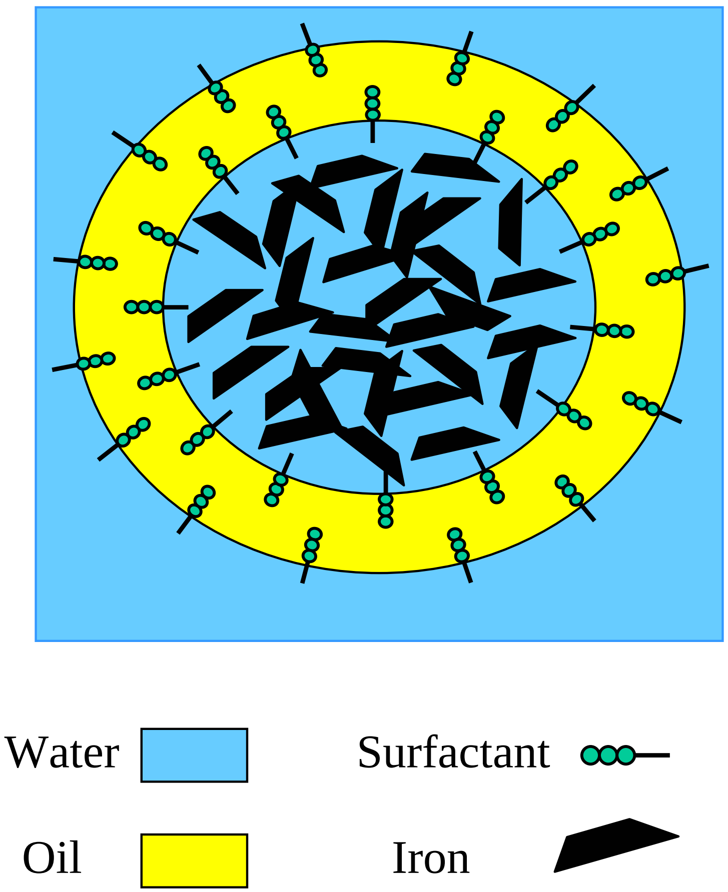
Objectives:

- 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

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

Nanoscale (UNH ZVI, RNIP, RNIP/Pd) — Micron size (Cerac, Mallinkrodt)