



Optimization and Performance of ZVI Amendments for In-Situ Chemical and Biological Reduction

Short Course: Optimization and Monitoring for Remediation of
Chlorinated and Related Compounds

Tuesday, November 12, 2019

Agenda

Optimization and Performance of ZVI Amendments

Iron Based Products

Review and applications

01

ZVI Suspensions

Engineered to accomplish the rapid and sustained degradation

03



02

eZVI

DNAPL source zone treatment

04

Sulfidated Iron

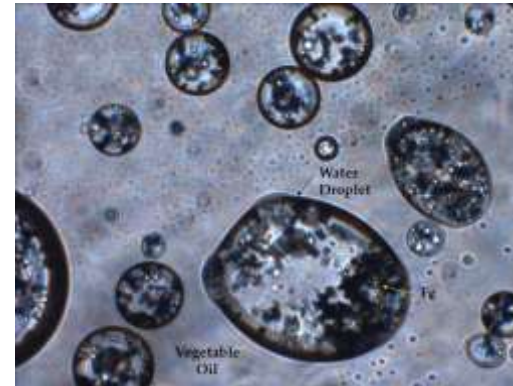
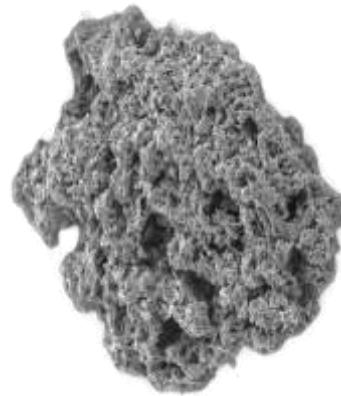
Higher contaminate removal efficiency

Iron Based Products

- ZVI Products

- eZVI

- ZVI Suspensions



Iron-Based Products

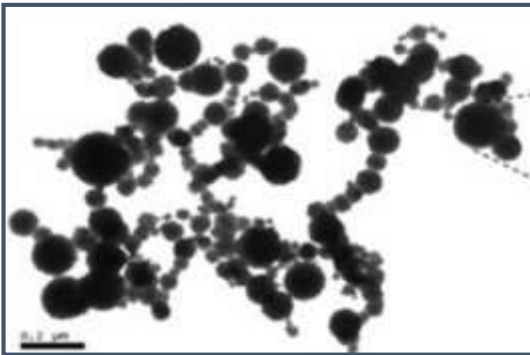
Soluble
Fe²⁺, Bicarb

Nano
nZVI

Microscale
mZVI liquids

Microscale
ZVI Slurries

Granular ZVI



0 μm

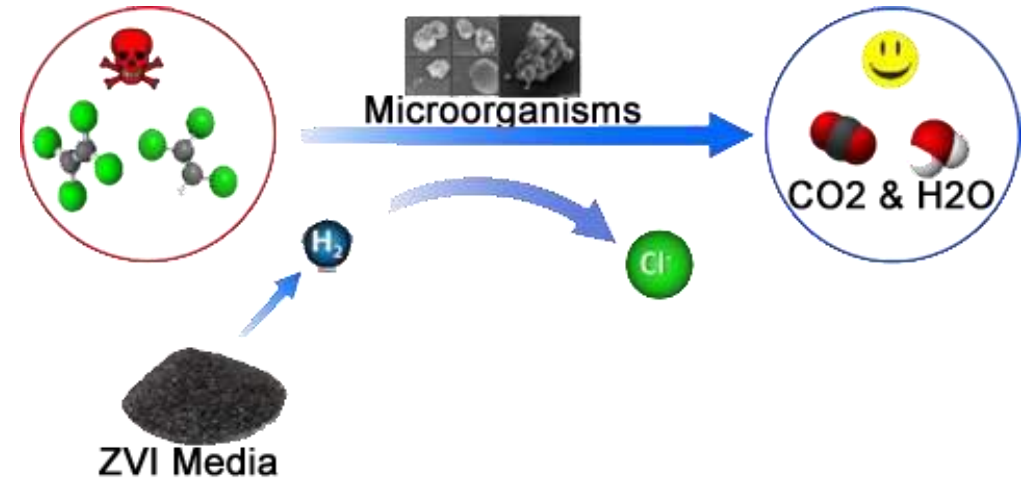
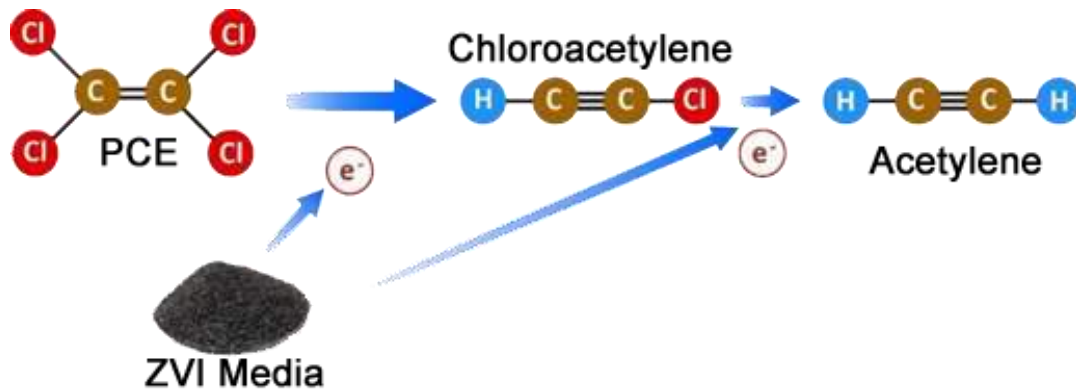
0.2 μm

< 5 μm

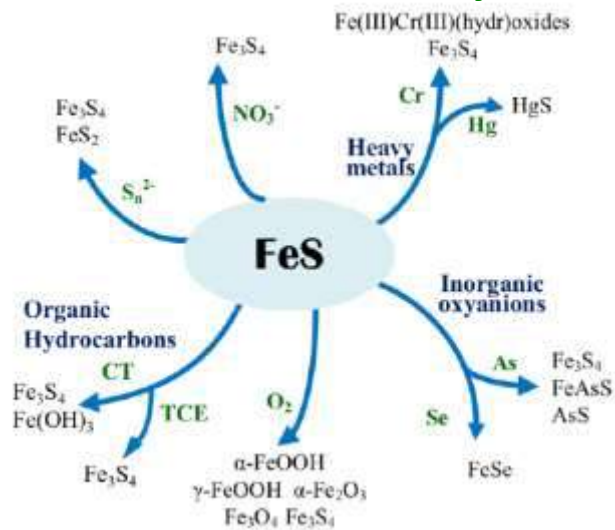
50 μm

2 mm

Iron-Based Products



Abiotic Reduction by FeS



Revised from Lan, Ying, Ph.D. dissertation, University of Oklahoma, 2016.

- Iron has strong oxidation-reduction potential in presence of water

Permeable Reactive Barriers (PRBs)

- Physical application methods
- Used for shallow depths



Photos: https://rtdf.clu-in.org/public/permbarr/prbsumms/more_info.cfm?mid=75



Photo: Dewind One-Pass Trenching

Soil Mixing

- Best suited for large material (granular/coarse iron, mulch)
- Trenching and soil mixing methods can be effective but are highly invasive



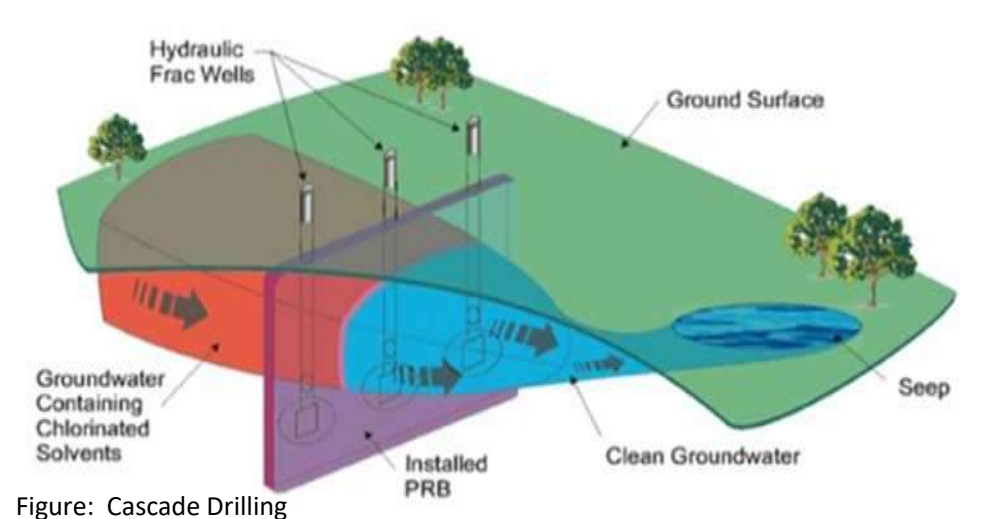
Photo: Geo-Solutions Inc.

Pneumatic / Hydraulic Fracturing

Controlled Vertical Inclusion Propagation (VIP)

- Passive treatment resulting in long-term cost savings
- Minimal site disturbance
- No excavation/disposal of contaminated material
- Deep application of treatment technology
- Minimal impact on groundwater flow regime
- Permanent remedy

Reactive barriers are installed to greater depths than conventional technologies with VIP



Direct Push

- Direct Push – Very flexible, small footprint
- Wide variety of injection tooling including water sampler screens
- Methodology can be used for a wide variety of applications
- Large areas can be treated quickly



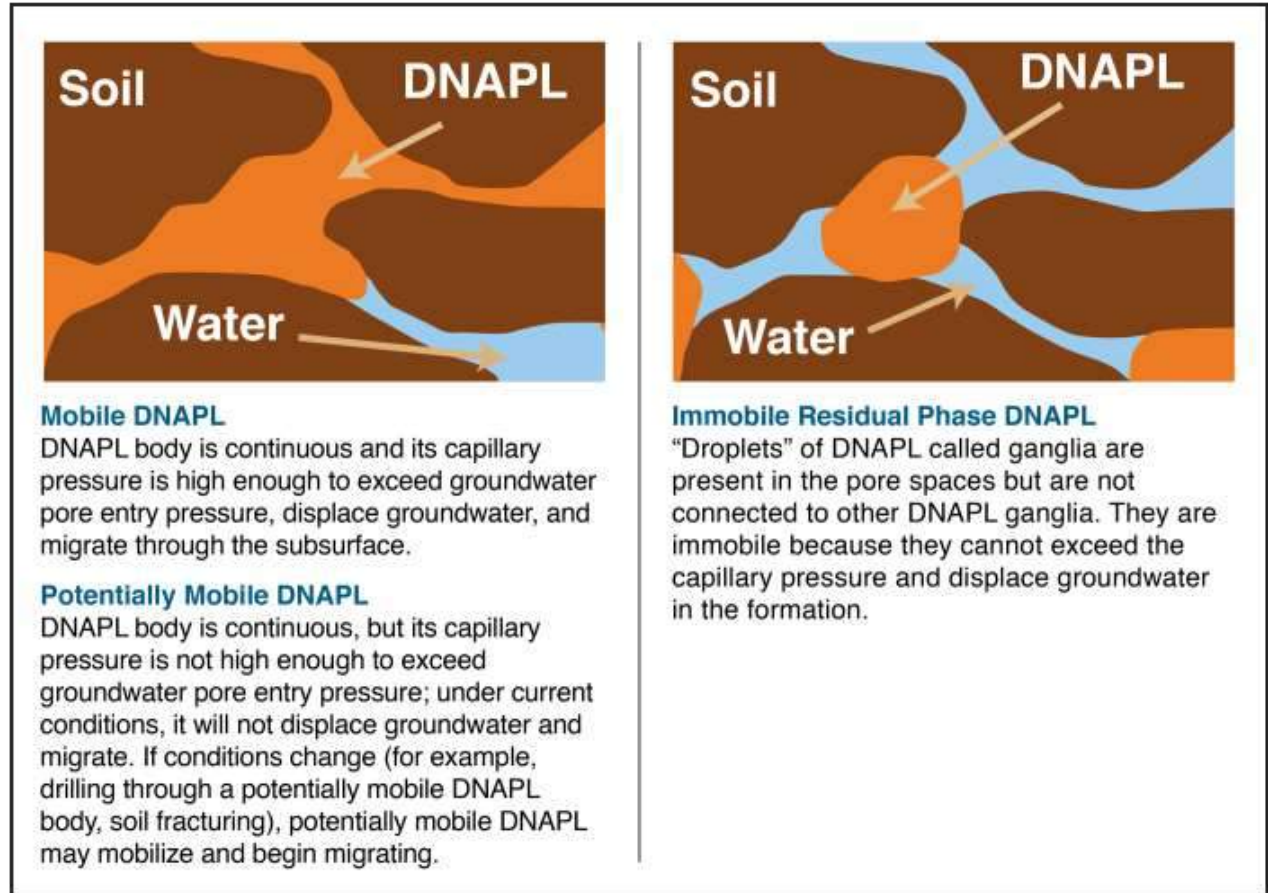
Wells

- Low pressure injection possible into more permeable zones
- Many sites have existing screened wells
- Must use small particle size / soluble material
- Good for repeat application
- Wells are permanent - eventual abandonment or removal
- If seal is compromised during injection subsequent attempts are usually futile



eZVI for DNAPLs

A Combination ISCR Technology for Source Zone Remediation

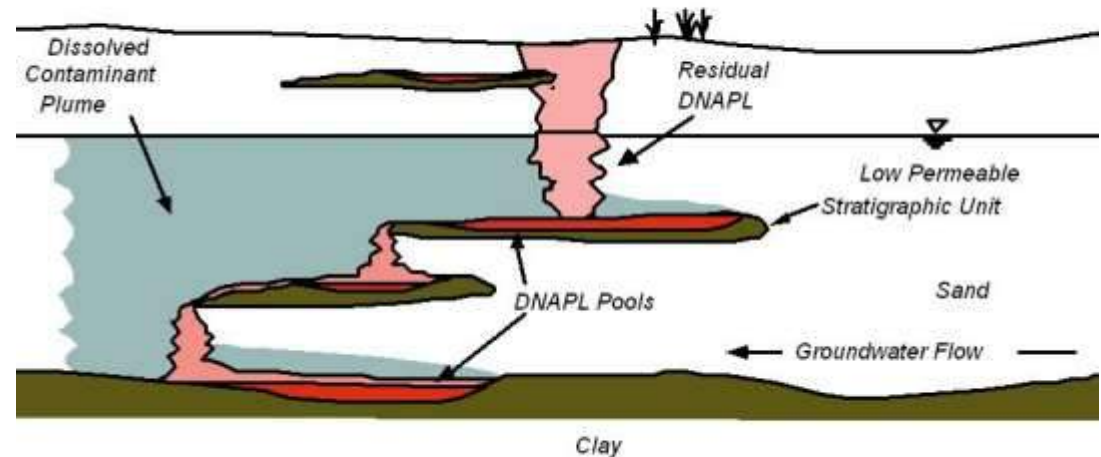


Ref: ITRC, Integrated DNAPL Site Characterization and Tools Selection, Figure 2-1
(www.itrcweb.org/DNAPL-ISC_tools-selection)

Do I have DNAPLs at My Site?

Suspected DNAPL Thresholds Based on Solubility Relative to 1 Percent of Aqueous Solubility

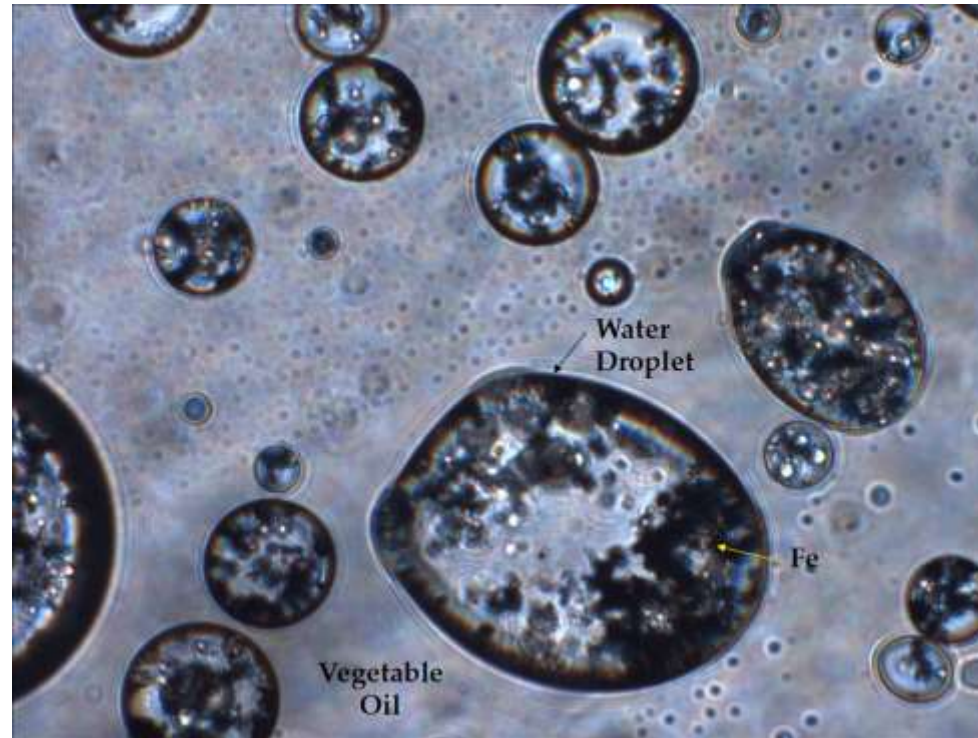
Chlorinated Solvent (CAS Number)	Aqueous Solubility ($\mu\text{g/L}$ @ 25 °C)	1% of Aqueous Solubility ($\mu\text{g/L}$ @ 25 °C)
PCE (127-18-4)	200,000	2,000
TCE (79-01-6)	1,472,000	14,720
cis-1,2-DCE (156-59-2)	3,500,000	35,000
trans-1,2-DCE (156-60-5)	6,300,000	63,000
1,1-DCE (75-35-4)	2,250,000	22,500
Vinyl Chloride (75-01-4)	8,800,000	88,000
1,1,1-TCA (71-55-6)	1,334,000	13,340



After Waterloo Centre for Groundwater Research, 1989.

Emulsified Zero-Valent Iron (EZVI)

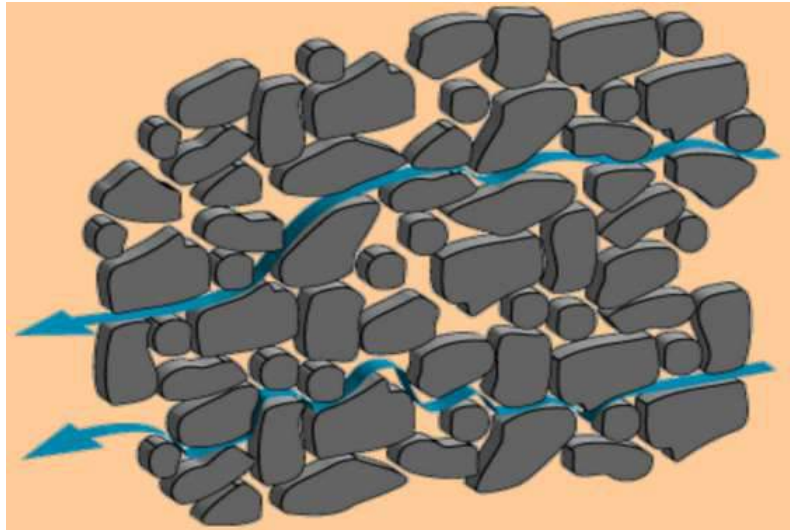
- A Combination ISCR Technology for Source Zone Remediation



STRUCTURE – What makes EZVI Unique?



Where, How Much, & How?

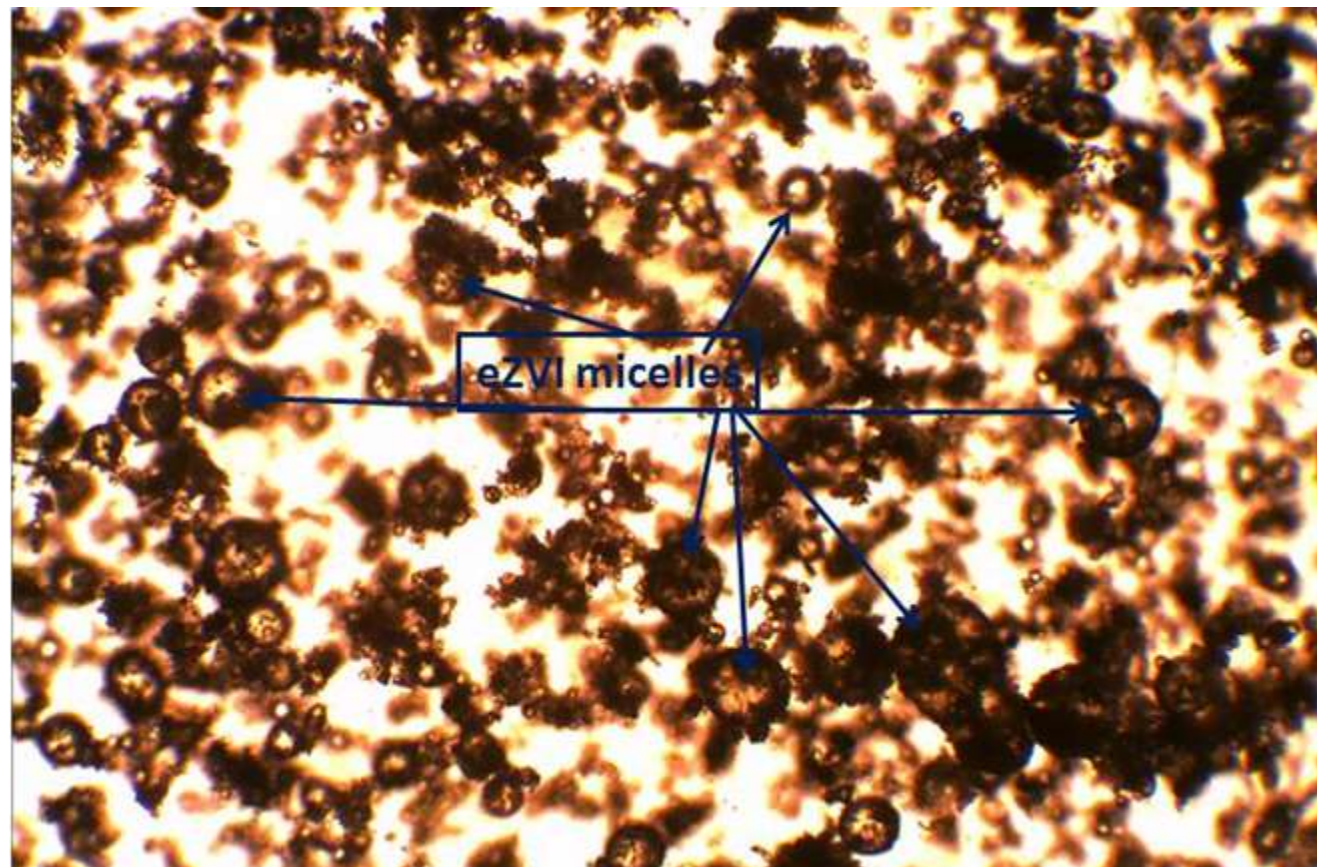


10% Effective Porosity



Direct Push Rig

Downgradient Monitoring Well



In Situ Chemical Reduction (ISCR)

Combines

- Biological processes
- Zero valent iron (ZVI) particle-driven abiotic pathways



MNA



Bio



mZVI Suspension,
EDS-ER™ & KB-1®

m-ZVI Suspensions

Micron-size ZVI suspension in a shear thinning fluid



*Sold under a License Agreement for U.S. Patent Nos. 7,129,388 and 7,531,709 relating to use of a mixture of organic hydrogen donors and zero valent metal used for environmental remediation applications.

Field prepared ZVI suspension

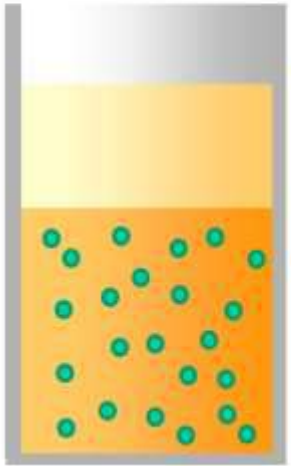


Products & Services for *In Situ* Remediation • tersusenv.com

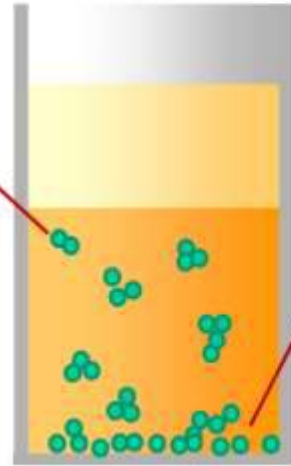
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Approaches

Example of a stable colloid



Example of an unstable colloid

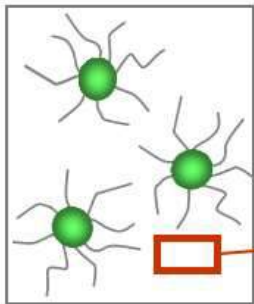


Aggregation

Challenges on ZVI suspension: ZVI is too heavy and simple viscosity increase does not help injectivity.

Sedimentation

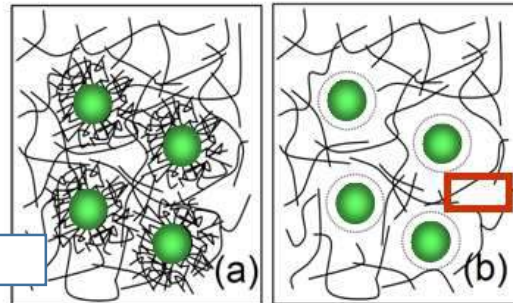
Steric stabilization



Liquid phase (water)

(Oil)

Dispersion in a gel network



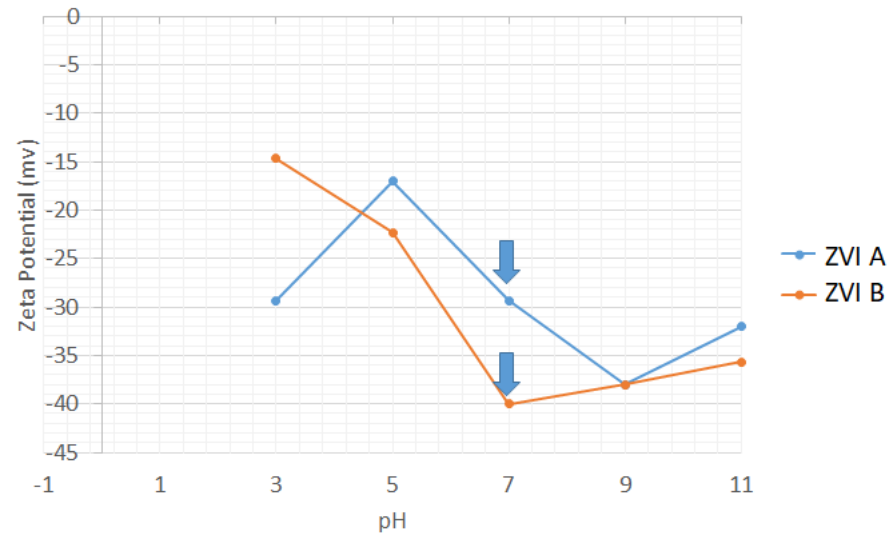
Network of polymer chains characterized by mechanical strength

- Solutions:** Increase steric repulsion between ZVI particles at the least increase in viscosity. Surfactant and oil thickener were used to increase positive buoyancy.

Dominant Forces in Dispersions

- Van der Waals attraction
 - Electrical double layer repulsion or attraction
 - Steric effects, mainly due to adsorbed polymers
 - Solid's particle size, density and shape
 - Liquid's viscosity and polarity
- “a suspension's stability is almost always improved by increasing the liquid's viscosity.”

ZVI Zeta Potentials



- At pH 7, $\zeta = -30 \text{ mV}$ & -40 mV
- At high pH, ZVI experiences deprotonation

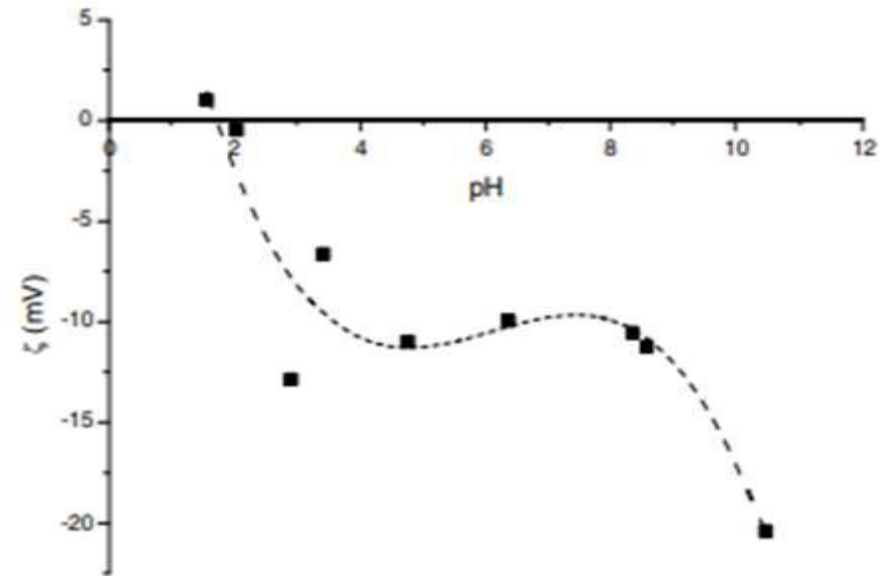


Fig. 5 – ζ potential as a function of pH.

Santos 2016, Journal of Materials Research and Technology

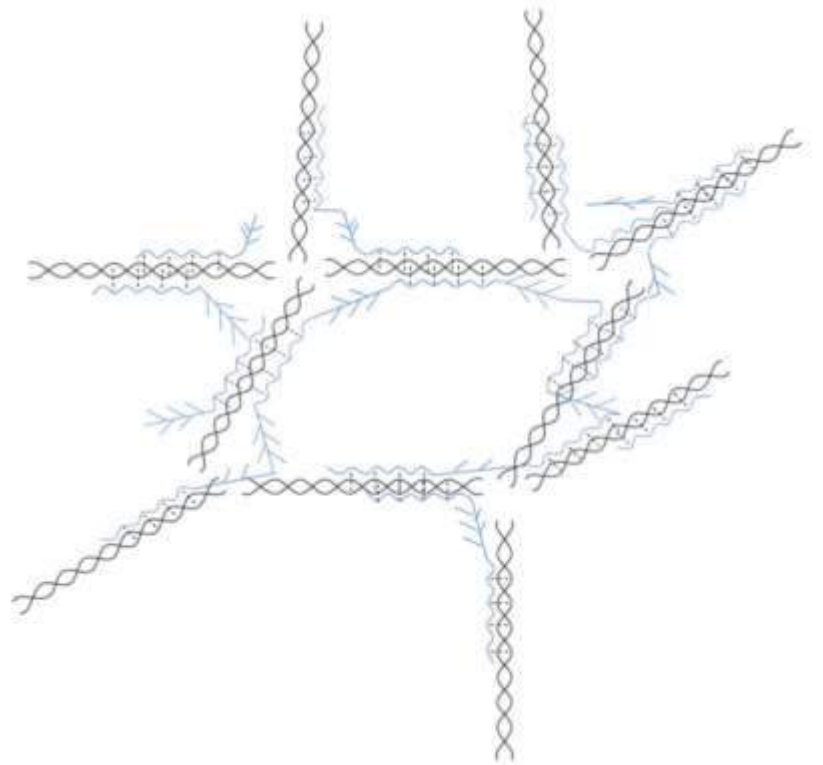
Viscoelastic Gels

Single Biopolymer Solution (SBS)

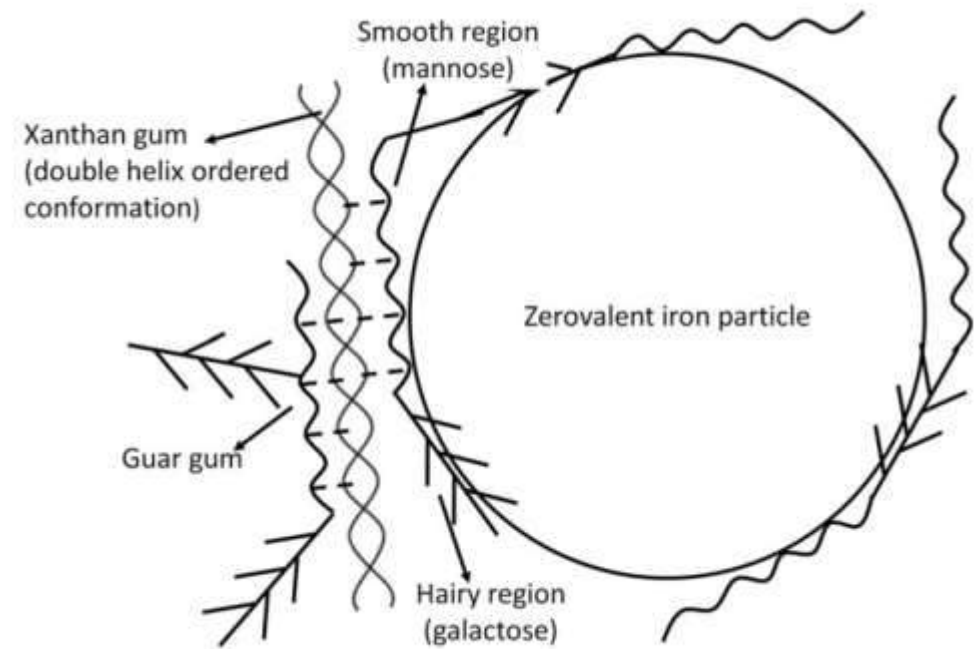
- ZVI dispersions with diluted SBS (XG or GG) are not stable over long periods of time (J Nanopart Res (2012) 14:1239)
- Adsorption affect
 - ZVI particles adsorb part of polymer to their surface
 - Decrease the viscosity of suspension
 - Reduces stability

Biopolymer Mixture Solution

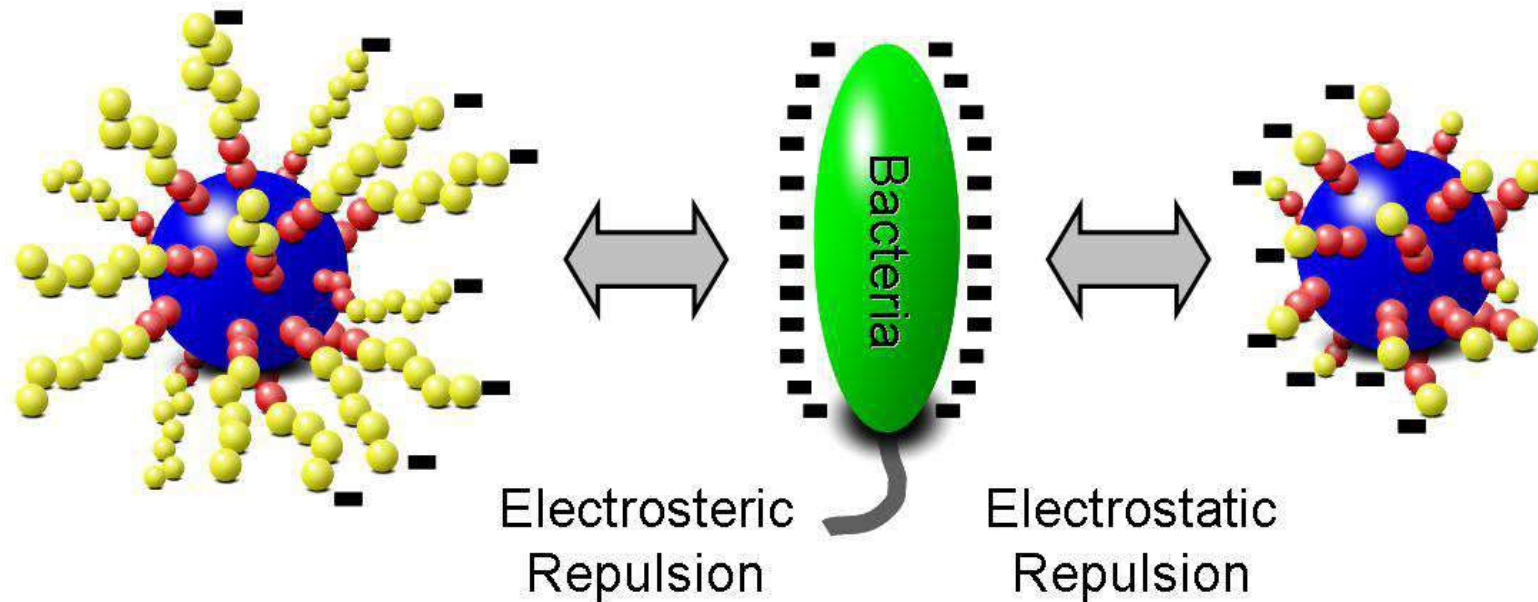
Interaction between XG and GG molecules forms a continuous network structure



GG molecules are able to adsorb to the ZVI surface (Tiraferri et al. 2008)

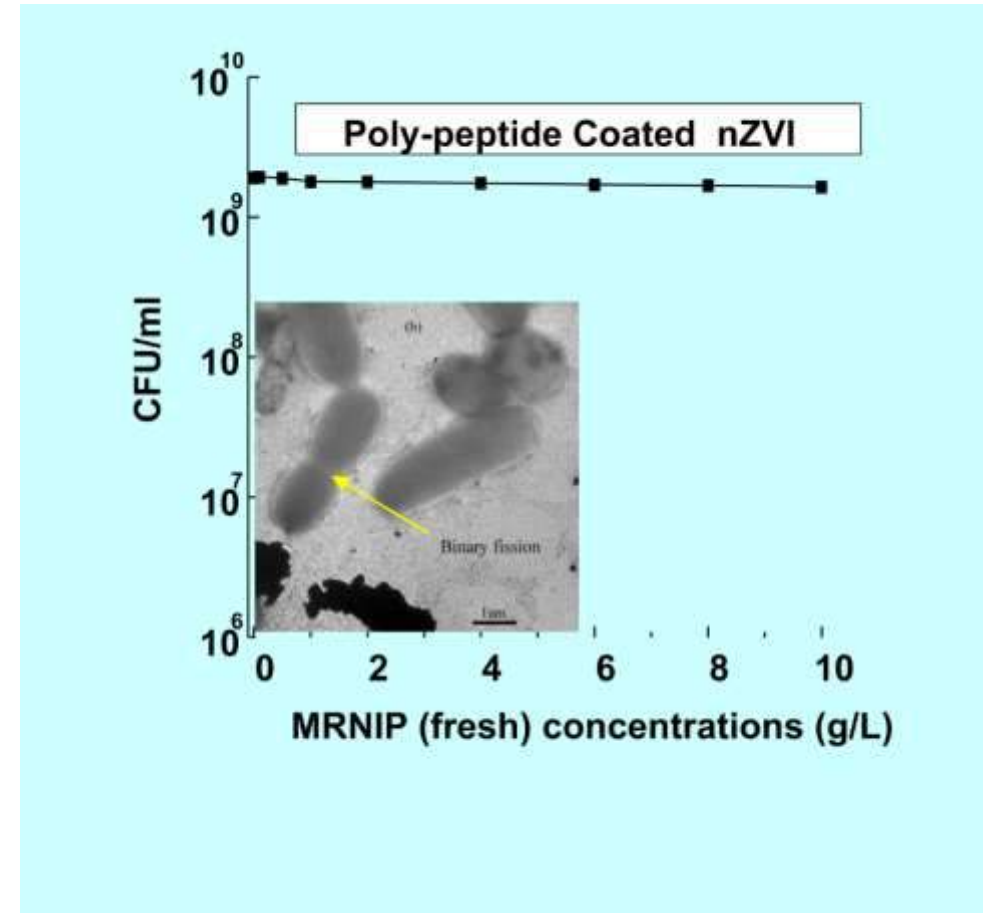
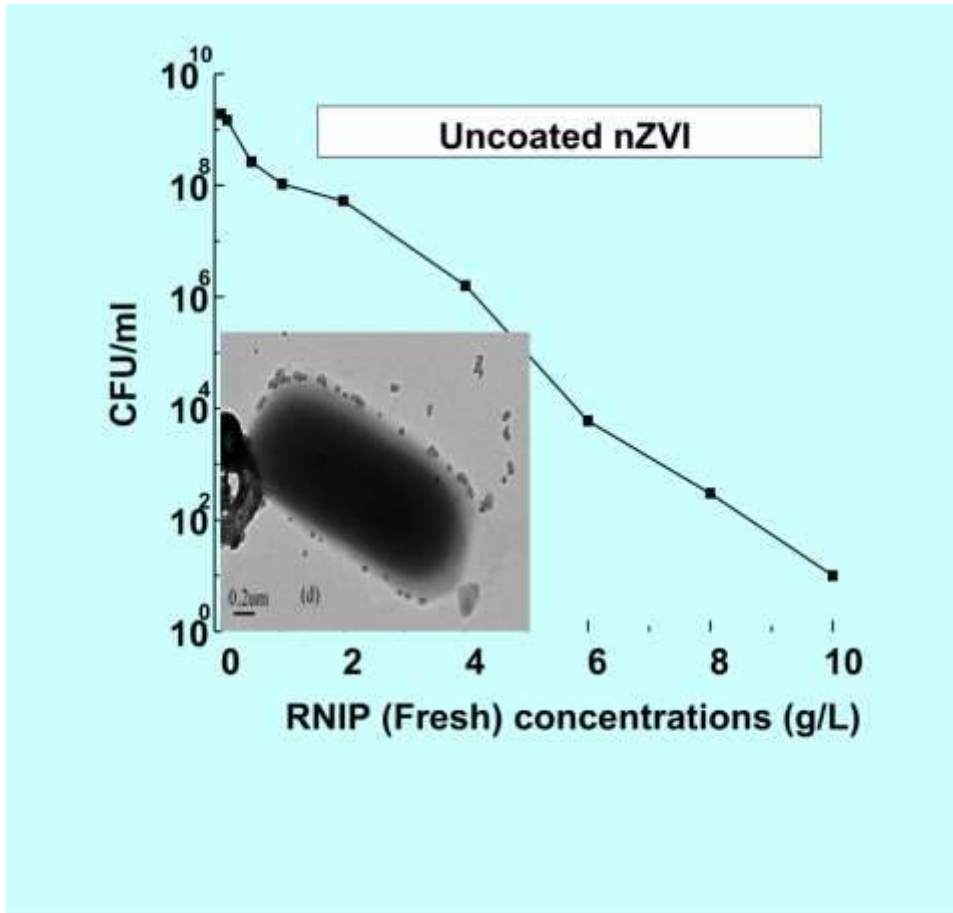


Polymer Coatings Mitigate nZVI Aggregation and Toxicity to Bacteria



Reference: Li Z., K. Greden, P.J.J. Alvarez, K.Gregory, and G.V. Lowry. Environ. Sci. Technol. 44 (9):3462–3467

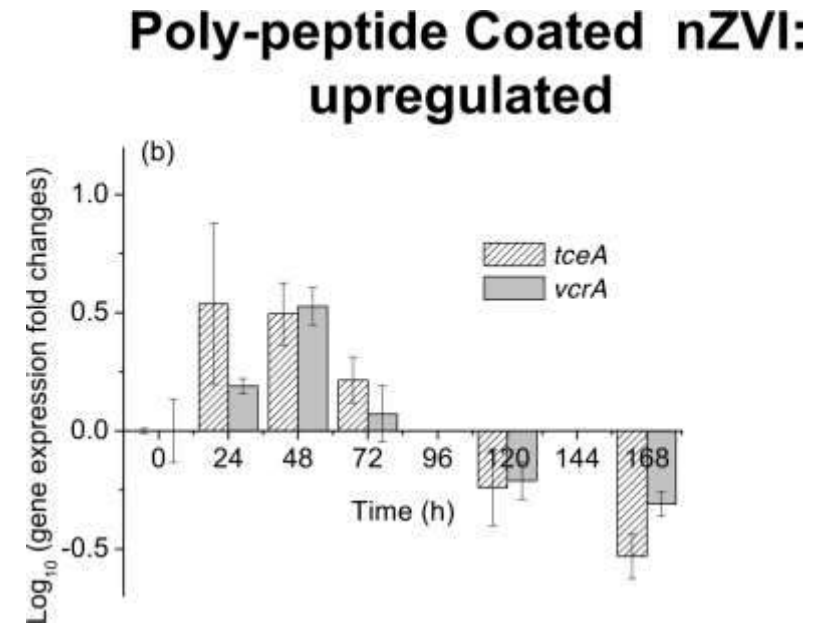
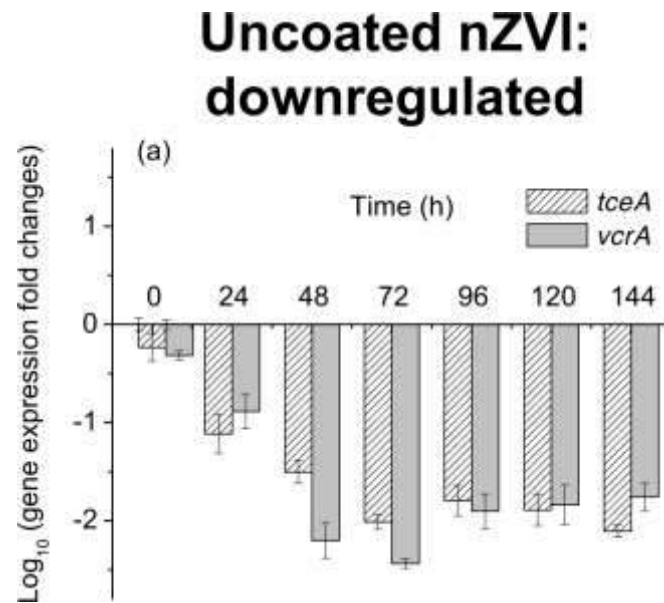
Dose response of *E. coli* exposed to nZVI



Reference: Xiu Z-M, Z-H Jin, T-L Li, S. Mahendra, G.V. Lowry, and P.J.J Alvarez. Bioresource Technology 101: 1141–1146

Coating the NZVI Enables Expression of Dehalogenase Genes as it Mitigates Toxicity

(Enables Microbial Reductive Dechlorination)



Reference: Xiu Z-M, K.B. Gregory, G.V. Lowry, and P.J.J. Alvarez. Environ. Sci. Technol. 44: 7647–7651

Typical Design

Suspension Preparation

- 3 to 7 g/L Biopolymer Mixture Solution
- 1.0 to 3.0 lbs. Crosslinker per 1,000 gallons (pH 8.5 to 10)
- 20 g/L ZVI

Post Injection Chase Water

- 1 pint to 1-gallon high pH enzyme breaker per 1,000 gallons

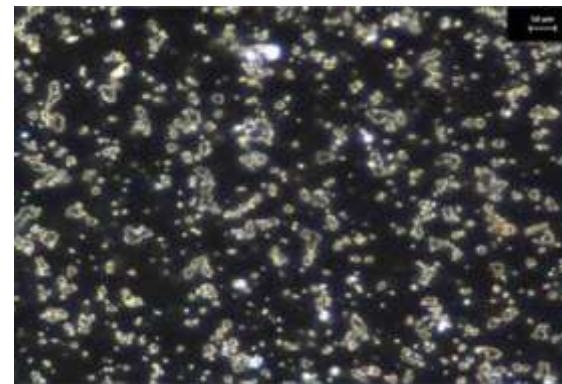
mZVI Suspension

- Uniform, low viscosity, liquid

- ✓ Pour
- ✓ Pump
- ✓ Field mix

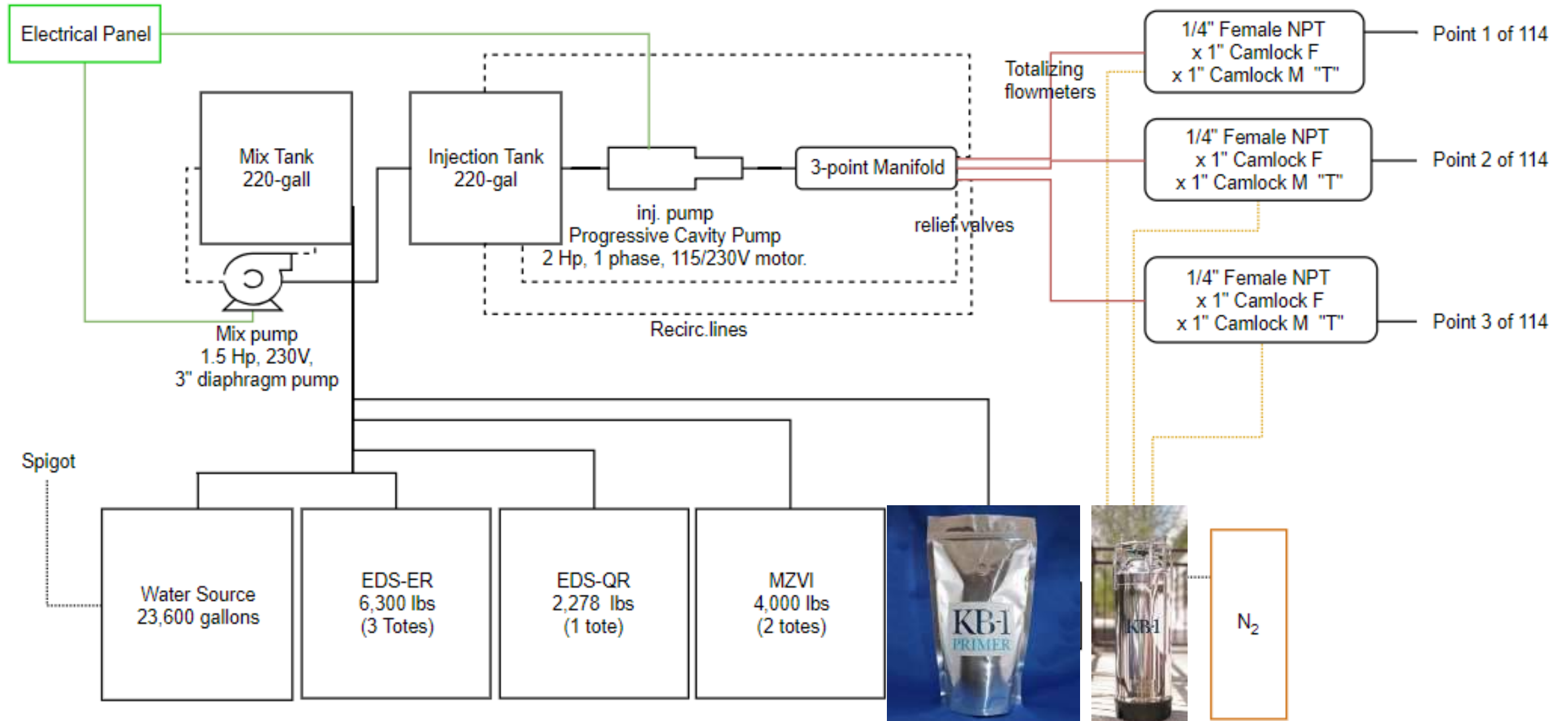
- Injection behavior is like EVO

<u>Parameter</u>	<u>Typical Values</u>
ZVI (% by wt.)	40
ZVI average particle size	<10 μm
Organic Carbon (% by wt.)	60
Specific Gravity (Density)	1.9 (15.8 lbs./gal)
Viscosity (cP)	~ 3,000
Water	0



*Sold under a License Agreement for U.S. Patent Nos. 7,129,388 and 7,531,709 relating to use of a mixture of organic hydrogen donors and zero valent metal used for environmental remediation applications.

Field Implementation



ISCR Injection Project

- Tight, challenging location



ZVI suspension-two totes, EDS-ER™-three totes, EDS-QR™-one tote, L-Cysteine- two buckets, KB-1® culture- 55L



Manifold assembly with a small pump



Mix pump



Injection Started

Dosing Considerations

- Commodity products are typically dosed on a soil mass basis (0.5 – 1.0 wt. %). Non-uniform emplacement requires overdosing.
- mZVI Suspension is dosed based on intragranular pore volume; 4.0 to 10.0 g/L – about 10-20 percent what is used for commodity iron products.
- Less material required = lower project cost

Iron Corrosion Reaction Stoichiometry

Reaction

Stoichiometry

Anaerobic iron corrosion

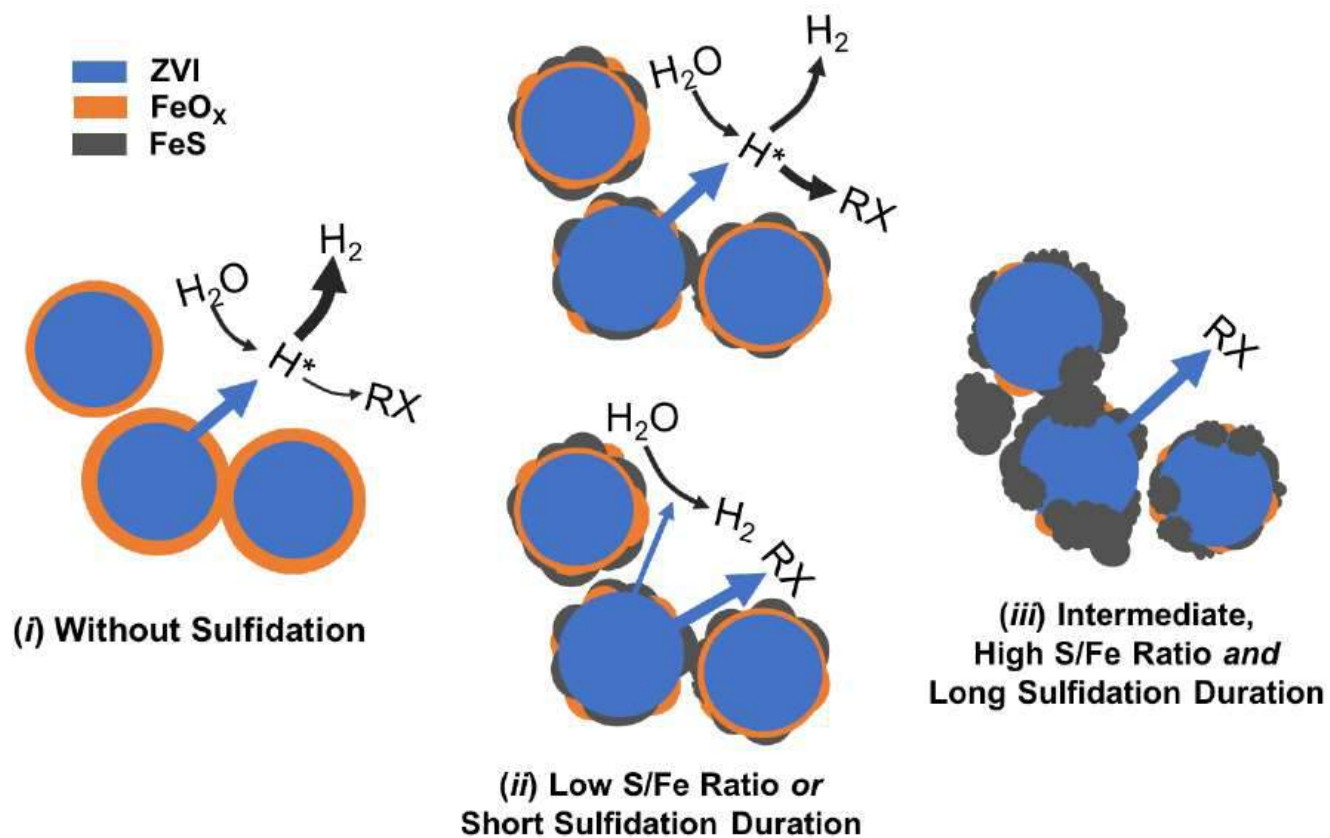


Mechanochemically Sulfidated Microscale Zero Valent Iron



Reference: Environ. Sci. Technol. 2017, 51, 12653-12662

Effects of Sulfidation



Fan, D., et al. (2017). *Environ Sci Technol*, 51(22), 13070-13085.

ISR-CI

Iron Sulfide Reagent

Provides

- Benefits of sulfidated ZVI
- Higher contaminant removal efficacy
- Lower cost

Specifications

- Physical form: colloidal suspension
- Specific gravity: 1.15 - 1.22
- ORP: -700 to -1300 mV

Sales and Technical Support



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