How to Choose the Appropriate Amendments for Your Chlorinated Solvent Sites

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tersus environmental

Thu, Jan 27, 2022
2:00 PM - 3:00 PM EST

Agenda

01 Contaminant Type

Chlorinated methanes, ethanes, and ethenes

02 Bioremediation

Biostimulation with Electron donor and Bioaugmentation with organohalide-respiring bacteria

03 ISCR

Geochemically enhanced biostimulation with ZVI (most widely used remediation amendment

04 ISCR Enhanced

Geochemically enhanced biostimulation with FeS (replicating true geochemical reactions)

How quickly do you need to close your site?

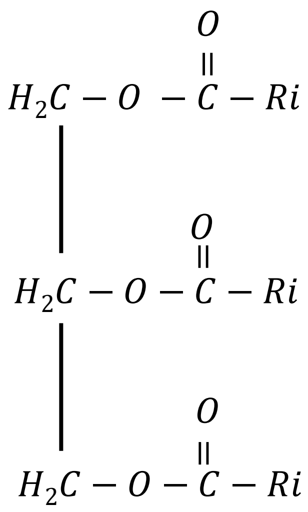
Performance Monitoring CSIA & MBTs	Biostimulation plus Bioaugmentation	ZVI plus Biostimulation & Bioaugmentation	FeS & ZVI plus Biostimulation & Bioaugmentation

Slow	Moderate	Fast	Faster

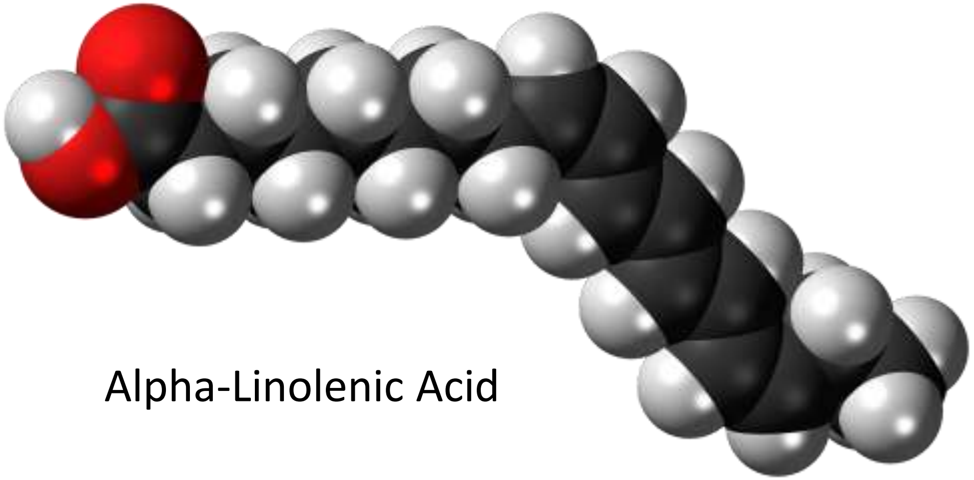
What is needed for enhanced reductive dechlorination?

Vegetable oils ferment to acetic acid and hydrogen

Soybean Fatty Acid Distribution



	Fatty Acid	**Percent**
C-16:0	Palmitic	11.0 %
C-18:0	Stearic	4.0 %
C-18:1	Oleic	24.0 %
C-18:2	Linoleic	54.0 %
C-18:3	Linolenic	7.0 %



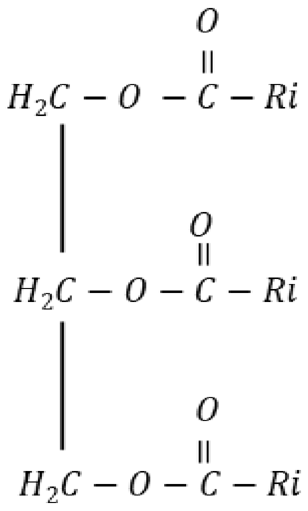
Alpha-Linolenic Acid

Vegetable Oil Fermentation

Two step process

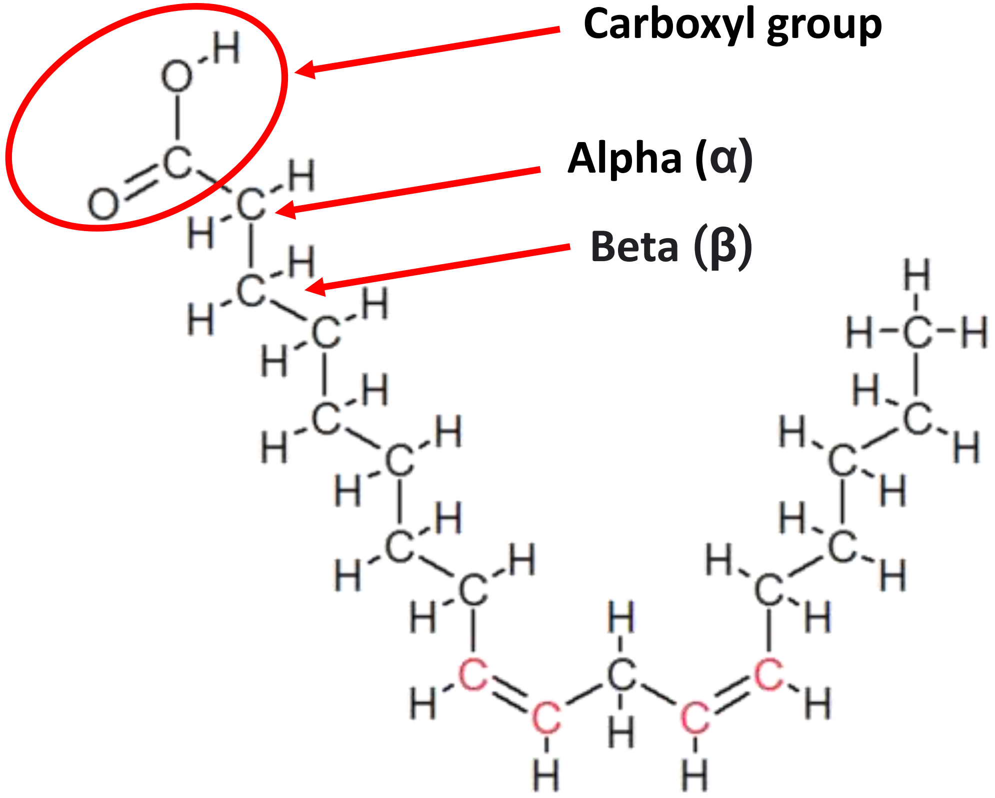
1. Long-chain fatty acids are hydrolyzed

2. Beta-oxidation



Fatty Acid Oxidation

Linoleic Acid



Multiple step metabolic process

$C_nH_{2n}O_2 + 2\ H_2O \Rightarrow C_{n-2}H_{2n-4}O_2 + 2\ H_2 + C_2H_4O_2$

- Removes two carbons from the chain
- Releases:
  - Four hydrogen atoms (H)
  - Acetic Acid ($C_2H_4O_2$)

Distribution of the Correct Type of Fatty Acids is Essential

Acetate

- Slow consumption
- Will migrate downgradient
- Stimulates PCE -> TCE -> cDCE
- Will not stimulate cDCE -> VC -> ethene

Hydrogen (H_2)

Produced from linolenic acid, propionate, butyrate, etc.

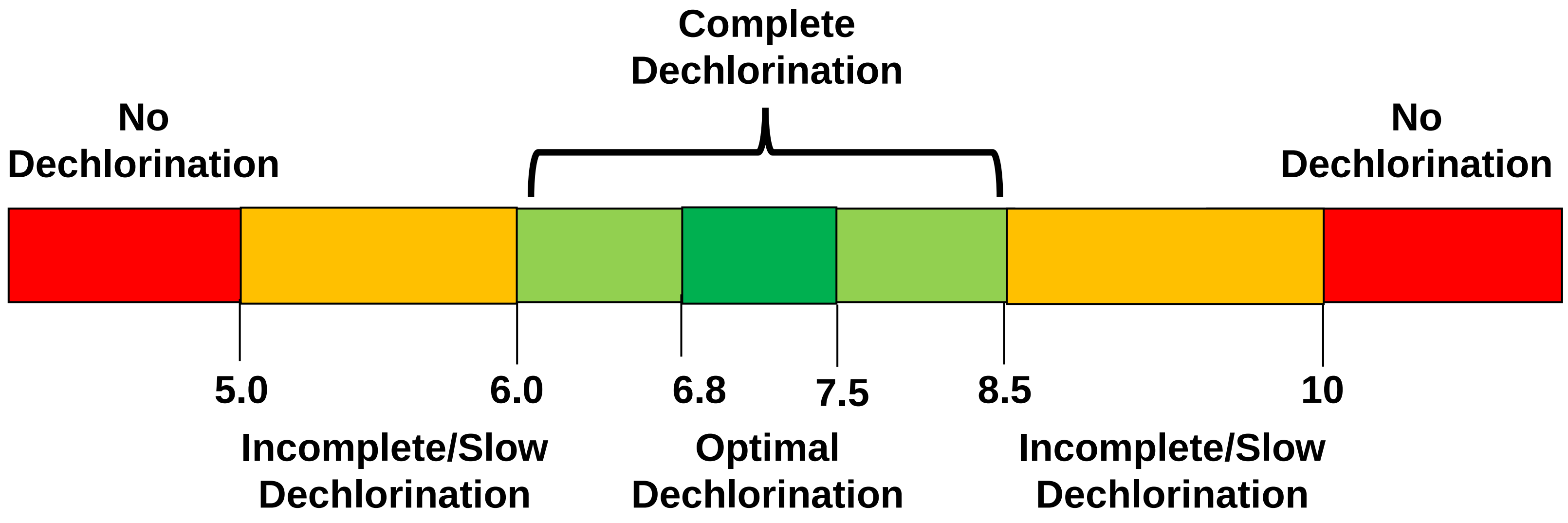
- Rapid consumption
- Does not migrate beyond injection zone
- Required for cDCE -> VC -> ethene

pH Plays a Key Role in VFA Production

Systems under alkaline conditions

- Enhances the activity of fatty acid-producing bacteria
- Inhibits methanogens
- Increases production of VFAs

Impact of pH on Dechlorination



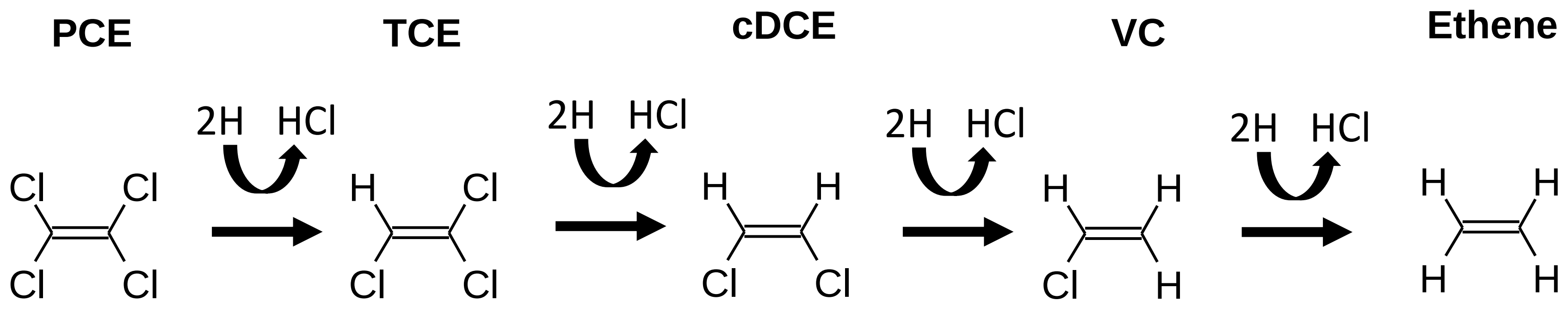
- pH of 6.0-8.5 is generally required for dechlorination to ethene*
- pH 6.8-7.5 is considered optimal range, 7.5 is best*
- Sites with low pH more likely to accumulate cDCE/VC

*Rowlands, 2004 (Slide Courtesy of SiREM)

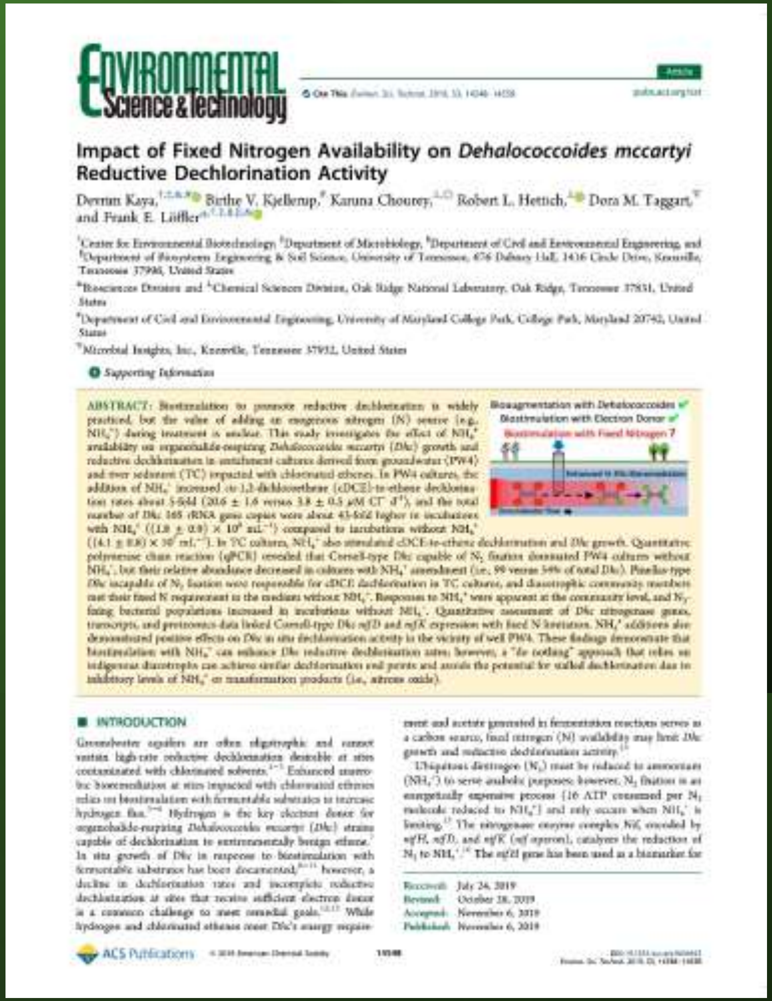
Why is low pH so Common?

- Some sites have intrinsic groundwater pH in the 5.0-6.0 range

- Reductive dechlorination produces hydrochloric acid



- Fermentation of electron donors generates acidic byproducts


Environmental Science & Technology

Impact of Fixed Nitrogen Availability on *Dehalococcoides mccartyi* Reductive Dechlorination Activity

Derya Kaya, Birthe V. Kjellerup, Karuna Chourey, Robert L. Hettich, Dora M. Taggart, and Frank E. Löffler

INTRODUCTION

ACS Publications

Nutrients

- Biostimulation benefits from adding an exogenous nitrogen (N) source (e.g., NH_4^+)
- Addition of addition of NH_4^+ increased cis-1,2-dichloroethene (cDCE)-to-ethene dichlorination rates about 5-fold
- Typical target dosing:
  - 20:1 BOD to NH_3 – N ratio
  - 100:1 BOD to PO_4 – P ratio

Available online at surbec.com

Surbec

TersOx™ Nutrients-QR

- Fast-acting soluble nutrient blend for bioremediation
- Blend of nitrogen, phosphorous and microbial growth enhancers that provide a source of urea, phosphate and potassium

Vitamin B_{12}

- Dehalococcoides mccartyi strains require vitamin B_{12} (Yan et al, 2013)

- Reported concentration for optimal dechlorination and growth: 25 to 50 µg/L (Stroo et al., 2013)

Stroo et al., 2013, Bioaugmentation for Groundwater Remediation, edited by Stroo, H.F., Leeson, A., Ward, C.H. HydroGeoLogic, Inc., Ashland, OR, USA

Yan et al, 2013, Yan J, Im J, Yang Y, Löffler FE. 2013 Guided cobalamin biosynthesis supports *Dehalococcoides mccartyi* reductive dechlorination activity. Phil Trans R Soc B 368: 20120320. http://dx.doi.org/10.1098/rstb.2012.0320

Saponification

The Process of Making Soap

+

=

Acid
(Oil)

Base
(Lye)

Salt
(Soap)

Biofouling

Nutrients in the vicinity of injection wells promote excessive biomass growth that reduce permeability

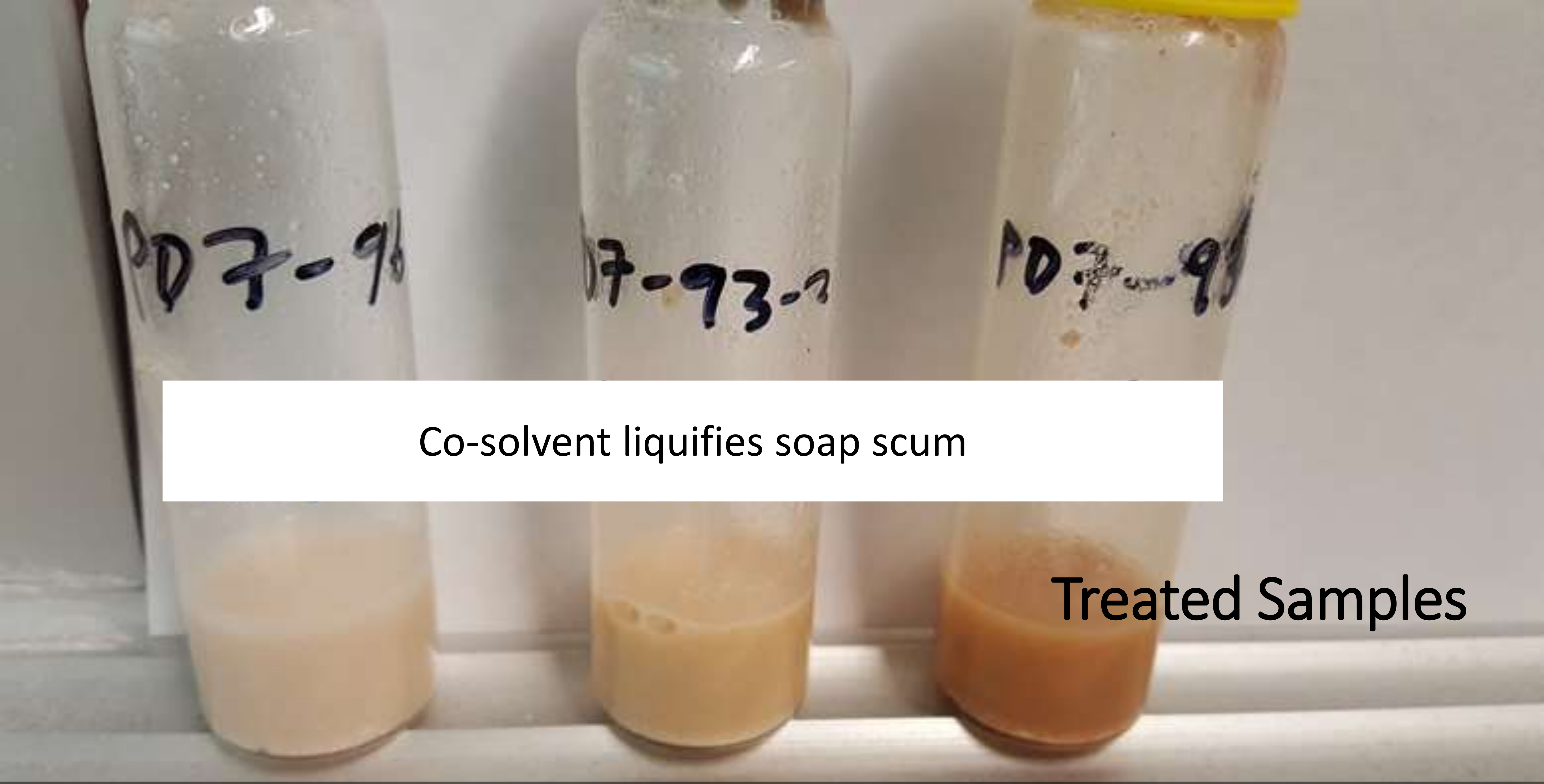
Bacterial growth within delivery wells

Hard Soap and Soap Scum

Hard Water

Calcium and Magnesium Ions

- React with the fatty acids to form an insoluble gelatinous curd



Co-solvent liquifies soap scum

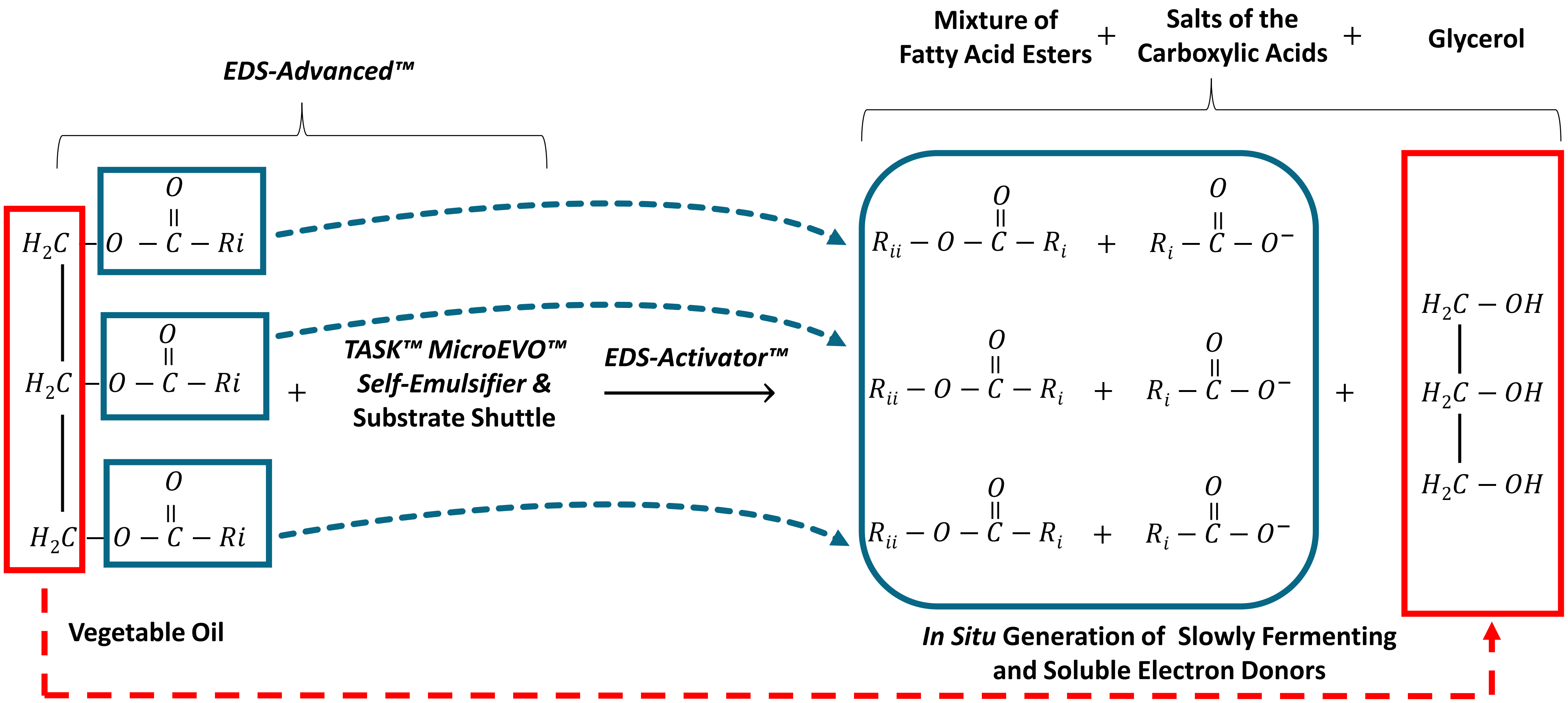
Treated Samples

Alkaline Groundwater

Bench test to liquify viscous material

- Samples mixed with co-solvent liquifies insoluble gelatinous curd
- Addition of water, forms an EVO

Anaerobic Bioremediation Deploying Electron Donor Via *In Situ* Alcoholysis



Activator Options

- Homogeneous Alkaline Catalyst
    - Alkyl oxides (RO^-)

- Heat
    - Steam hydrolysis
    - Electrical resistance heating
    - Thermal conduction heating
    - Gas thermal heating
    - Residual heat from an in-situ thermal remediation project

- Biocatalyst
    - Enzyme (triglyceride lipases)

EDS-Advanced™

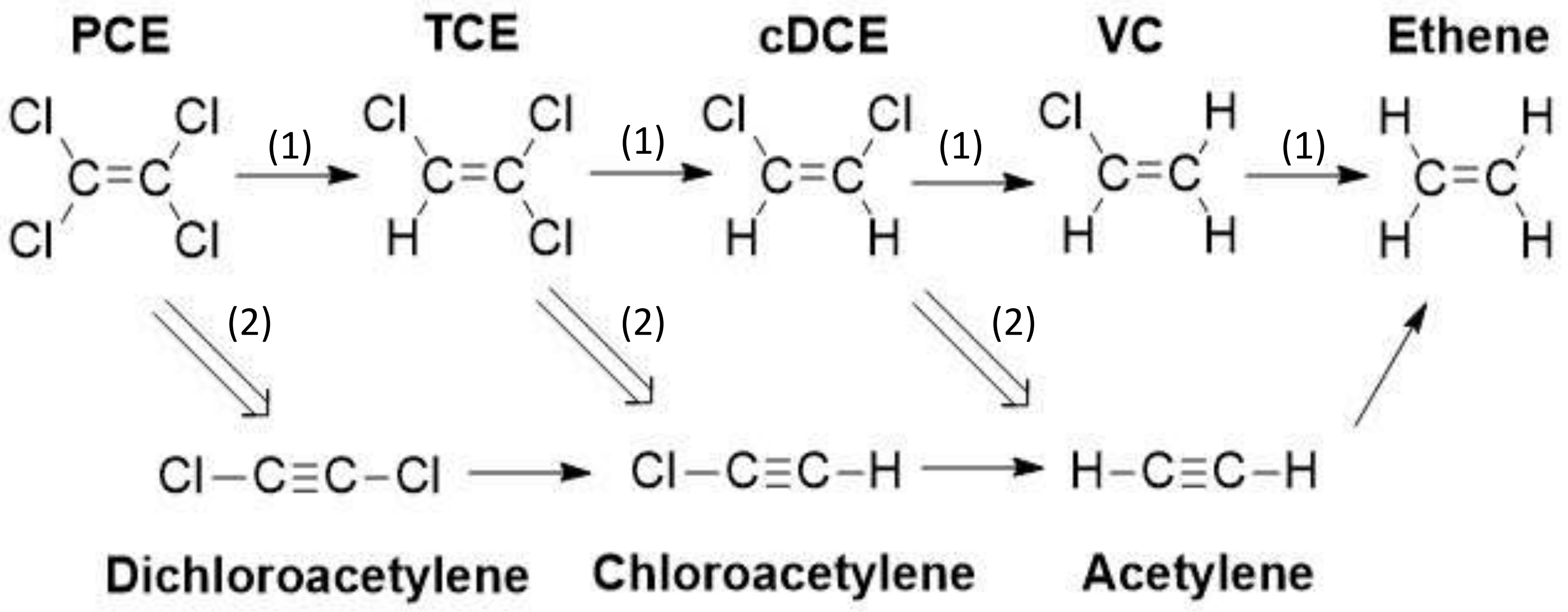
Unrestricted Electron Donor Subsurface Distribution for Anaerobic Bioremediation

- Improved subsurface distribution of a vegetable oil-based electron donor
- Improved ROI, fatty acid distribution and TOC when compared to EVO
- Eliminates dependence on EVO droplet size
- Aids in reducing cVOC inhibitory concentrations by sequestering DNAPL
- High alcohol content and high solubility reduces injection well biofouling risk

Typical Application Rates

EDS-ER™ (Soybean Oil and TASK™ MicroEVO™ Self-Emulsifier	2 to 8 g/L
EDS-Activator™	16 to 20% of EDS-ER Dose
EDS Substrate Shuttle (Co-Solvent)	0.4 g/L
Microscale Zero-Valent Iron (mZVI)	4 to 6 g/L

ZVI Destructive Process



Pathway 1, Biotic Degradation (e.g., dichlorination of solvents)
Pathway 2, Abiotic Degradation (e.g.,β elimination by ZVI or iron sulfides)

Abiotic Reduction by Iron Sulfide (FeS)

ZVI can react directly with sulfate via abiotic reaction

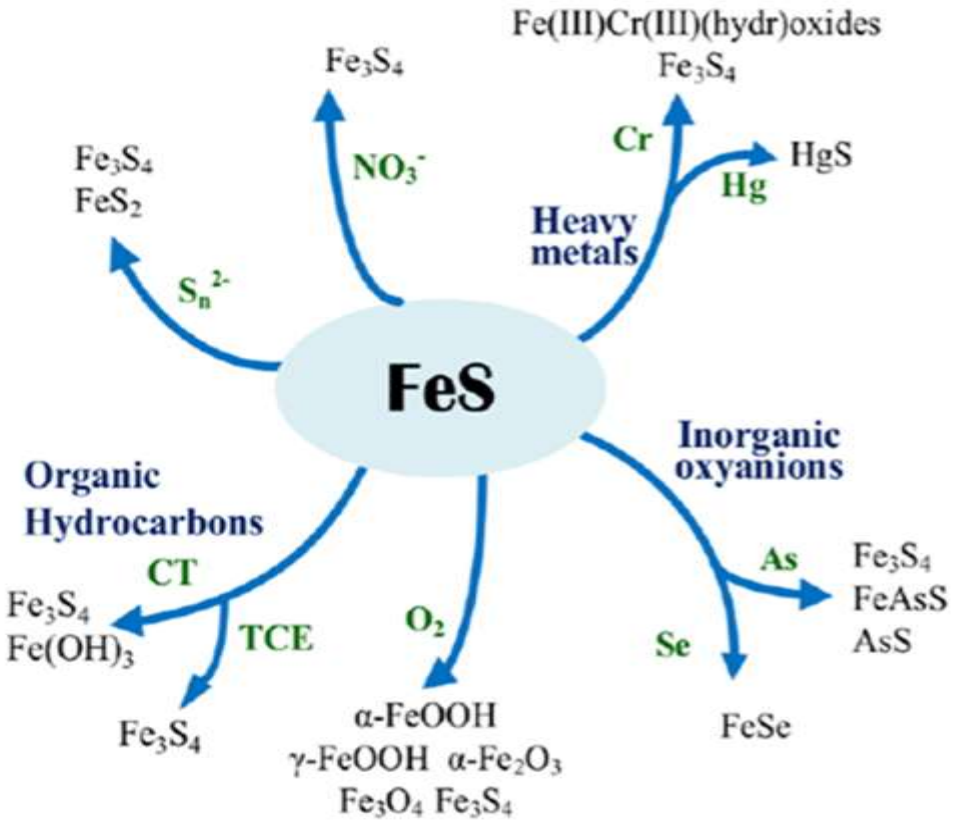
$$Fe^0(S) + 1/4\ SO_4^{2-} + 2H + \rightarrow 1/4\ FeS(S) + 3/4\ Fe^{2+} + 10\ H_2O$$

ZVI reacts with water to produce ferrous and H_2

$$Fe^0(S) + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^-$$

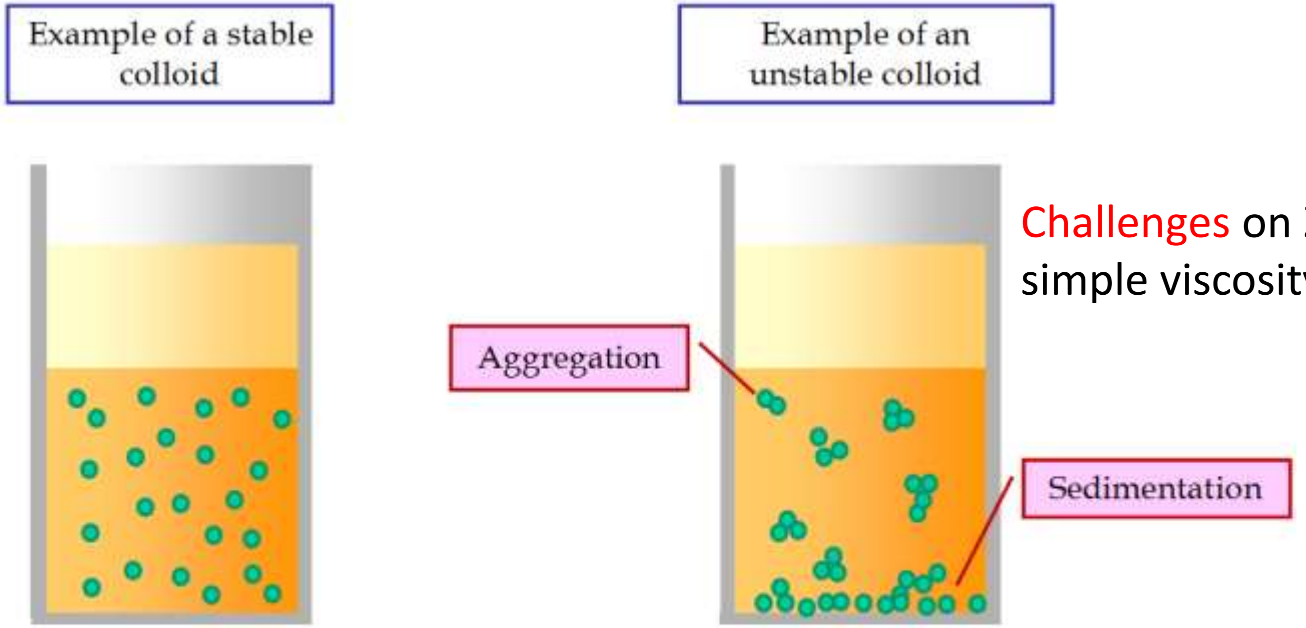
After which sulfate is reduced by H_2 to sulfide via microbially mediated reactions and forms iron sulfide precipitates

$$2Fe^{2+} + SO_4^{2-} + 4H_2 \rightarrow Fe\ S(S) + 4H_2O$$

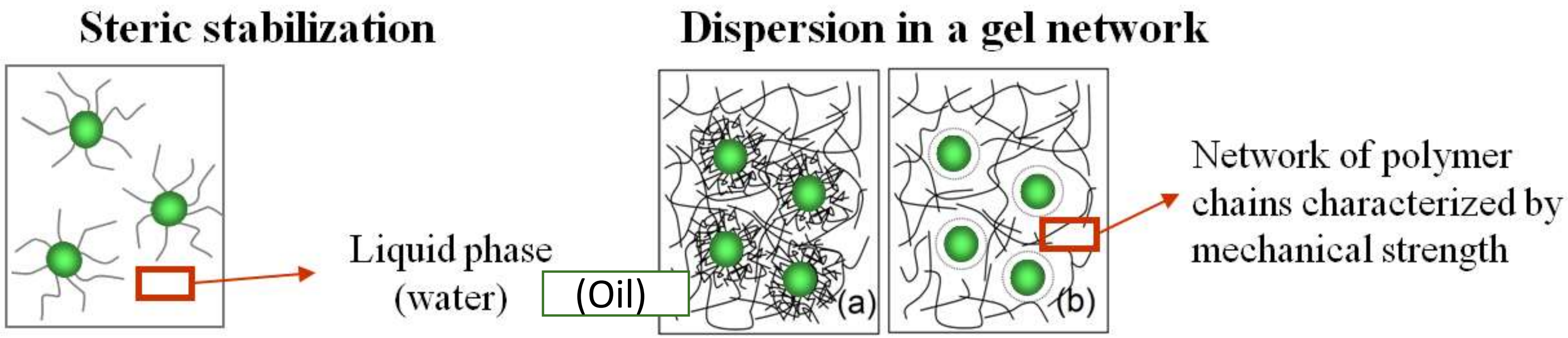


Revised from Lan, Ying, Ph.D. dissertation, University of Oklahoma, 2016.

Approaches



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



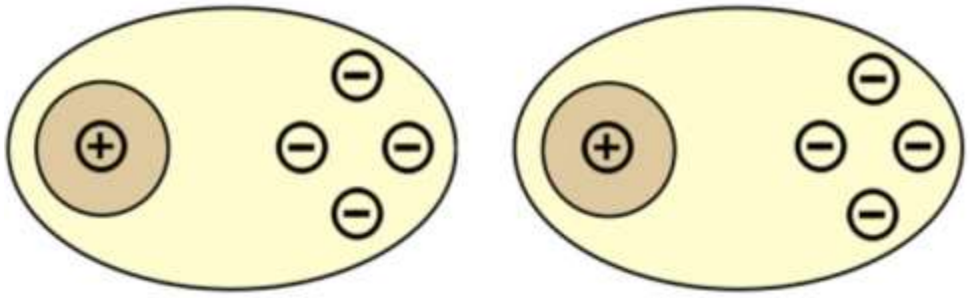
Solution: Increase steric repulsion between ZVI particles at the least increase in viscosity. Surfactant and oil thickener were used to increase positive buoyancy.

Dominant Forces in Dispersions

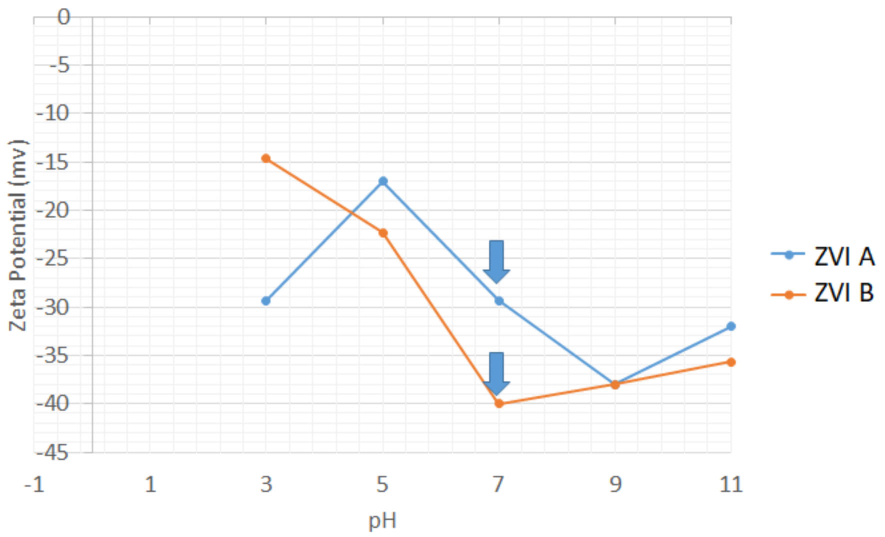
- Van der Waals attraction
- Electrical double layer repulsion or attraction
- Steric effects, mainly due to adsorbed polymers
- Solid's particle size, density and shape
- Liquid's viscosity and polarity

➢ "a suspension's stability is almost always improved by increasing the liquid's viscosity."

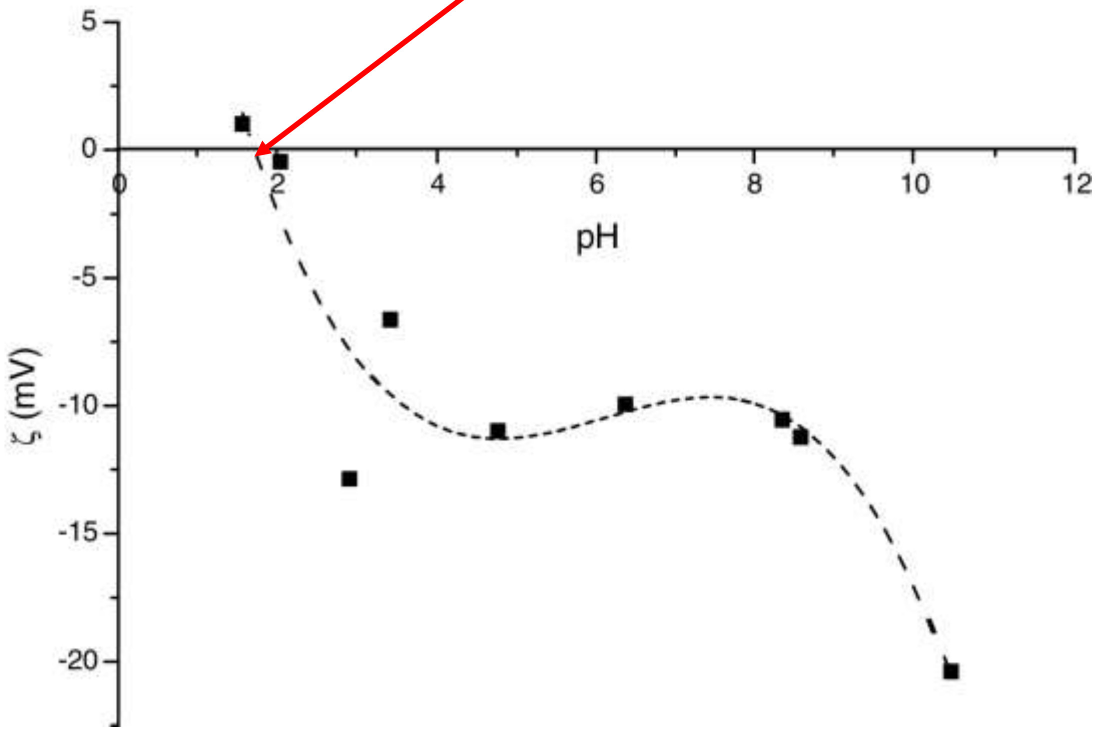
Attraction of Polarized Atoms



ZVI Zeta Potentials



Isoelectric point, pH at which a ZVI carries no net electrical charge



- At pH 7, *ζ = -30 mv & -40 mv*
- At high pH, ZVI experiences deprotonation (H^+)

Reference: Felipe Sombra dos Santos , Fernanda Rodrigues Lago, Lídia Yokoyama, Fabiana Valéria Fonseca. Synthesis and characterization of zero-valent iron nanoparticles supported on SBA-15. J Mater Res Technol. 2017; 6(2): 178–183

Microscale Zero-Valent Iron (mZVI) Suspensions

mZVI suspension in a shear thinning fluid

Field prepared mZVI suspension

Viscoelastic Gels
Single Biopolymer Solution (SBS)

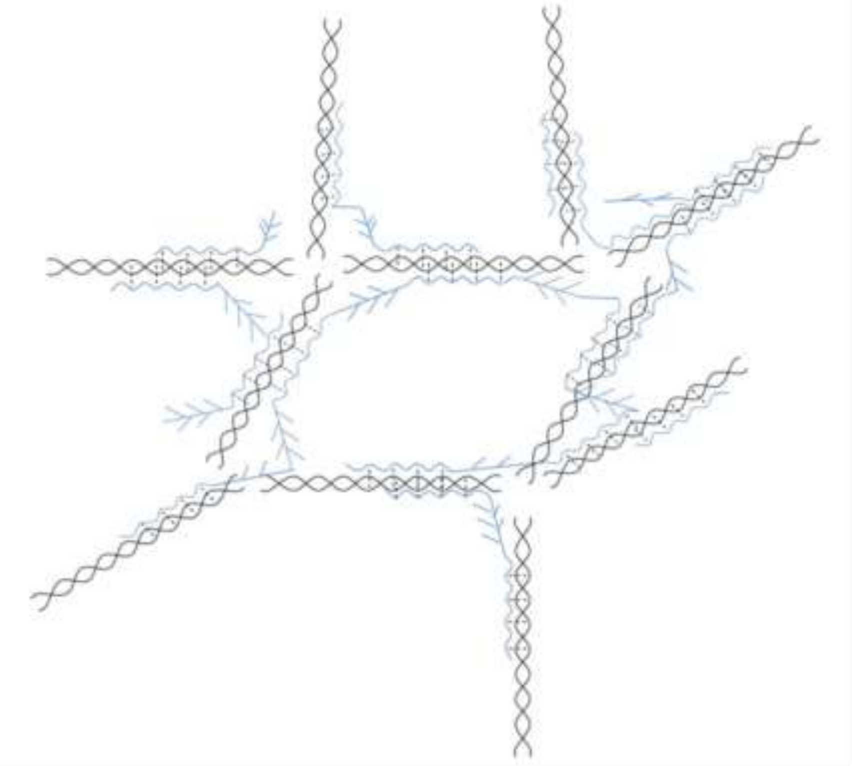
- ZVI dispersions with diluted SBS (XG or GG) are unable to prevent sedimentation of ZVI particles (J Nanopart Res (2012) 14:1239)
  - Unfavorable alignment
  - Weak interaction among molecules

- Adsorption affect
  - ZVI particles adsorb part of polymer to their surface
  - Decrease the viscosity of suspension
  - Reduces stability

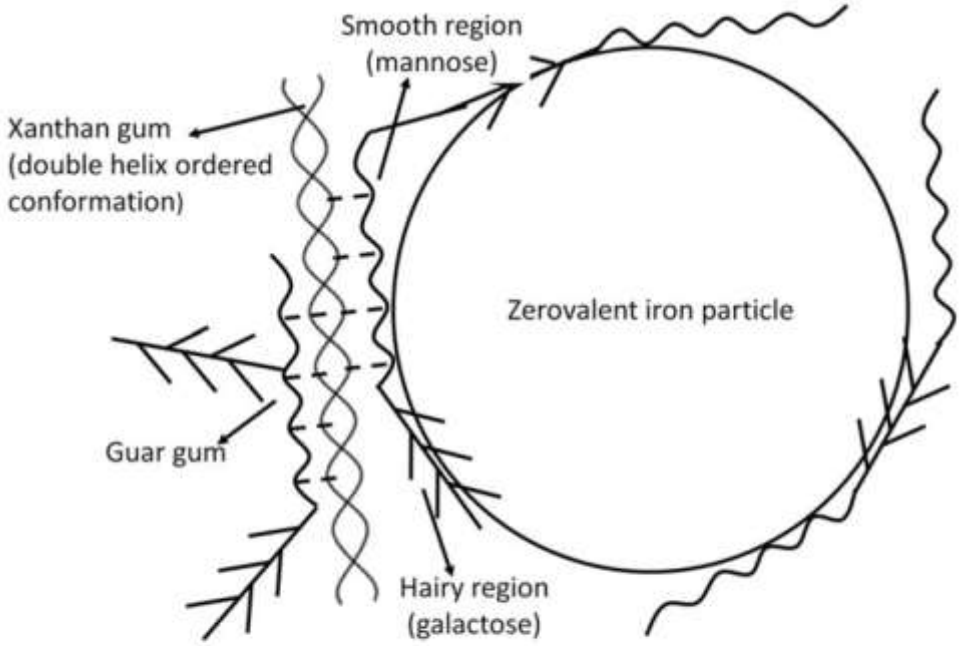
Reference: Dingqi Xue and Rajandrea Sethi. Viscoelastic gels of guar and xanthan gum mixtures provide long-term stabilization of iron micro- and nanoparticles. J Nanopart Res (2012) 14:1239

Biopolymer Mixture Solution (BMS)

Interaction between XG and GG molecules forms a continuous network structure

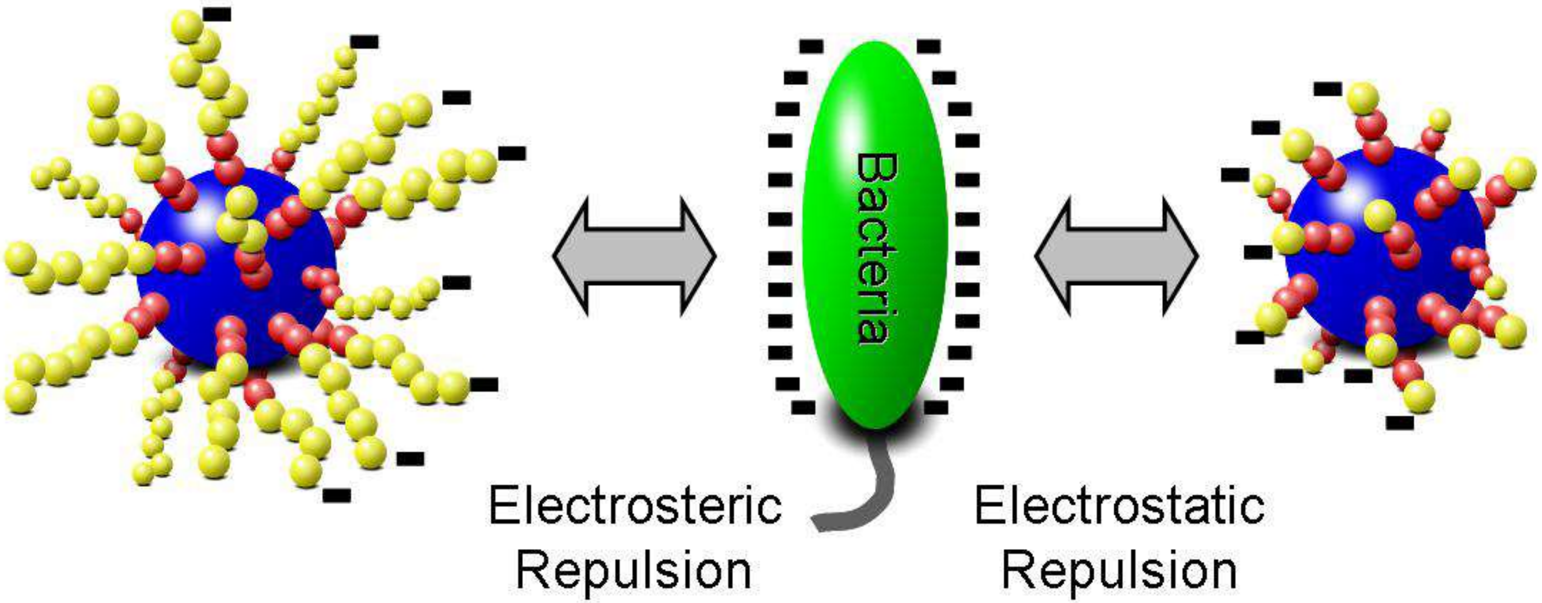


GG molecules are able to adsorb to the ZVI surface (Tiraferri et al. 2008)



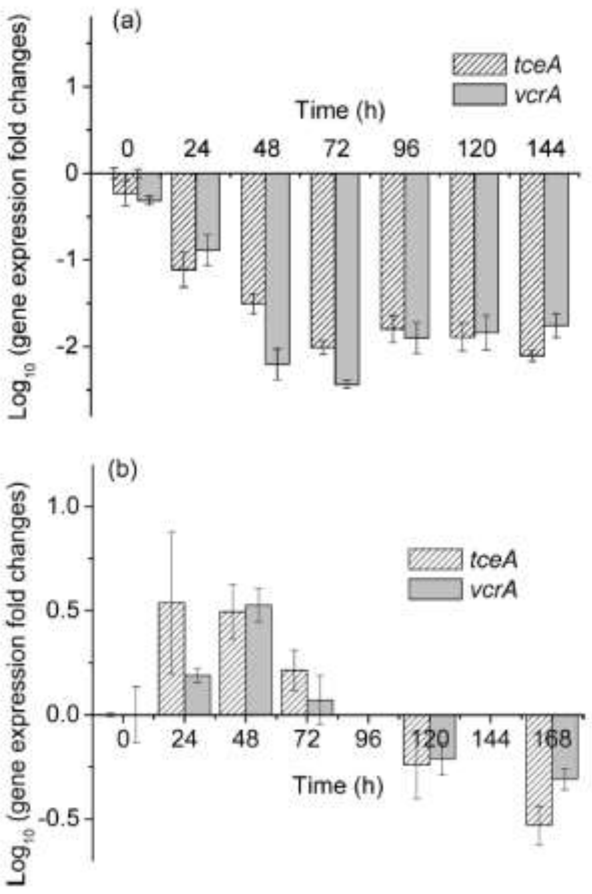
J Nanopart Res (2012) 14:1239

Polymer Coatings Mitigate nZVI Aggregation and Toxicity to Bacteria



Reference: Li Z., K. Greden, P.J.J. Alvarez, K.Gregory, and G.V. Lowry. Transformations of Nanomaterials in the Environment. *Environ. Sci. Technol.* 2012, 46, 13, 6893–6899

Relative tceA and vcrA expression after exposure to (a) bare NZVI and (b) coated NZVI (1 g NZVI/L)



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

- Enables Microbial Reductive Dechlorination

Reference: Zong-ming Xiu, Kelvin B. Gregory, Gregory V. Lowry, and Pedro J. J. Alvarez. Effect of Bare and Coated Nanoscale Zerovalent Iron on *tceA* and *vcrA* Gene Expression in *Dehalococcoides* spp. Environmental Science & Technology 2010 44 (19), 7647-7651

Typical Design

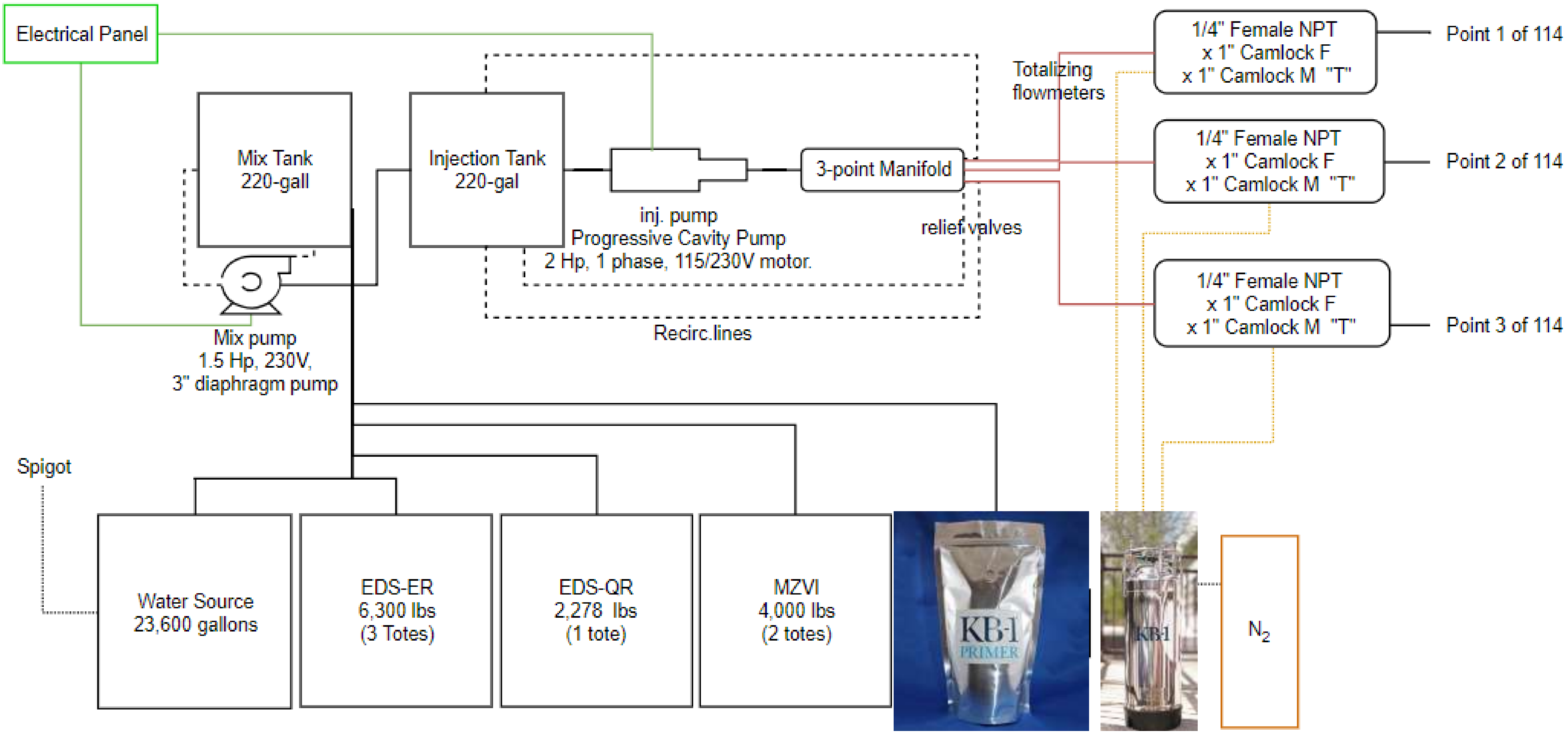
Suspension Preparation

- 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

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

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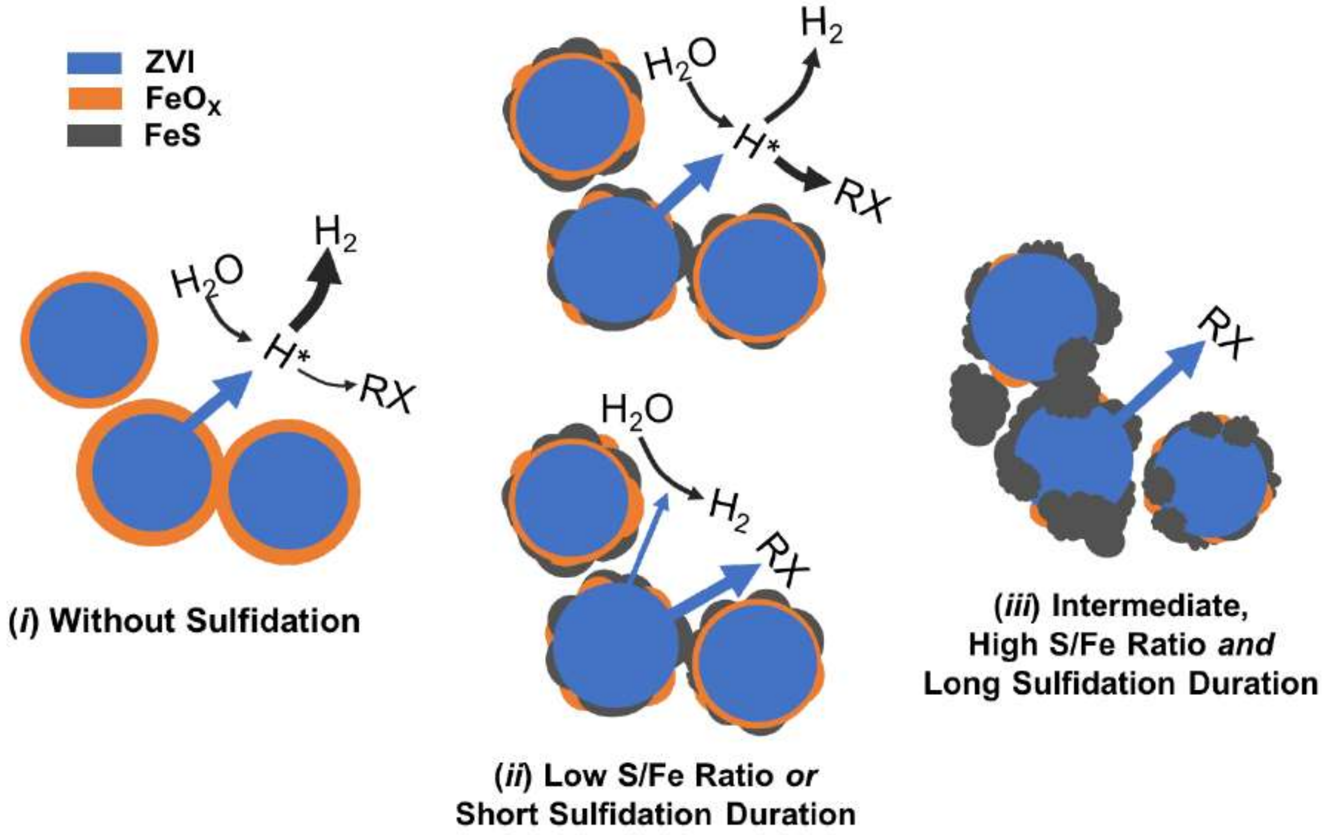
Mechanochemically Sulfidated Microscale Zero Valent Iron

Reference: Yawei Gu, Binbin Wang, Feng He, Miranda J. Bradley, and Paul G. Tratnyek. Mechanochemically Sulfidated Microscale Zero Valent Iron: Pathways, Kinetics, Mechanism, and Efficiency of Trichloroethylene Dechlorination. *Environmental Science & Technology* 2017 *51* (21), 12653-12662

Effects of Sulfidation



Reference: Dimin Fan, Ying Lan, Paul G. Tratnyek, Richard L. Johnson, Jan Filip, Denis M. O'Carroll, Ariel Nunez Garcia, and Abinash Agrawal. Sulfidation of Iron-Based Materials: A Review of Processes and Implications for Water Treatment and Remediation. Environmental Science & Technology 2017 51 (22), 13070-13085.

Iron Sulfide Reagent

ISR-Cl

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

FeS Biotic vs. Abiotic

Biotic

- Formed *in situ* by sulfate reducing microorganisms
- Must create and maintain chemical and physical ecosystem
- Requires phosphate as nutrient

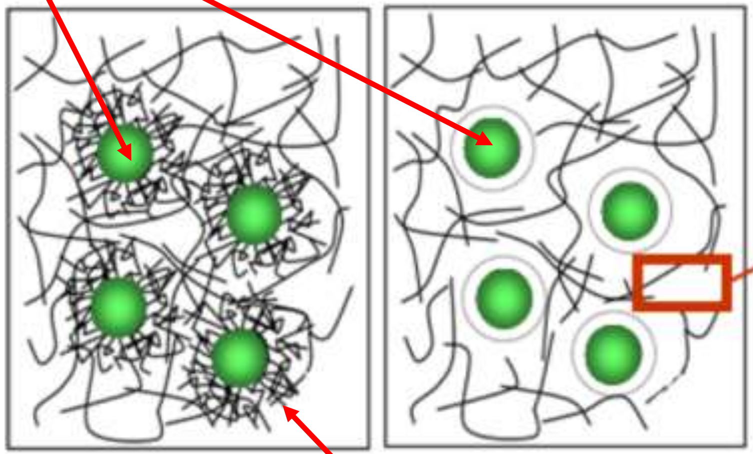
Abiotic (ISR-Cl)

- Manufactured / formulated to a specification in a chemical reactor and delivered to site
- Transformation of FeS to Fe_3S_4 is generally faster

Packaging

Method and a Chemical Composition for Accelerated In Situ Biochemical Remediation, US 11,123,779 B2

Ferrous sulfide and zero-valent metal particles



Network of polymer chains in aqueous solution

Vegetable oil, an oil thickening agent, and a surfactant forming suspension networks

The United States of America

The Director of the United States Patent and Trademark Office

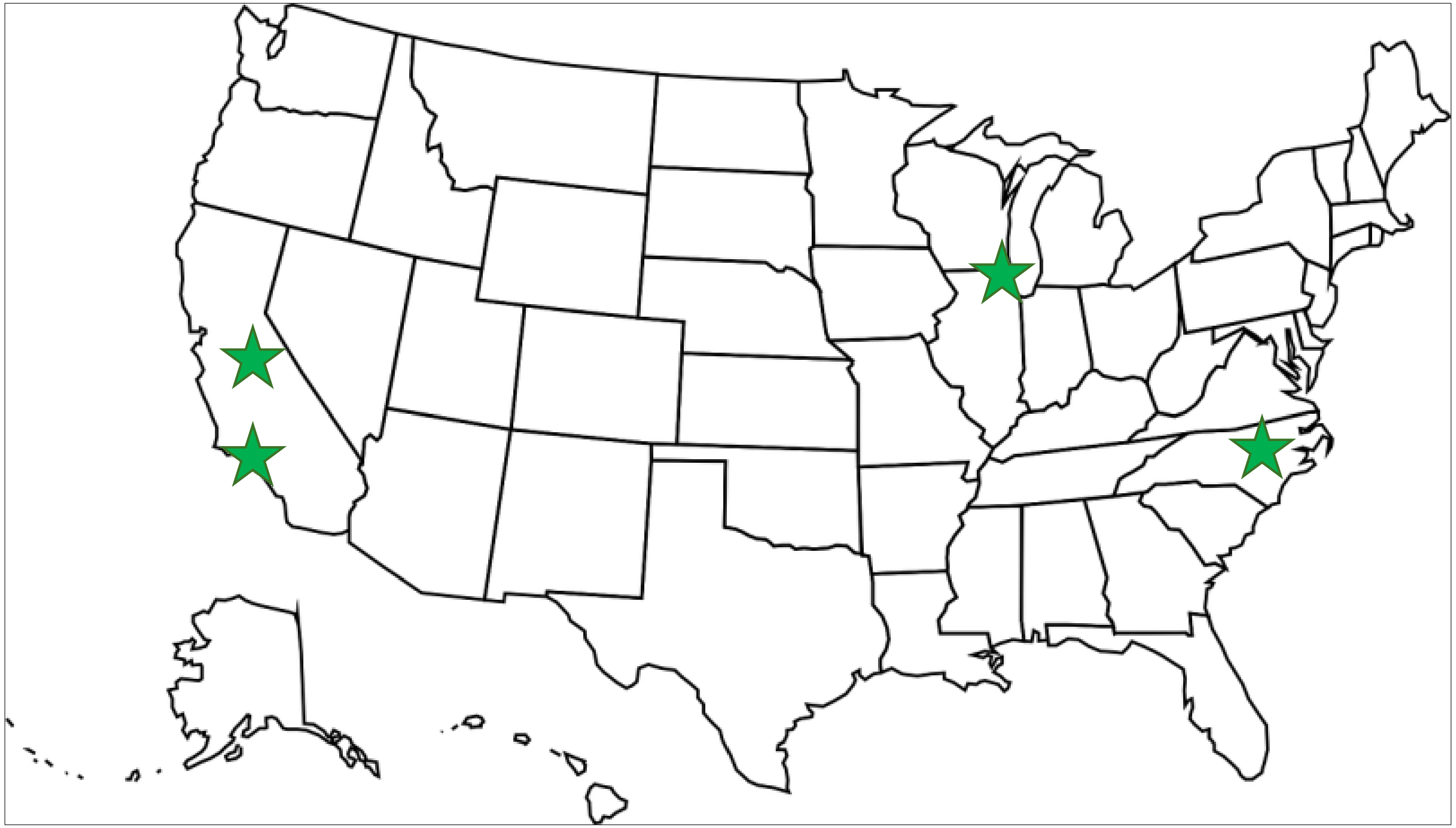
Has received an application for a patent for a new and useful invention. The title and description of the invention are enclosed. The requirements of law have been complied with, and it has been determined that a patent on the invention shall be granted under the law.

Therefore, this

United States Patent

Grants to the person(s) having title to this patent the right to exclude others from making, using, offering for sale, or selling the invention throughout the United States of America or importing the invention into the United States of America, and if the invention is a process, of the right to exclude others from using, offering for sale or selling throughout the United States of America, or importing into the United States of America, products made by that process, for the term set forth in 35 U.S.C. 154(a)(2) or (c)(1), subject to the payment of maintenance fees as provided by 35 U.S.C. 41(b). See the Maintenance Fee Notice on the inside of the cover.

Distribution Centers



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PRODUCTS AND SERVICES

ISCO

Modulated TersOx™ Liquid
Activated and Controlled Exothermic (ACE)

AEROBIC BIOREMEDIATION

TersOx™ Family of Products

ELECTRON ACCEPTORS FOR ANAEROBIC BIOREMEDIATION

Sulfate Enhanced *In Situ* Remediation of Petroleum Hydrocarbons using *Nuristulfate®* and *NutriBind®*

ELECTRON DONORS

Enhanced Anaerobic Bioremediation of Chlorinated Solvents

ZVI AND ISCR

ZVI Powders, mZVI, & ISR-Cl

NAPL REMEDIATION

Tersus Advanced Surface Kinetics (TASK™)
Liberates NAPL and captures them with enhanced recovery techniques

EQUIPMENT

Subsurface Delivery Systems
Additive injection and groundwater recirculation trailers available for short- or long-term leases

PERFORMANCE MONITORING

Compound Specific Isotope Analysis (CSIA) and Molecular Diagnostic Tools (MDT)

TECHNICAL SUPPORT

Professional technical services

Thank you

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