How to Choose the Appropriate Amendments for Your Chlorinated Solvent Sites

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



Agenda

Contaminant Type

Chlorinated methanes, ethanes, and ethenes



02

Bioremediation

Biostimulation with Electron donor and Bioaugmentation with organohaliderespiring bacteria



ISCR Enhanced

Geochemically enhanced biostimulation with FeS (replicating true geochemical reactions)

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03

Geochemically enhanced biostimulation with ZVI (most widely used remediation amendment

How quickly do you need to close your site?





What is needed for enhanced reductive dechlorination?

Vegetable oils ferment to acetic acid and hydrogen

Soybean Fatty Acid Distribution

 $\begin{array}{c}
0\\
H_2C - O - C - Ri\\
0\\
H_2C - O - C - Ri\\
0\\
H_2C - O - C - Ri\\
H_2C - Ri
\end{array}$

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 %





Vegetable Oil Fermentation

Two step process

1. Long-chain fatty acids are hydrolyzed



2. Beta-oxidation



Fatty Acid Oxidation



Multiple step metabolic process

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

- Removes two carbons from the chain
- Releases:
 - Four hydrogen atoms (H)
 - Acetic Acid (C₂H₄O₂)

Distribution of the Correct Type of Fatty Acids is Essential

Acetate

Hydrogen (H₂)

Rapid consumption

Produced from linolenic acid, propionate, butyrate, etc.

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

- 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)

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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





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

Derrun Kaya, 128,800 Birthe V, Kjellerup,⁷ Karuna Chourey,^{2,0} Robert L, Hettich,²⁴⁰ Dora M, Taggart,⁷⁷ and Frank E. Löffler^{10,1,1,2,0,0}

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Department of Civil and Environmental Engineering, University of Maryland College Park, College Park, Maryland 20742, United

"Microbial Insights, Inc., Knowelle, Tennessee 37932, United States

Supporting Information

ABSTRACT: Bustanulation to promote reductive daublostnation is widely Busagrountation with Detablocaccoides of practiced, but the value of adding an enogeneous nitrogen (N) sensue (e.g. NH,") during instruct is unclear. This ready investigates the effect of NH," analability on organoitalide cospiting Deballococcesion security (Die) growth and reductive decklorination in antichment cultures derived from groundwater (PW4) and tiver sedanters (TC) impacted with chlorinatud observes. In PW4 cultures, the addition of NH," increased or 1.2-dichlocortheae (cDCE) to othere decklosingtion rates about 5-564 (20.6 \pm 1.6 versus 3.8 \pm 0.5 μM CT $J^{4}\lambda$ and the total randwo of Dis. 165 (BNA game copus wore alreat 615-626 logitor in socialization. "Beautimeters with NR4," ((1.8 ± 0.8) × 10° mL⁻¹) compared to increduction without NR4," ((1.8 ± 0.8) × 10° mL⁻¹), to Contrare, NR4," (4.1 ± 0.8) × 10° mL⁻¹). To Contrare, NR4, "



publication phase

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INTRODUCTION

Groundwater agailers are often oligatoophic and cannot ventues lagbrate reductive decidormation destrable at sties contaminated with chlorinated solvents.1-1 Enhanced murinc bioremulation at stics impacted with chlorouted ethrelies on bootendation with fermintable substrates to men hydrogen flan.⁹⁻⁴ Hydrogen is the key electron donor organoloside-rospiting Debalococcellos recortis (Dhc) stra capable of dechlorization to entronesentally bonign effort In sits growth of Div in rangeous to biostimulation w ferminable inherator has been documented.⁸⁻¹¹ however, ducline in dechloritation rates and incontribut reductive dechlastration it vive that receive sufficient electron donor is a common challenge to meet nemedial goals.^{12,12} While hydrogen and chlavingted otherate meet Dic's margy require

ACS Publications - + Hit Instance Denot Ione

ment and acetate generated in fermentation reactions serves as a carbon searce, fixed retregen (N) availability may limit Die greach and metactive deditorination activity.

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Nutrients

- Biostimulation benefits from adding an exogenous nitrogen (N) source (e.g., NH_4^+)
- Addition of addition of NH₄⁺ increased cis-1,2dichloroethene (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



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 B₁₂



- Dehalococcoides mccartyi strains require vitamin B₁₂ (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. <u>http://dx.doi.org/10.1098/rstb.2012.0320</u>





The Process of Making 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

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Alkaline Groundwater

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Bench test to liquify viscous material

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

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Anaerobic Bioremediation Deploying Electron Donor Via In Situ Alcoholysis





Activator Options

• Homogeneous Alkaline Catalyst • Alkyl oxides (RO–)

• Heat

- \odot Steam hydrolysis
- \odot Electrical resistance heating
- $\ensuremath{\circ}$ Thermal conduction heating
- \odot Gas thermal heating
- \odot Residual heat from an in-situ thermal remediation project
- Biocatalyst
 - \circ 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

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

ZVI reacts with water to produce ferrous and H₂

 $Fe^{0}(S) + 2H_{2}O \rightarrow Fe^{2+} + H_{2} + 2OH^{-}$

After which sulfate is reduced by H₂ to sulfide via microbially mediated reactions and forms iron sulfide precipitates

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





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Approaches

Sedimentation

Example of a stable colloid





Example of an

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

Steric stabilization

Liquid phase

(water)



Dispersion in a gel network



 Network of polymer
 chains characterized by mechanical strength



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

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- 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 <u>almost always improved</u> by increasing the liquid's viscosity."

Attraction of Polarized Atoms

ZVI Zeta Potentials



- 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)



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



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-CI

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

Abiotic (ISR-CI)

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

- Manufactured / formulated to a specification in a chemical reactor and delivered to site
- Transformation of FeS to Fe₃S₄ is generally faster









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



Network of polymer Chains in aqueous solution

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



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Enhanced Anaerobic Bioremediation of Chlorinated Solvents

ELECTRON ACCEPTORS FOR

ANAEROBIC BIOREMEDIATION

AEROBIC BIOREMEDIATION

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

Thank you

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