ZVI Amendments for In-Situ Chemical and Biological Reduction

Tersus Environmental

Presented by David Alden, P.E.

Friday, May 1, 2020

CHAPTER 10

IN SITU CHEMICAL REDUCTION FOR SOURCE REMEDIATION

Paul G. **Tratnyek**,[1] Richard L. **Johnson**,[1] Gregory V. **Lowry**[2] and Richard A. **Brown**[3]

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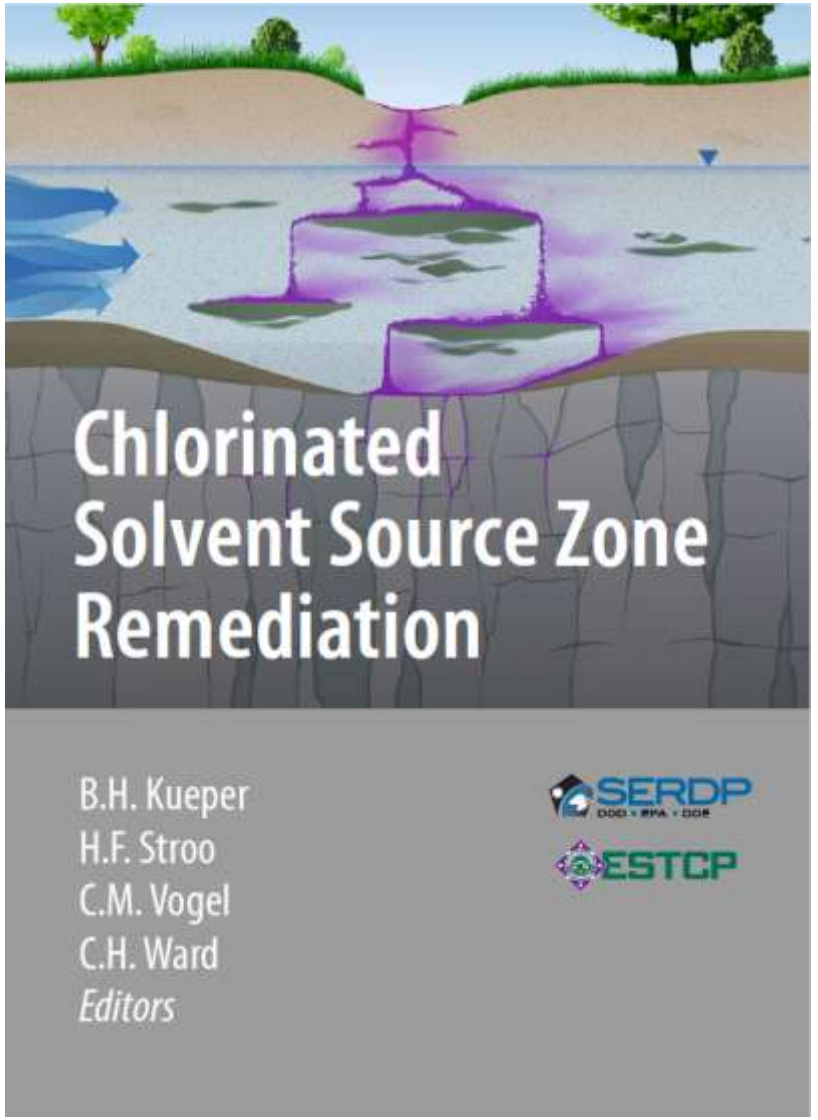
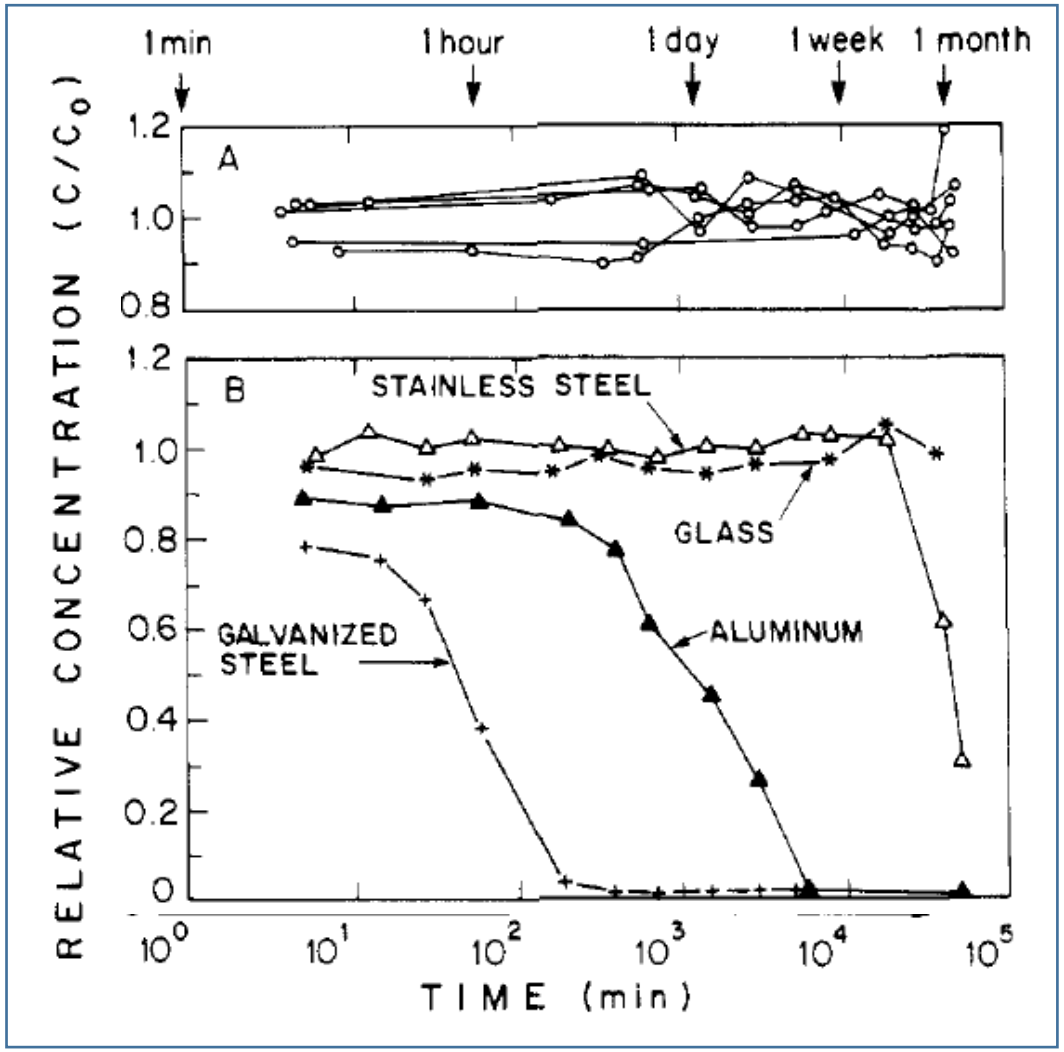
[2]Carnegie Mellon University, Pittsburgh, PA 15213, USA;
[3]Environmental Resources Management, Ewing, NJ 08618, USA



Environ. Sci. Technol. **1990**, *24*, 135–142

Sampling Bias Caused by Materials Used To Monitor Halocarbons in Groundwater

Glenn W. Reynolds,† John T. Hoff,* and Robert W. Gillham



Relative concentration of bromoform, C/C_0, versus time

Dr. Gillham

Waterloo Centre for Groundwater Research and Department of Earth Sciences, University of Waterloo, Waterloo, Ontario, Canada, N2L 3G1

Agenda

ZVI Amendments for In-Situ Chemical and Biological Reduction

ISCR Concept 01

02 PRBs

Types of ZVI-based products 03

04 Design and Case Studies

01 ISCR Concept

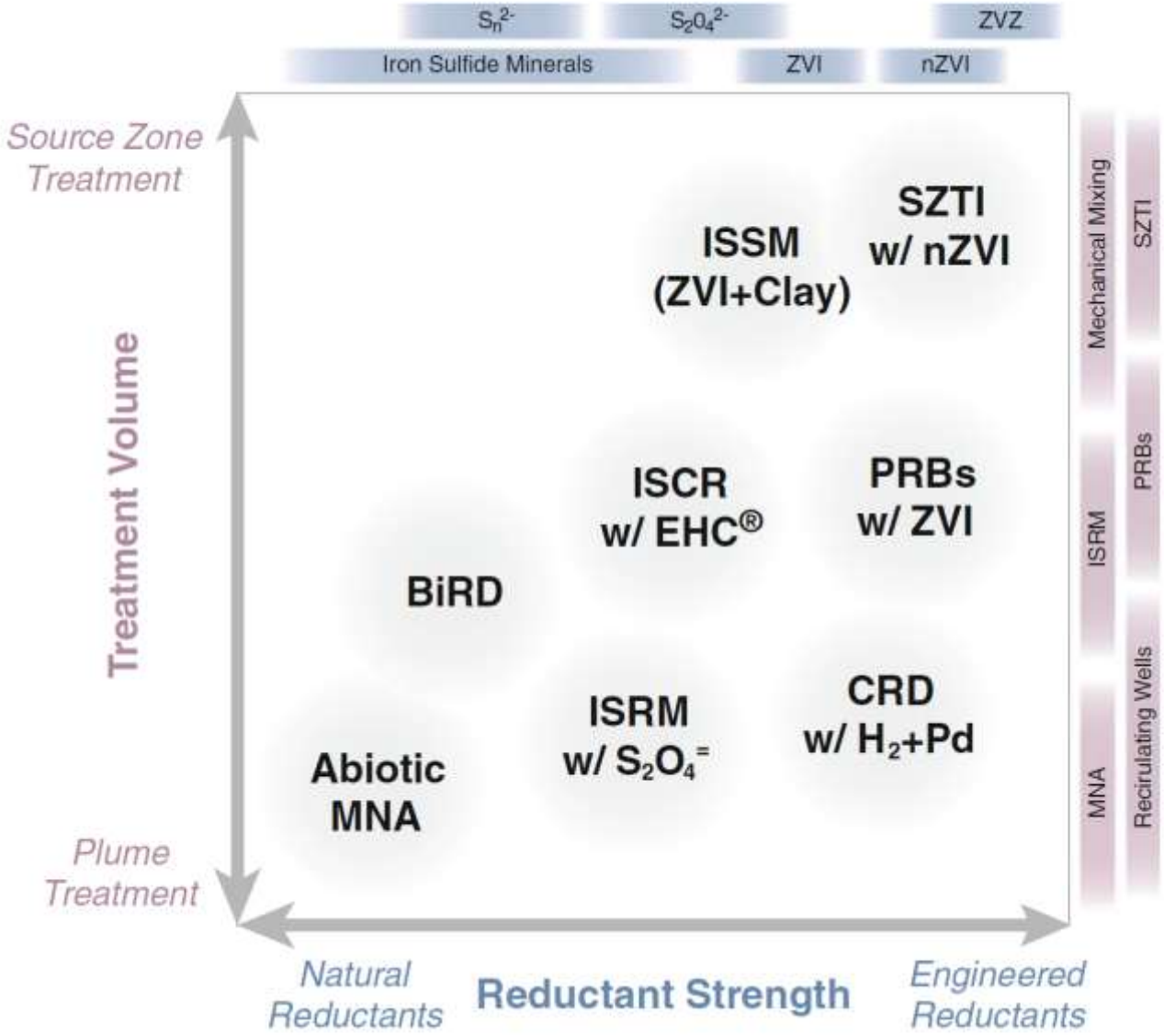
Necessary reducing conditions (ISCR)

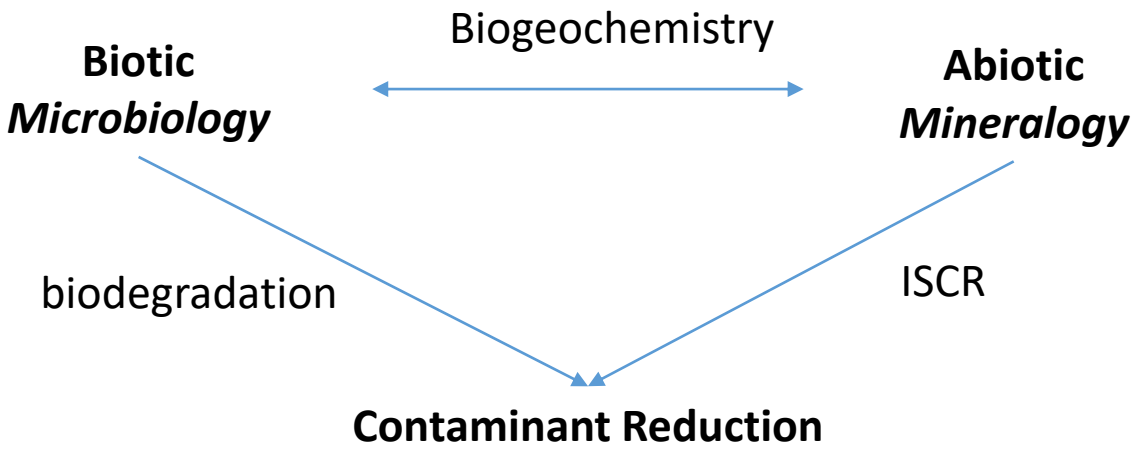
intrinsic biogeochemical processes

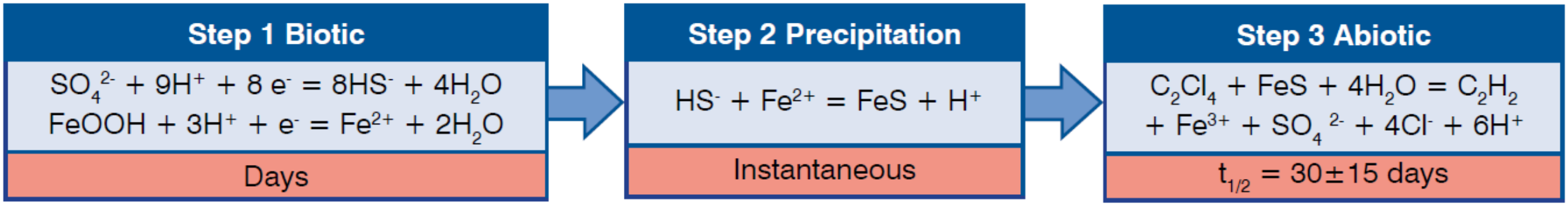
biostimulation

strong chemical reductant

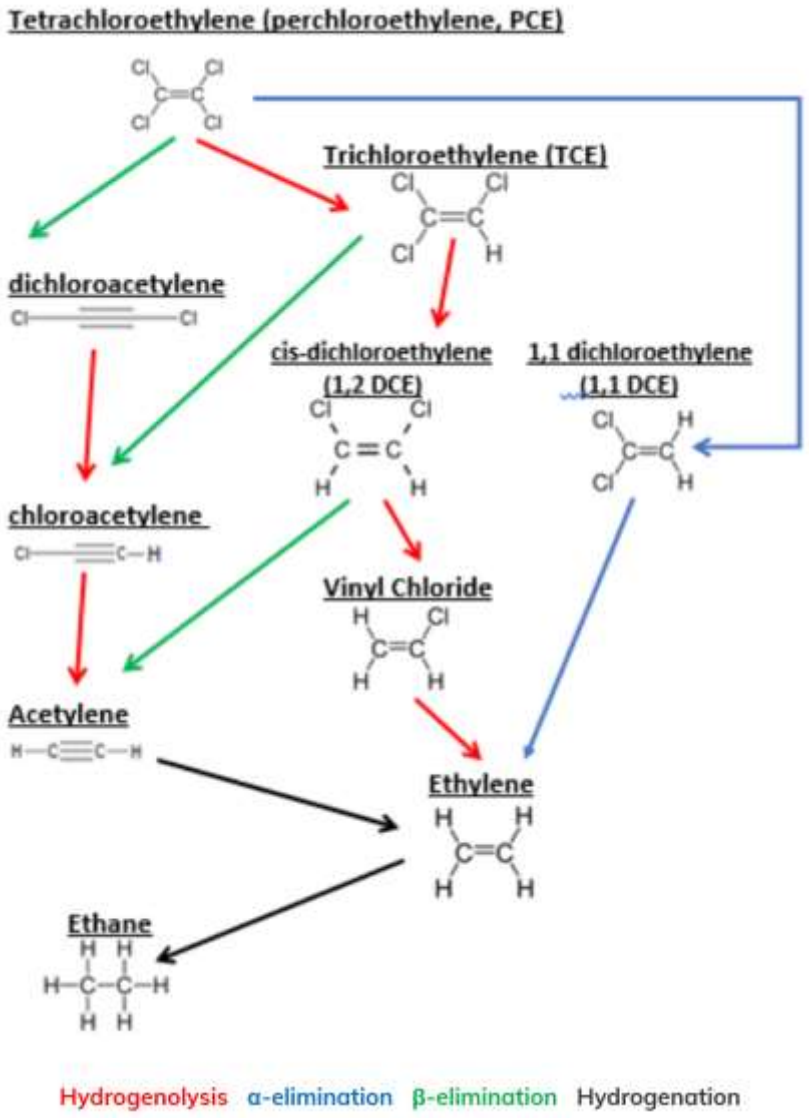
Source: ITRC 2011

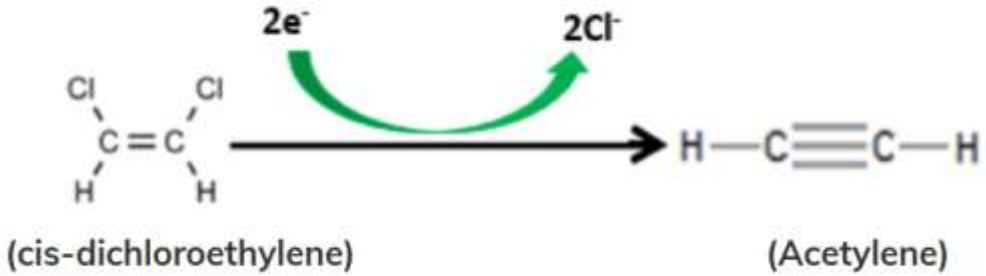


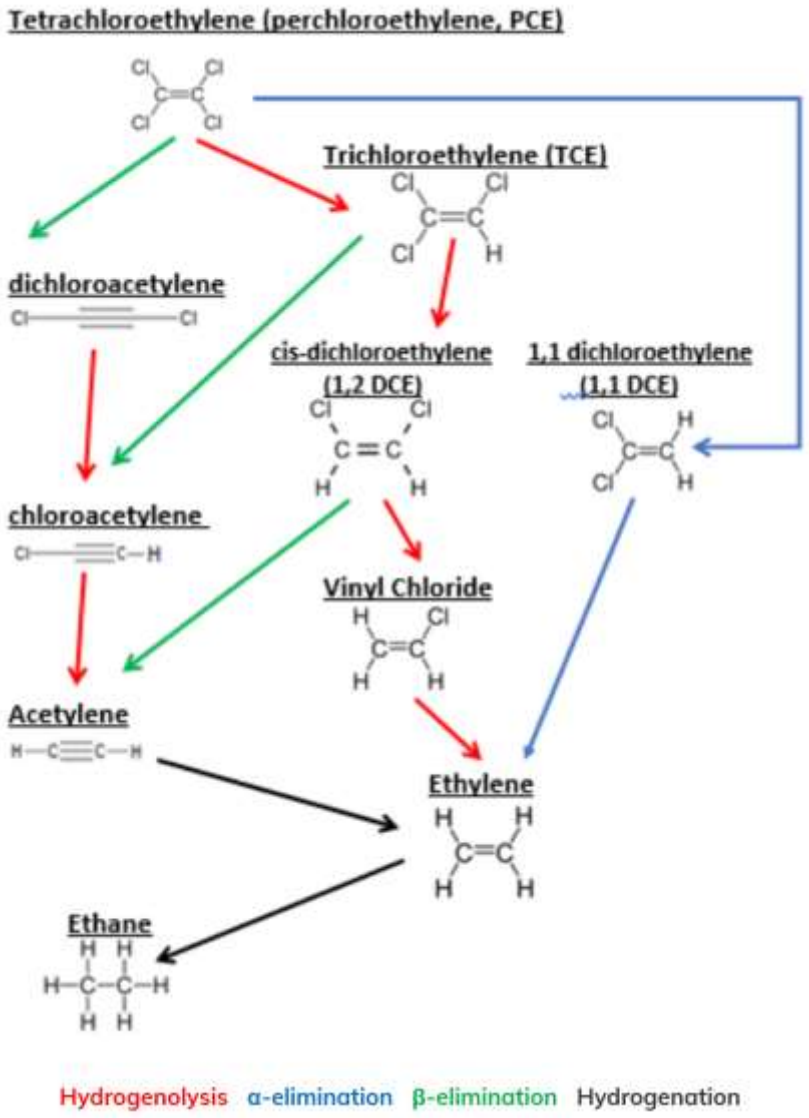


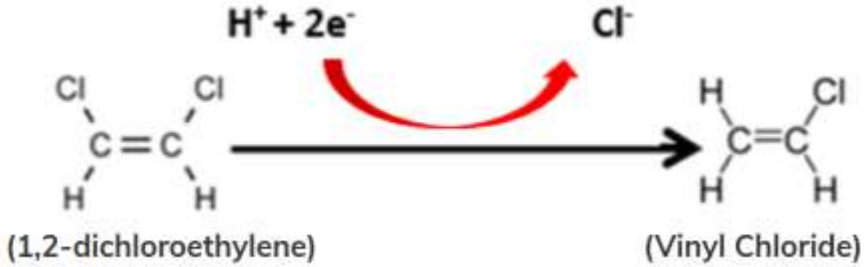


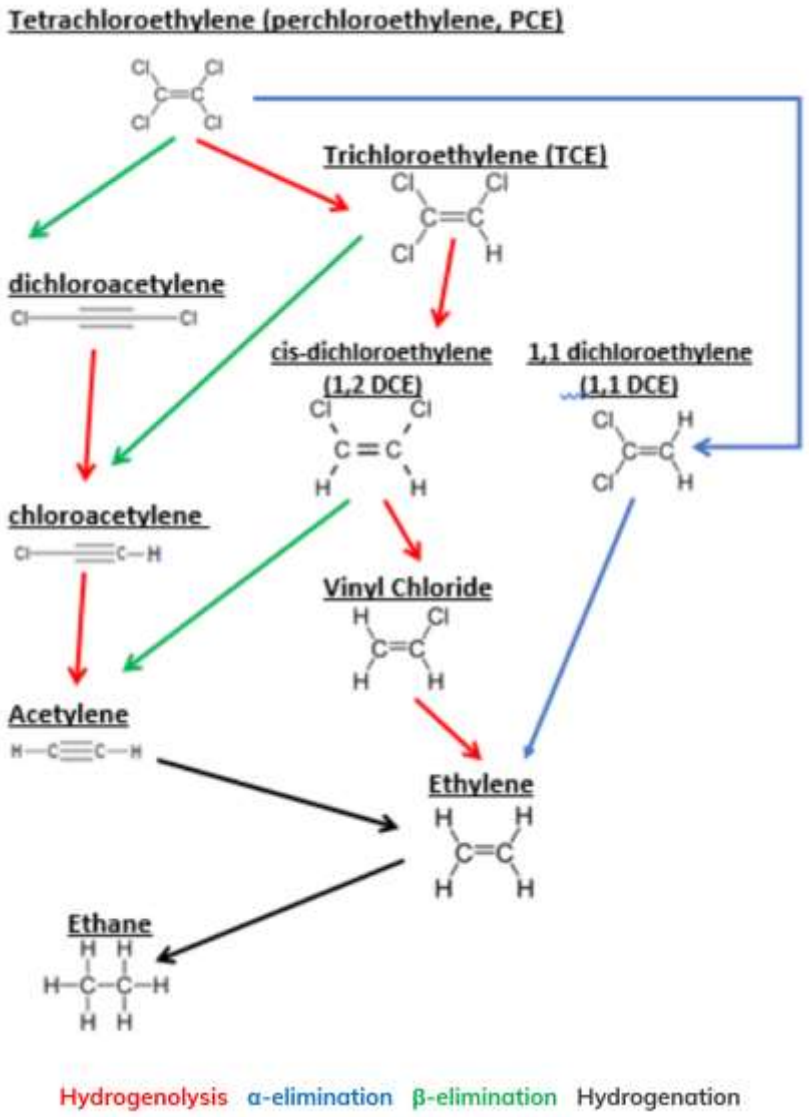
Source: NAVFAC Fact Sheet ISBGT

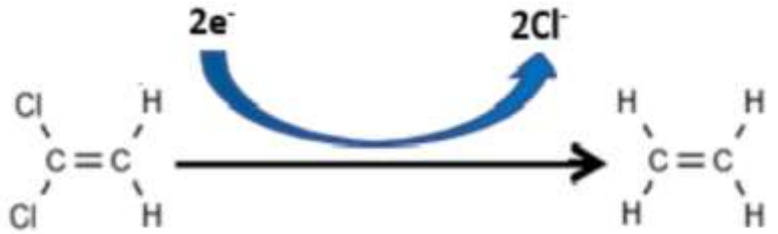




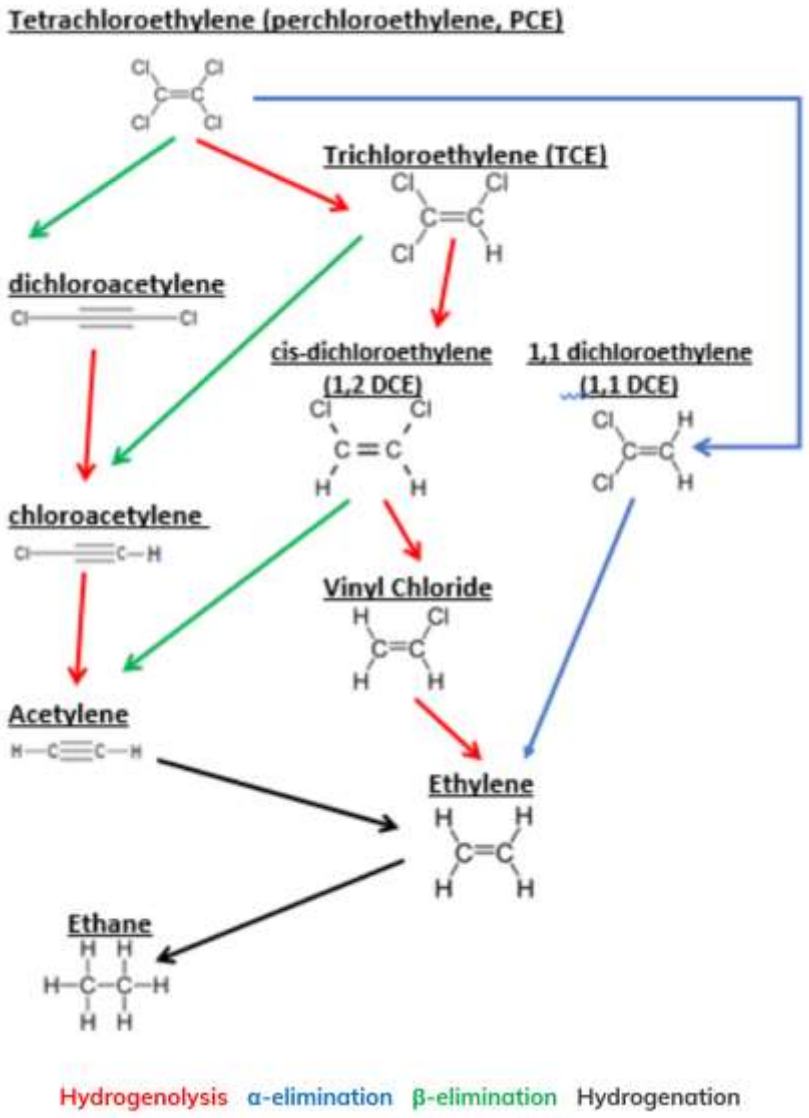


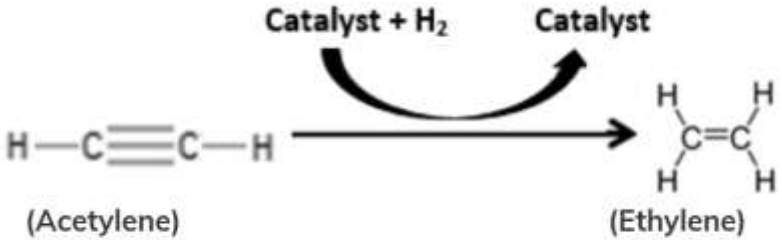




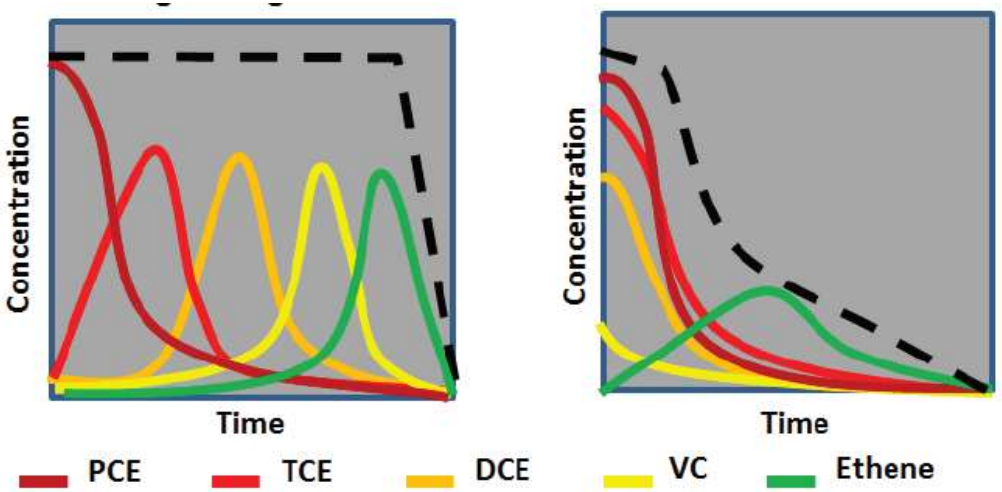


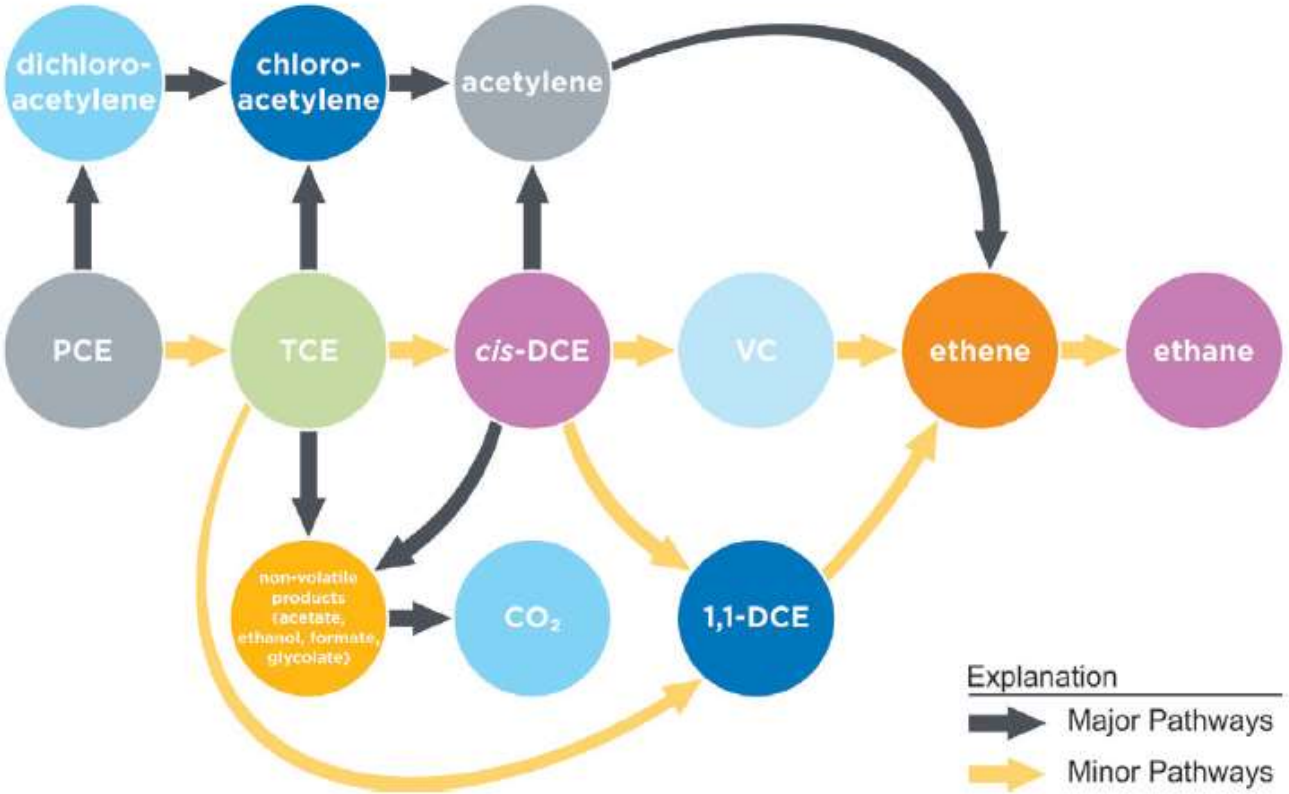
1,1, DCE **Ethylene**





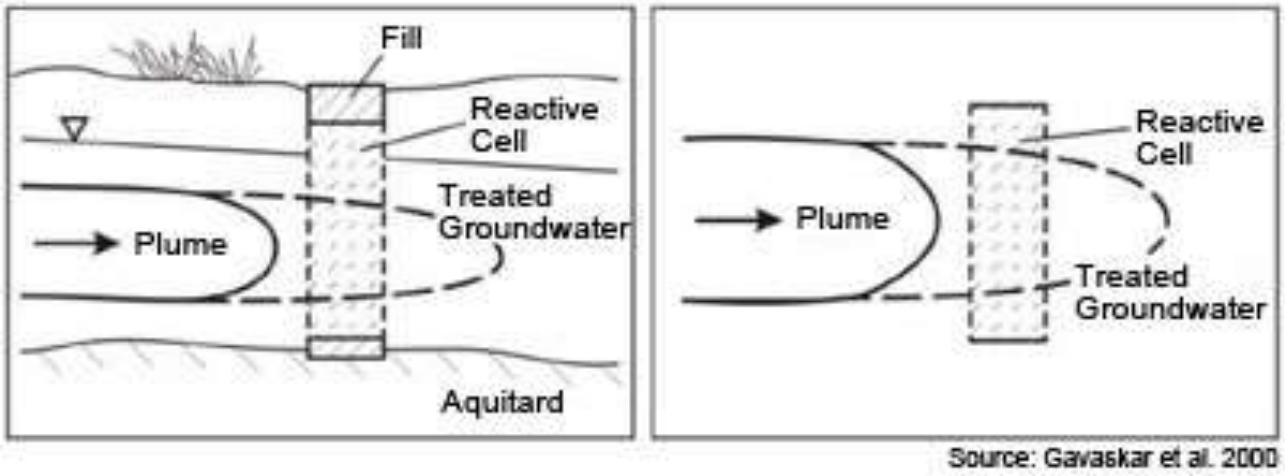
Chlorinated Ethene Abiotic Transformation Pathways





Source: NAVFAC Fact Sheet ISBGT

02 PRBs



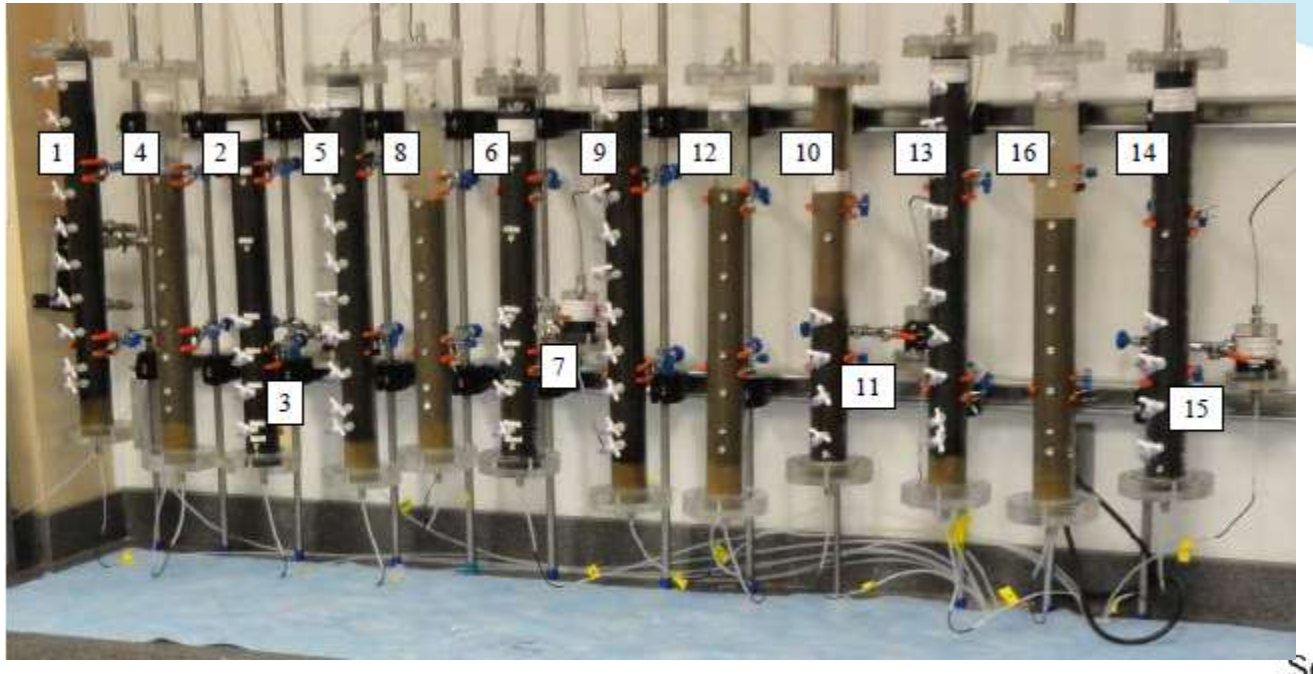
Source: Gavaskar et al. 2000

1. **Site delineation and characterization**
   a. **Are contaminants amenable to ISCR?**
   - Solvents
   - Metal oxyanions
   - Non-metal inorganics such as perchlorate

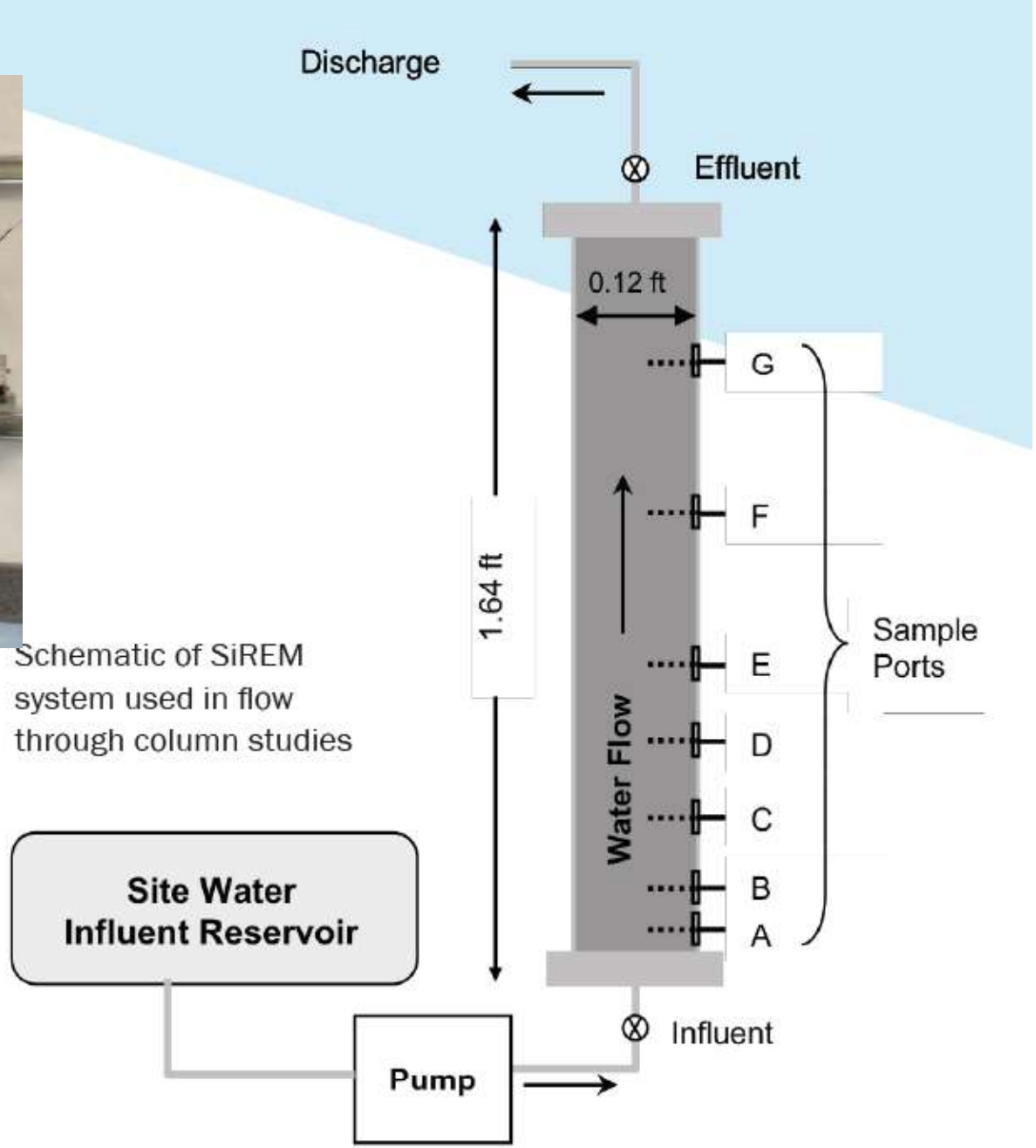
   b. **Site Conditions**
   - Size
   - natural reductant demand (NRD)
     pH, Carbonate, TEAPs, ORP

2. **Technology assessment**
   a. Treatment goal
   b. Time needed to treat
   c. Preliminary Cost

3. **Design and implementation**



Schematic of SiREM system used in flow through column studies



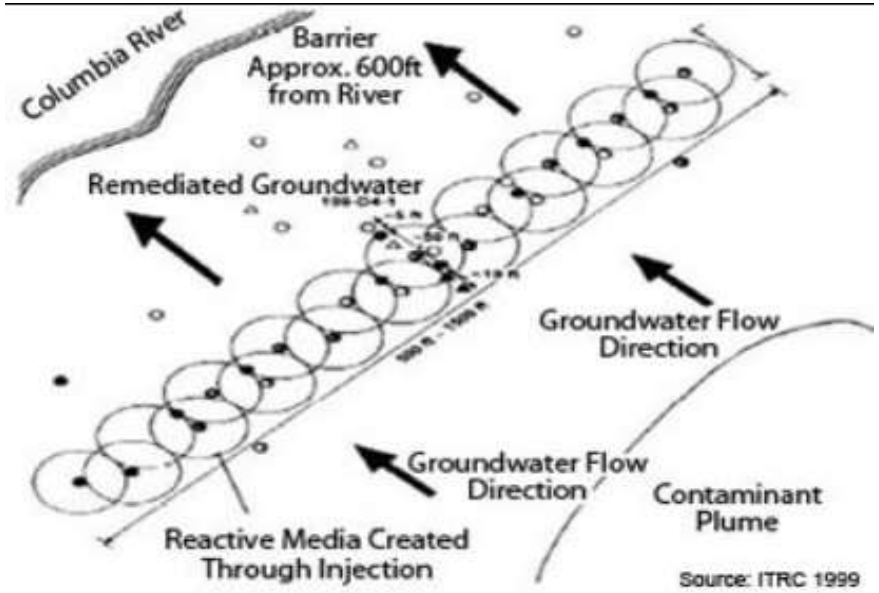


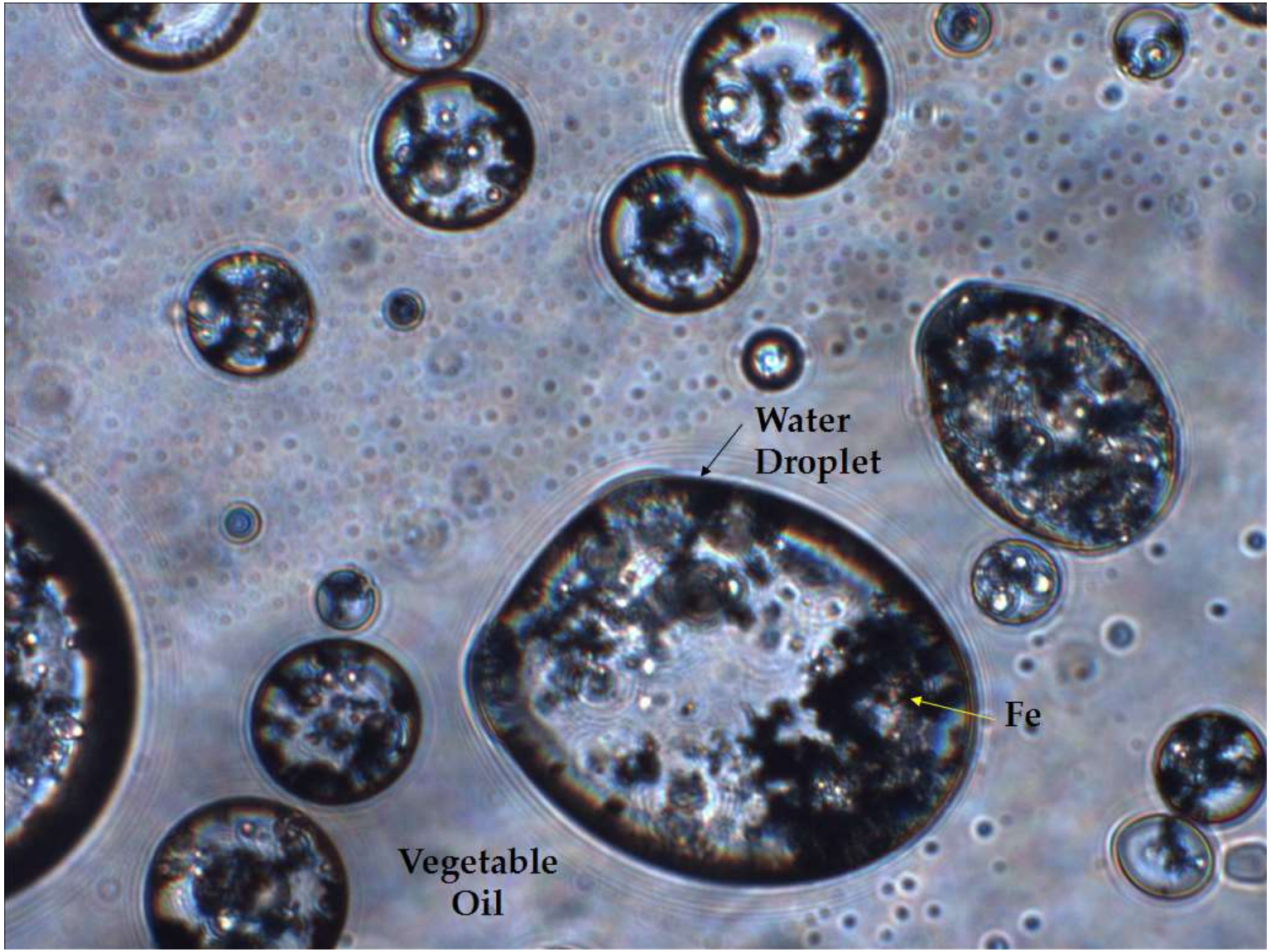
Photo: Dewind One-Pass Trenching

03 Types of ZVI-based products

EZVI

Suzanne O'Hara, Thomas Krug, GeoSyntec Consultants;
Cherie Geiger, Christian Clausen, University of Central Florida;
Jacqueline Quinn, NASA.

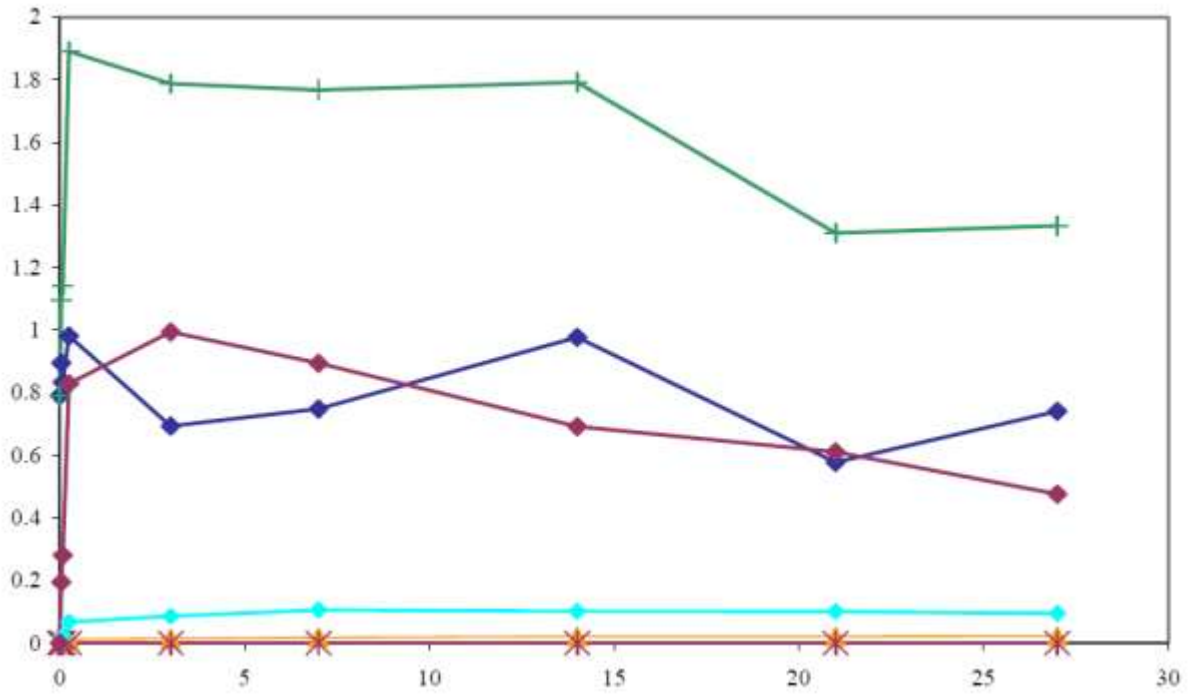
EZVI



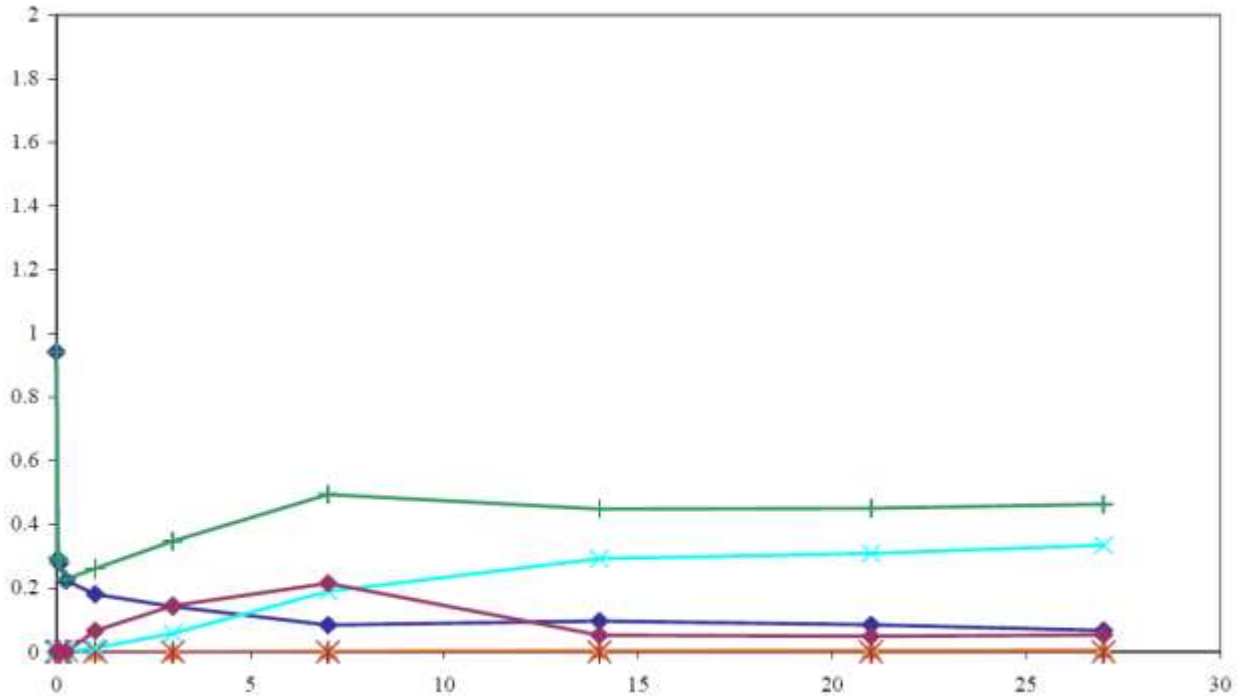
EZVI

EZVI

EZVI



ZVI and KB-1 - DNAPL



eZVI and KB-1 - DNAPL

TCE cis-1,2-DCE VC Ethene Ethane total ethene+ethane

O'Hara et al. EZVI

EZVI

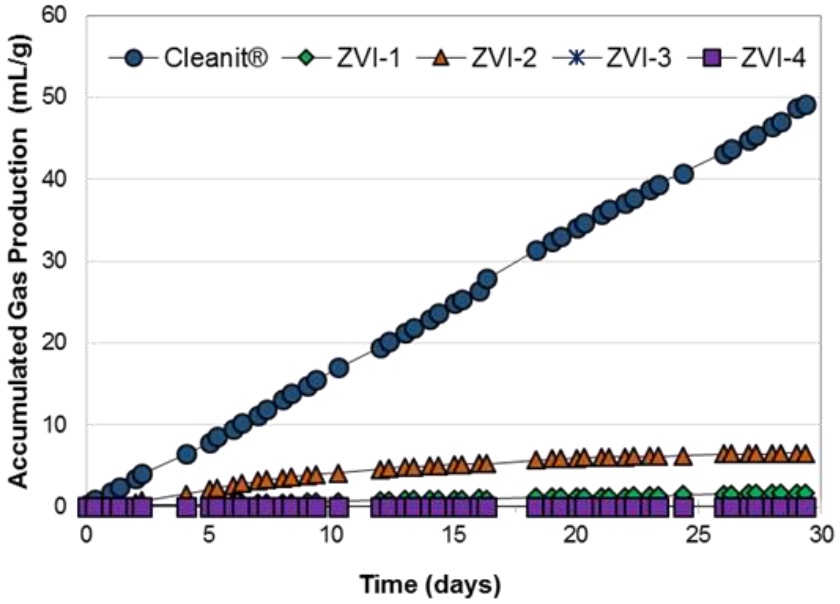
Launch Complex 34 in Cape Canaveral Air Force Station Florida Innovative Technology Evaluation Report

EPA Field Innovative Technology Report. Sept. 2004

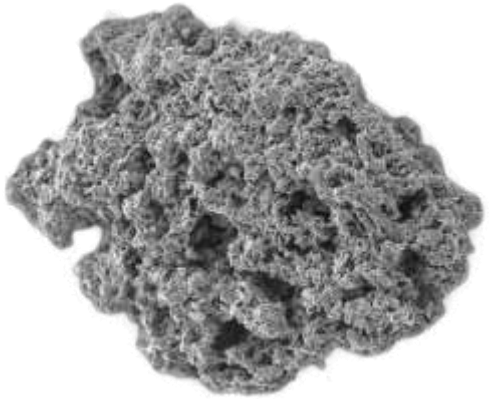
eZVI PCE/TCE DNAPL Site 45, South Carolina

ESTCP Cost and Performance Report Sept. 2010

ZVI

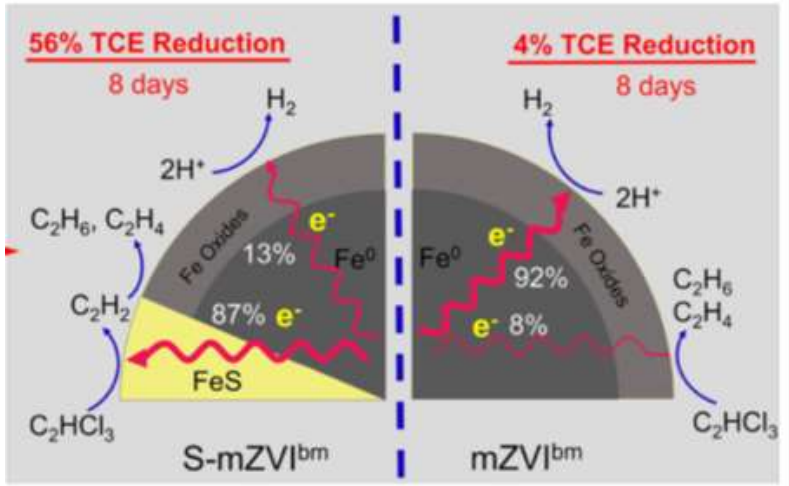


Hydrogen Gas Production (corrosion)



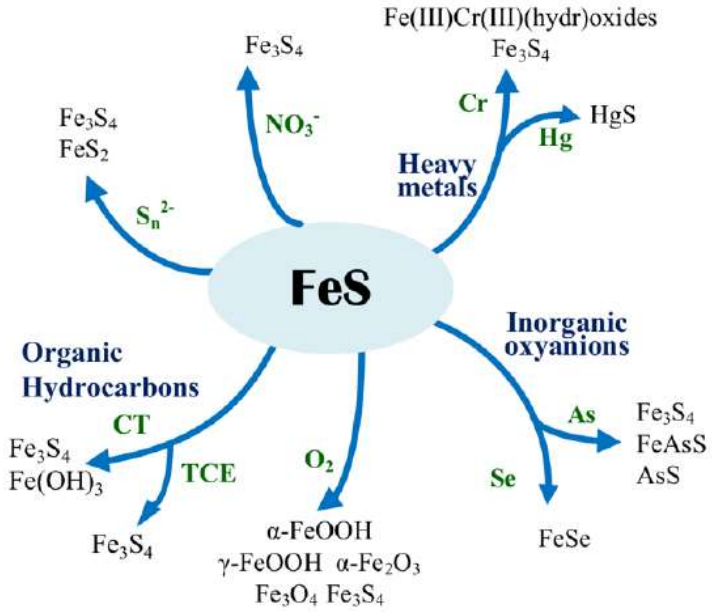
Högänäs

Sulfidated micro (and nano) ZVI



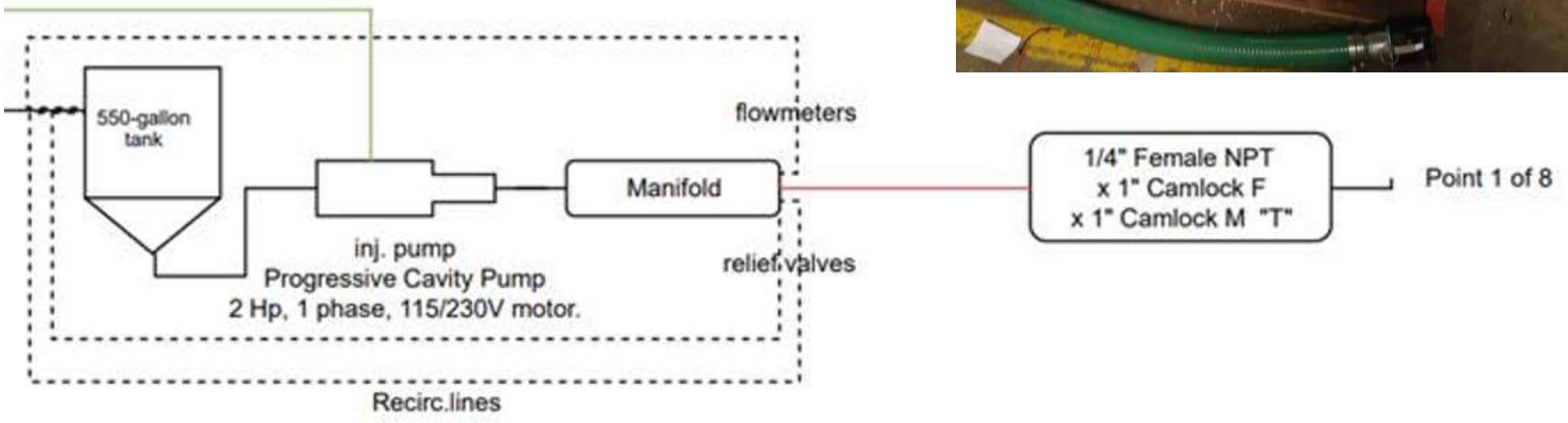
Gu, Wang, He, et al. (2017) Env. Sci. Technol. 51: 12653-12662 Mechanochemically Sulfidated mZVI: Pathways, Kinetics, Mechanisms, Selectivity

ISR



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

Micron-size ZVI suspension in a shear thinning fluid



mZVI Suspension

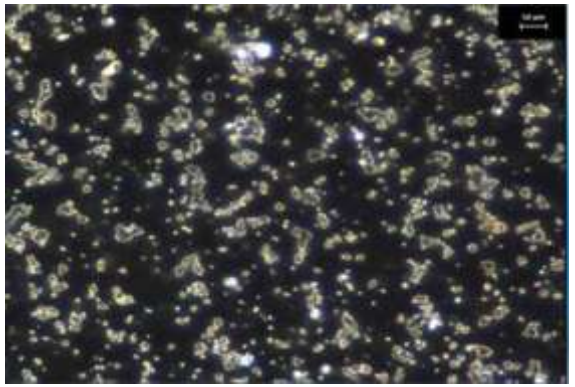
- Uniform, low viscosity, liquid

  - ✓ Pour
  - ✓ Pump
  - ✓ Field mix

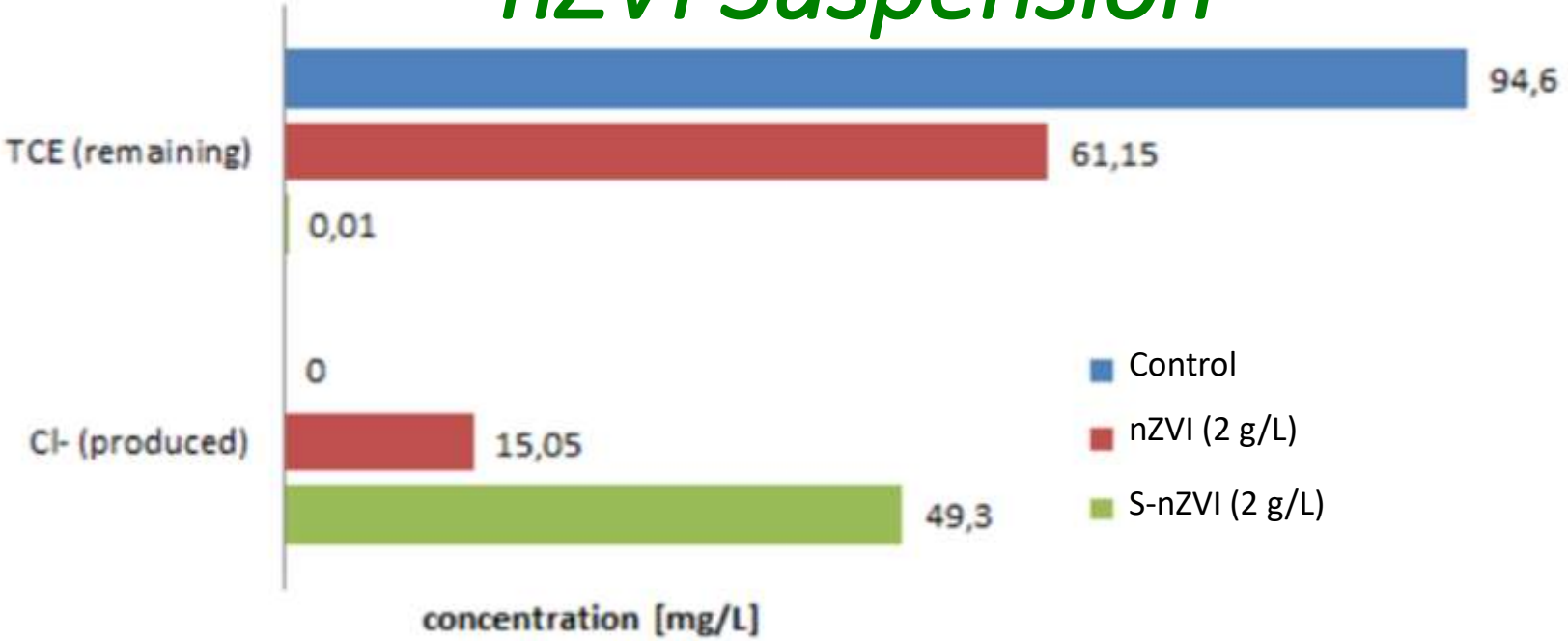
- Injection behavior is similar to EVO

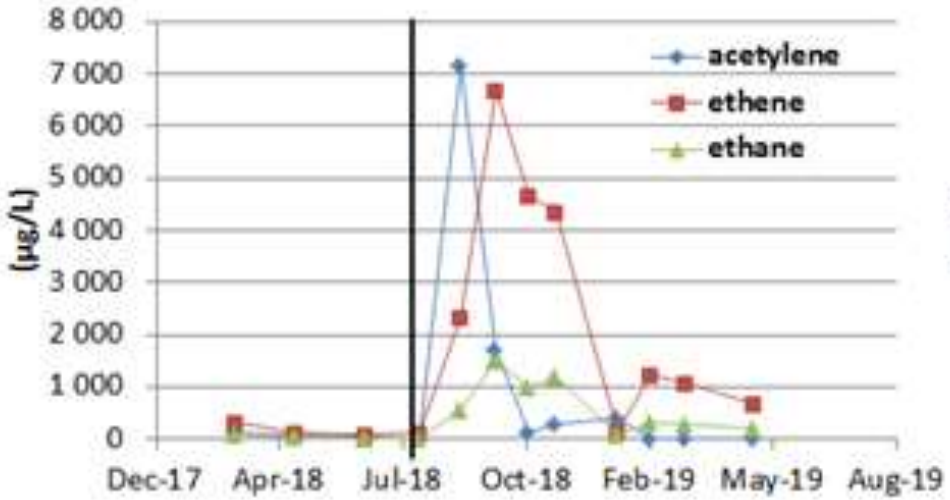
- Sulfidated version

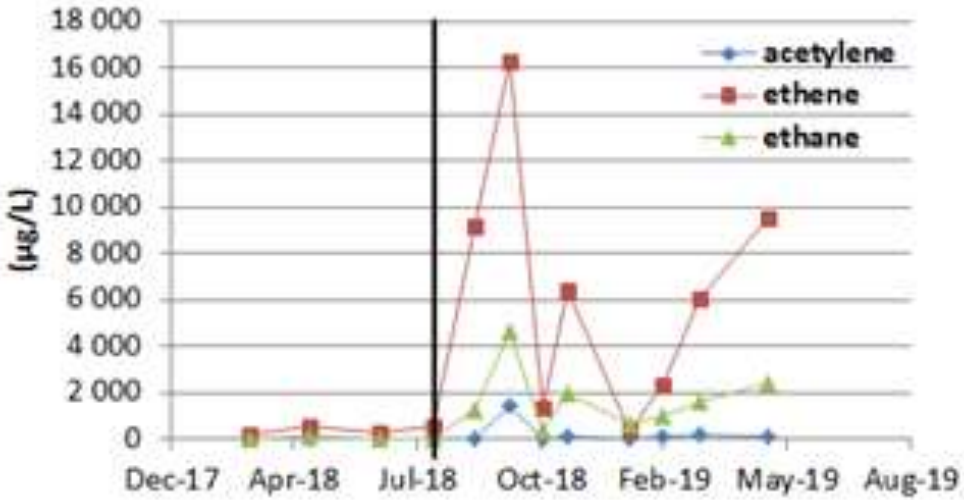
Parameter	Typical Values
ZVI (% by wt.)	40
ZVI average particle size	<5 µm
Organic Carbon (% by wt.)	60
Specific Gravity (Density)	1.9 (15.8 lbs./gal)
Viscosity (cP)	~ 3,000
Water	0



nZVI Suspension







ISR
Iron Sulfide Reactant

Iron Sulfide Reactant

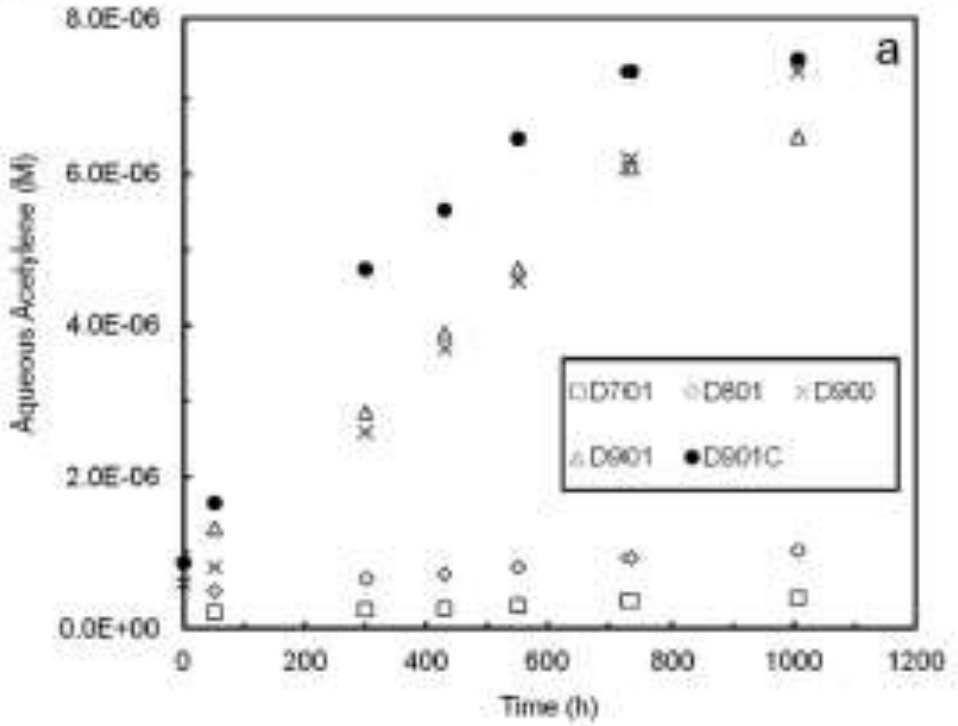
Liquid that mimics naturally-occurring FeS

promotes abiotic and biotic activity that degrades chlorinated ethenes, ethanes and explosives, precipitates toxic metals and neutralizes radioactive materials.

KEY: Has to be freshly prepared.

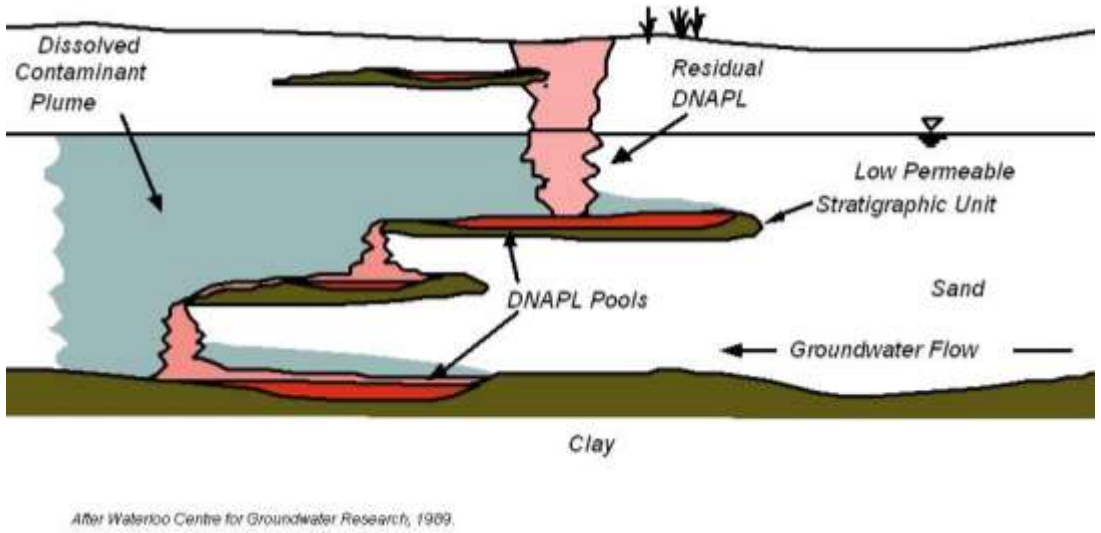
Abiotic reductive dechlorination of *cis*-DCE by ferrous monosulfide

Sung Pil Hyun[1,2] · Kim F. Hayes[2]



Acetylene production from abiotic cis-DCE degradation by the FeS suspension
Freshly made FeS vs. freeze-dried Mackenawite

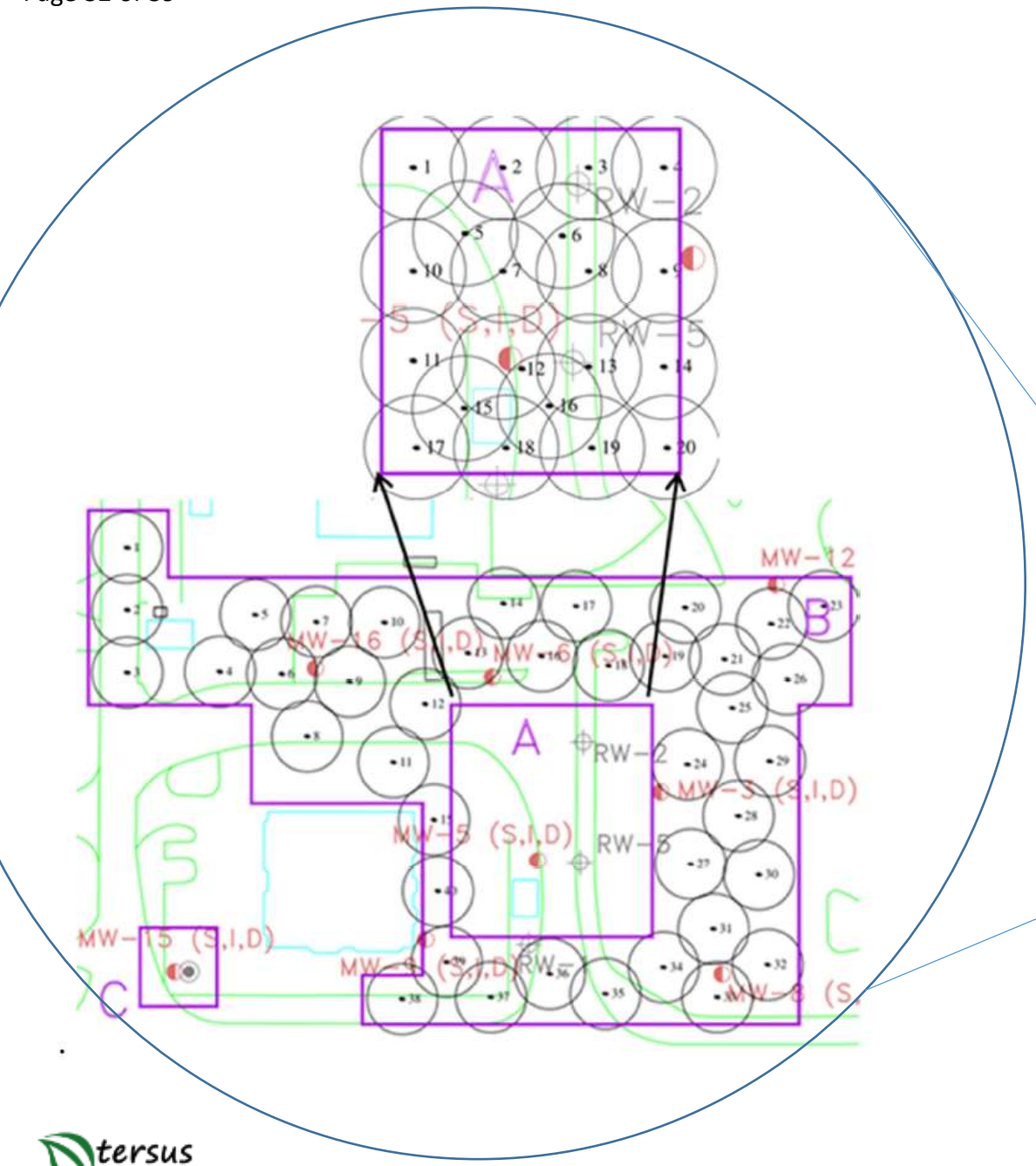
04 Design and Case Studies

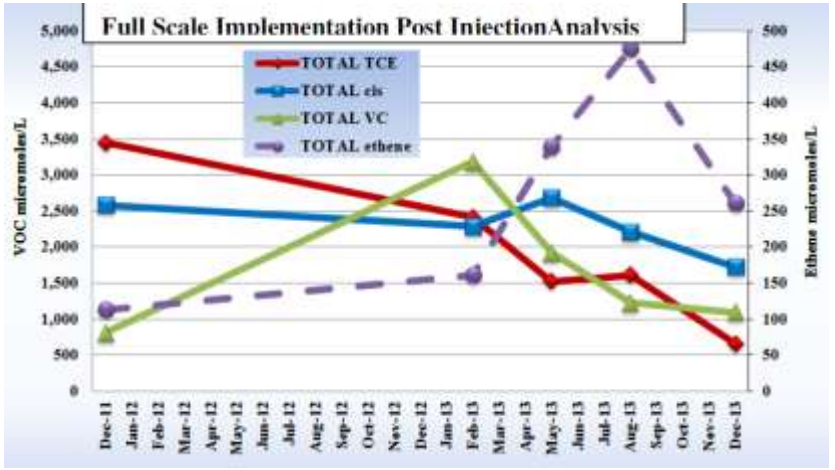


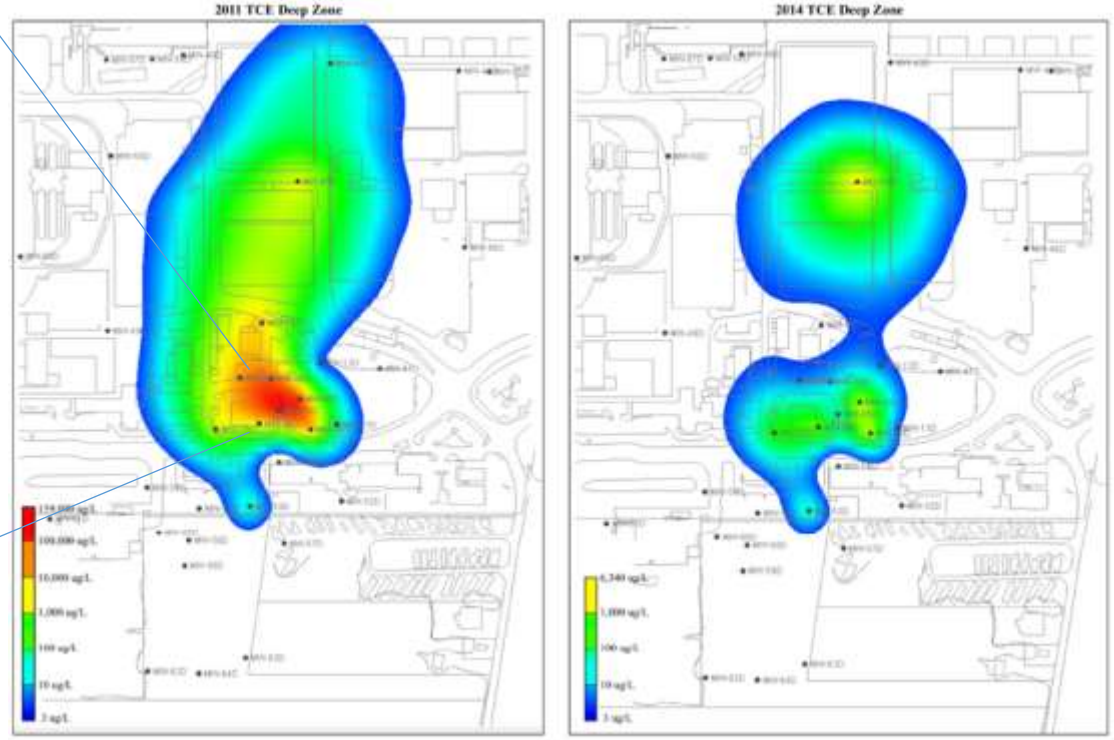
After Waterloo Centre for Groundwater Research, 1989.

Chlorinated Solvent (CAS Number)	Aqueous Solubility (µg/L @ 25 °C)
PCE (127-18-4)	200,000
TCE (79-01-6)	1,472,000
cis-1,2-DCE (156-59-2)	3,500,000
trans-1,2-DCE (156-60-5)	6,300,000
1,1-DCE (75-35-4)	2,250,000
Vinyl Chloride (75-01-4)	8,800,000
1,1,1-TCA (71-55-6)	1,334,000

- Outside-In, Bottom-up Direct Push Injection
- Material Injected neat, or (diluted with veg. oil)
- Inject where DNAPL is suspected
- Volume of Injected fluid should replace 10% of the mobile pore volume (n_e)



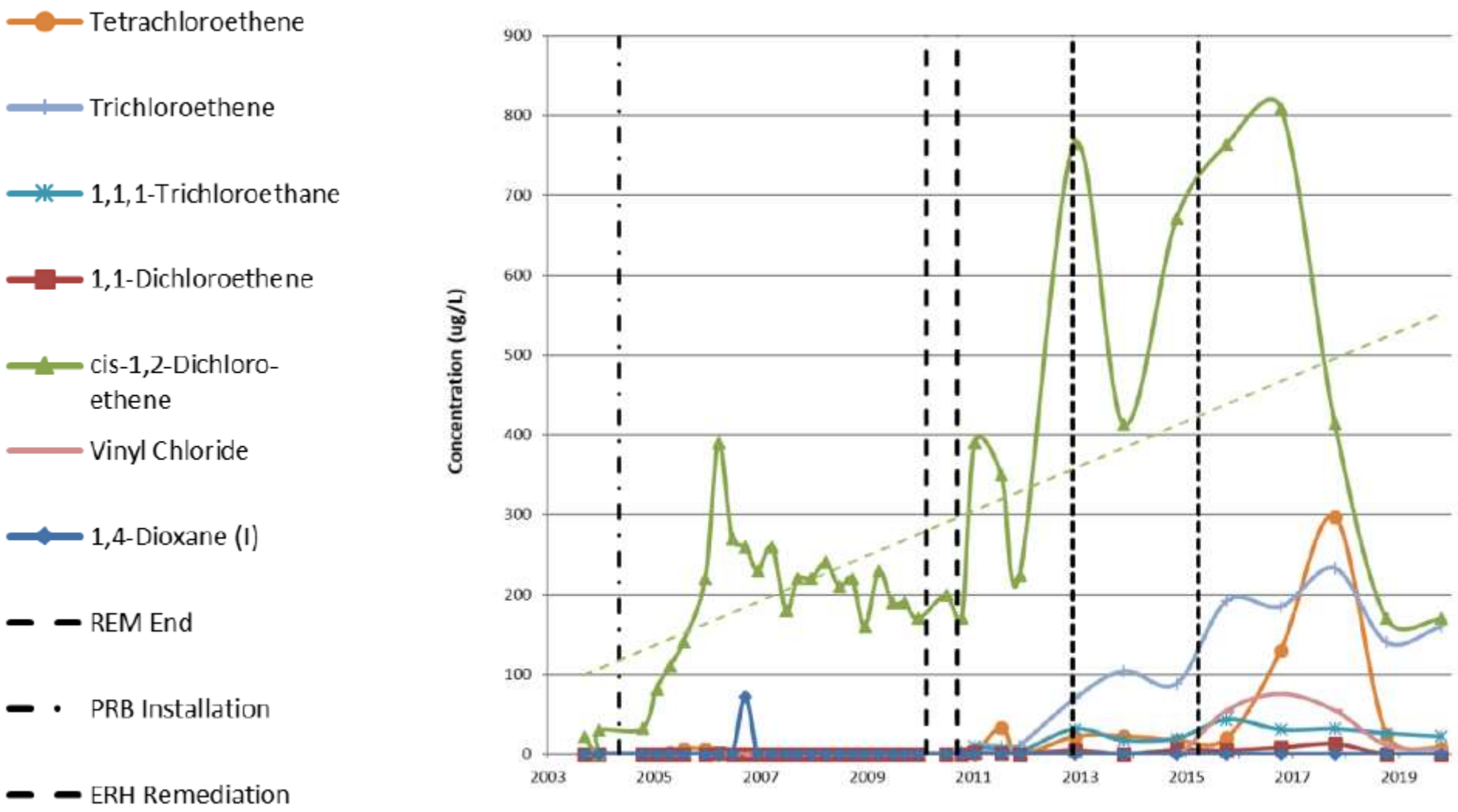




Bench Scale Test Results		
ZVI Weight	1066.85	g
ZVI % by weight	50%	
Flowrate	1.96	L/day
Contaminant Concentration	100	mg/L
Residence time	2.5	Hours
Breakthrough Time	7	Days

14 mg/g removal

Composition Calcs.		
Average Groundwater Flux	0.0147	ft3/ft2/day
Assumed Porosity	49%	
Velocity	0.03	ft/day
Theoretical wall width	0.5	Ft
Residence Time	17	Days
ZVI Composition	50%	percent by weight
Mass of ZVI per ft^2 of cross area	75	lbs/ft2
Time to Breakthrough	11.5	Years
Target Lifetime	10	Years

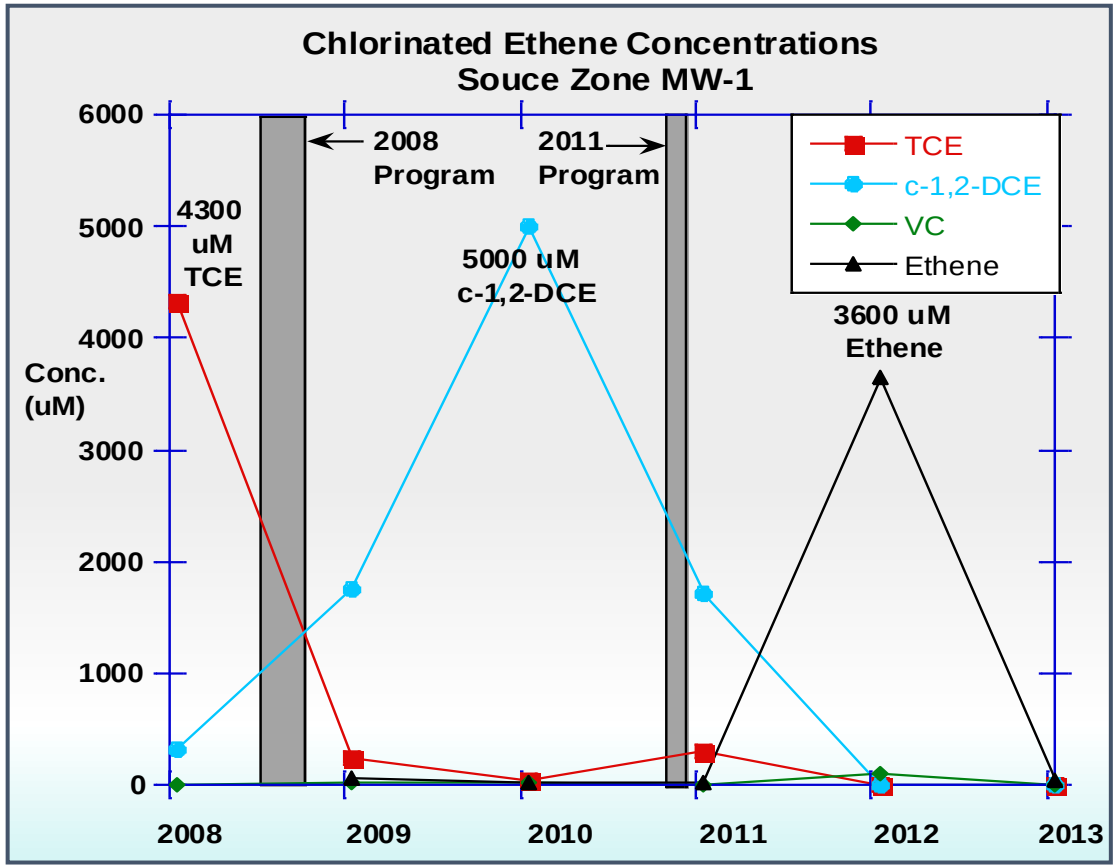


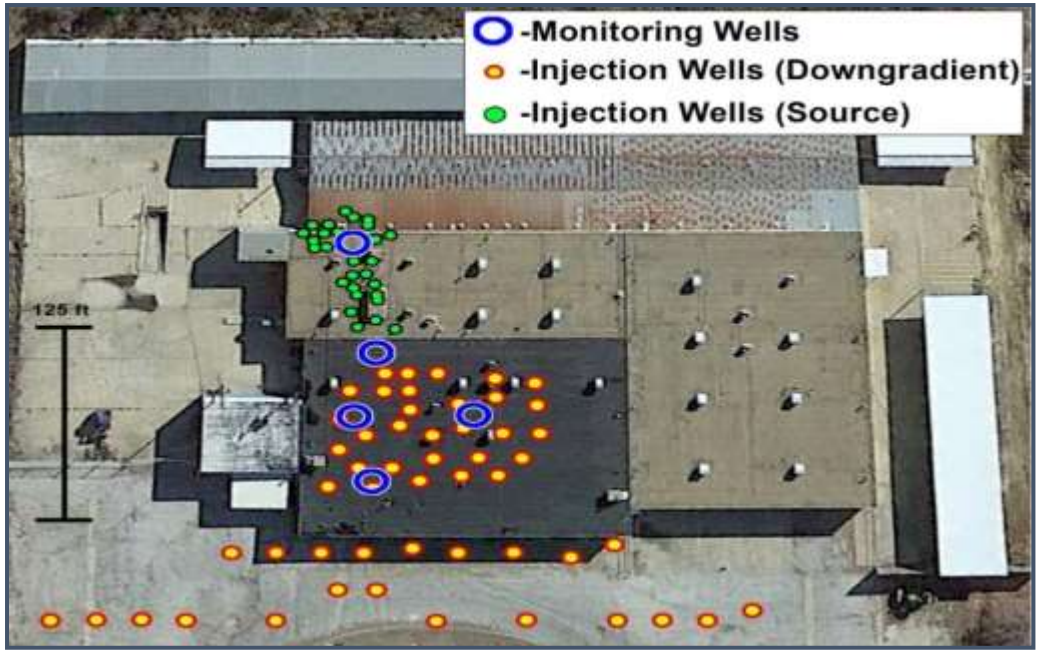
Injection volume	mZVI™	EDS-ER™	50% KOH	KB-1®	KB-1® Primer
gal/pt	Gal	Gal	Gal	Liters	pouches
1,200	(2 drums)	(1 tote 3 drums)	(2 drums)	24 (1 vessel)	24

Product	lbs. H_2 per lb. of electron donor	H_2 demand (lbs.) Using ESTCP tool	Total Electron Donor demand (lbs.)
EDS-ER™ (EVO) Soybean oil-based	0.359	2,186	6,089

Points	ROI	thickness	Porosity	PV	Injection Volume	Injection Volume
each	ft	ft	%	gal	% of PV	Gal
24	7.5	14	15%	66,600	43%	28,800

Implementation: Injection was done in two phases based on baseline and monitoring data.

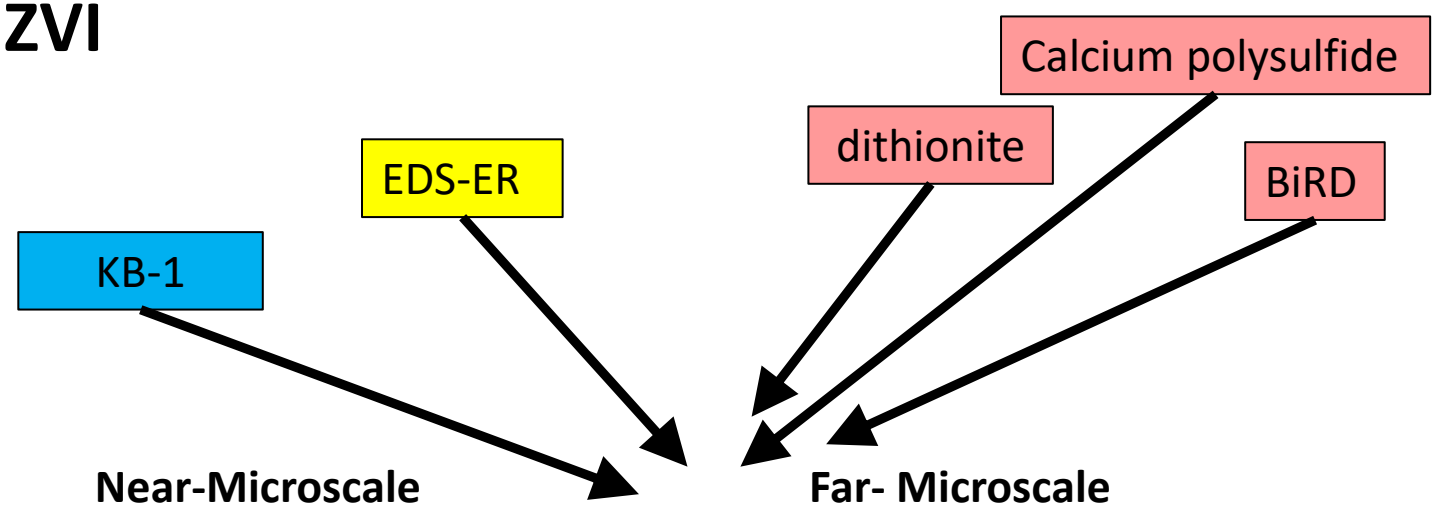




Results: 5-year monitoring data tells an interesting story. A large spike in ethene shows complete biotic degradation after 2011 injection event

Summary

- **Many types of ZVI**
- **ZVI → ISCR**
- **ZVI + BIO**



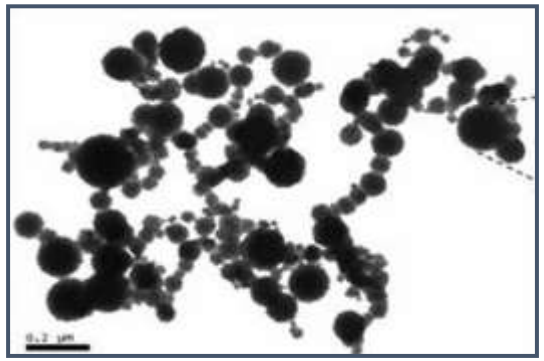
Soluble
Fe^{+2}, Bicarb

Nano
nZVI

Near-Microscale
ZVI liquids

Far- Microscale
ZVI Slurries

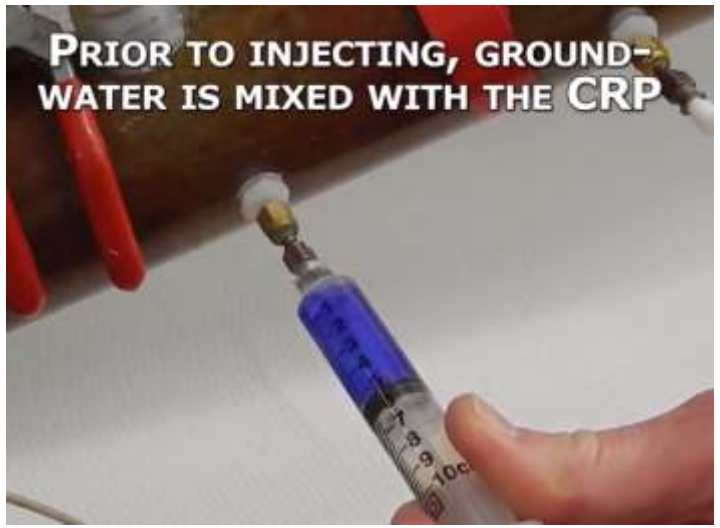
Scrap Iron

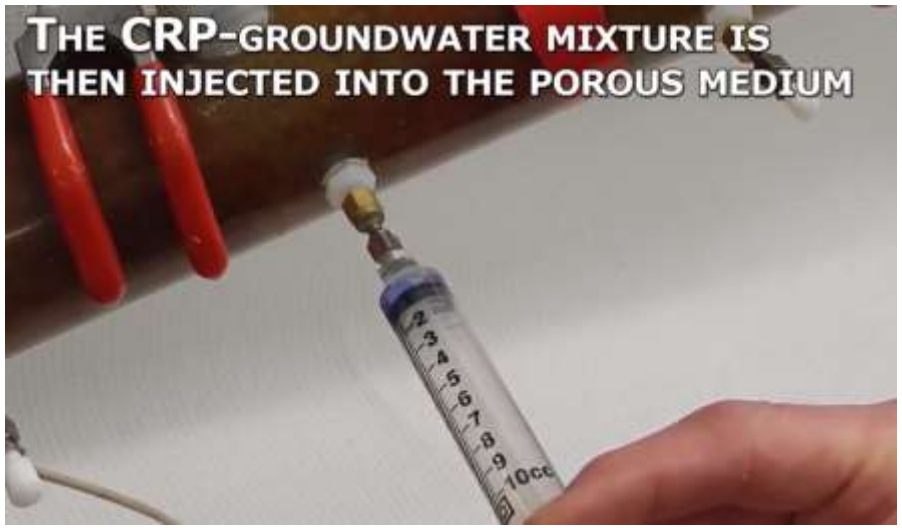


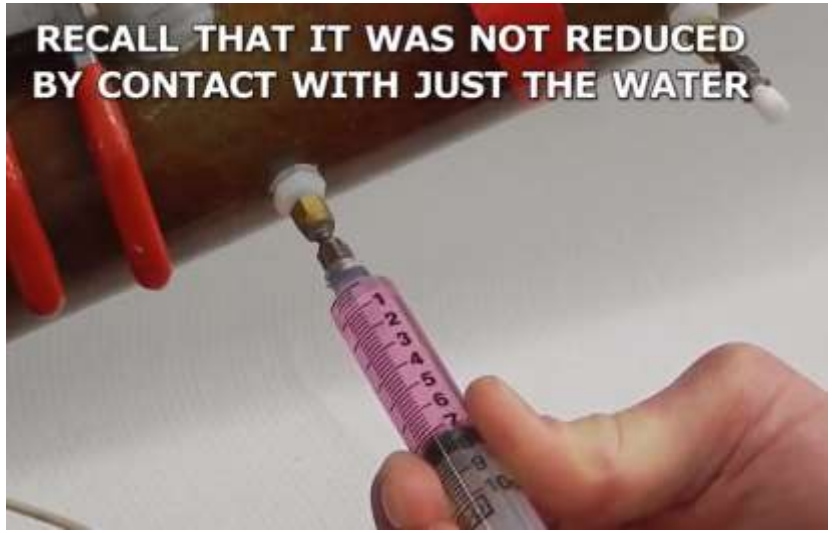
0 µm | 0.2 µm | 2-3 µm | 50 µm | 1 mm

General Considerations

MNA **BIO** **ISCR-BIO**







Tratnyec's presentation

Thank You!

David F. Alden, P.E.
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