Sulfidated Colloidal Zero-Valent Iron For Groundwater Treatment Gareth Leonard RemTech 2020



# What is In Situ Chemical Reduction (ISCR)?

- Term used since the 1990's
- Category of in situ groundwater remediation technologies where treatment occurs primarily by chemical reduction of contaminants
- Emphasis on abiotic reduction:
- Reductant supplies electrons
- Contaminant accepts electrons: TCE loses Cl, gains H
- Can occur naturally, when stimulating anaerobic biological degradation or by addition of strong chemical reductants



# What is Zero Valent Iron (ZVI)?

- Strong 'engineered' reductant
- Iron typically exists as Fe<sup>2</sup> and Fe<sup>3</sup> oxides
- Fe<sup>0</sup> is manufactured to be reactive

# What are we trying to improve upon?

- ZVI has been used since the 1990's
- Address challenges of:
  - 1. Reactivity
  - 2. Persistence
  - 3. Delivery
  - 4. Ease of Use

• Resulting in a significant improvement in efficacy, utility and economy



# New ZVI Substrate

### Engineered Zero Valent Iron product:

- Colloidal particle size <5µm</li>
- Sulfidated particle coating
- Glycerol suspension

This combination results in:

- Abiotic degradation
- ISCR enhanced biological degradation







## 1) Reactivity: Focus on Sulfidation

Electron Efficiency (%)

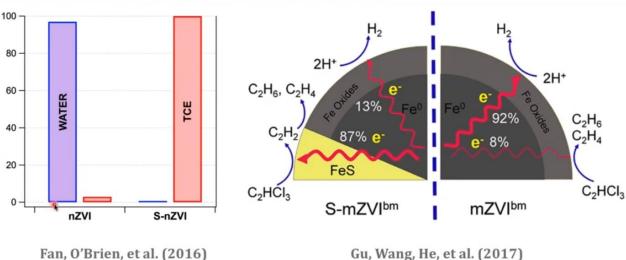
Env. Sci. Technol. 50: 9558-9565

Sulfidation of nZVI for Improved

Selectivity during ISCR

# ZVI also reacts with water = H<sub>2</sub> • Results in:

- passivation
- decreased persistence
- Less treatment of the contaminant



Env. Sci. Technol. 51: 12653-12662

Mechanochemically Sulfidated mZVI:

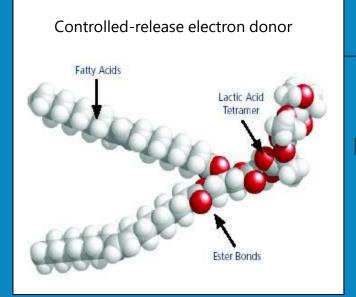
Pathways, Kinetics, Mechanisms, Selectivity

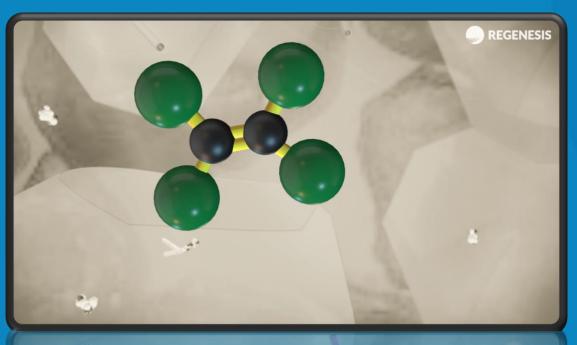
#### Answer = sulfidate the ZVI surface

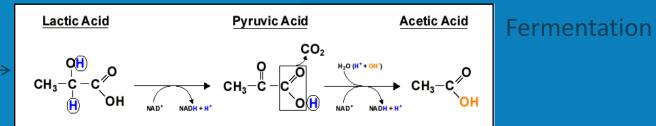
- Coats the surface of the ZVI particle with iron sulfide
- Results in an increase in Electron Efficiency (EE):
  - Minimizes reaction rate with water
  - Maximizes reaction rate with contaminants
- Sulfidation enhances reaction rate with chlorinated ethenes



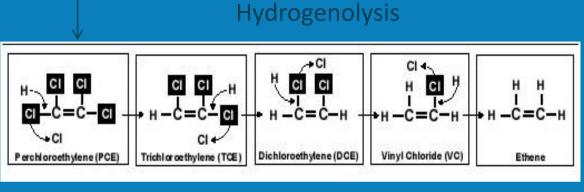
### **ISCR-Assisted Bioremediation**







Dissolution



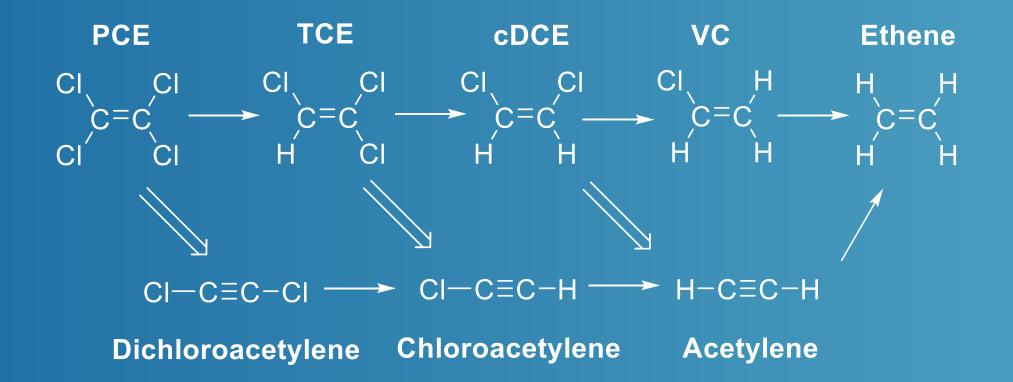
 $PCE \longrightarrow TCE \longrightarrow DCE \longrightarrow VC \longrightarrow Ethene$ 

### **ISCR** enhancement

- Rapidly create anaerobic conditions
- Remove dissolved oxygen
- Glycerol layer provides dissolved hydrogen
- Able to address greater mass abiotic destruction of parent compounds

### CHEMICAL (ABIOTIC) REDUCTION:

#### **Reaction pathway can bypass toxic daughter products**





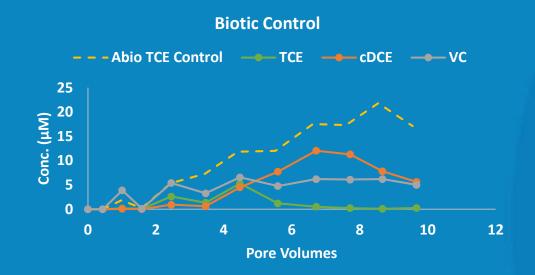
OPTIMIZATION FOR ZVI TECHNOLOGY FOR IN SITU REMEDIATION OF CHLORINATED CONTAMINANTS

### **ISCR-ASSISTED BIOREMEDIATION**

### **BIOTIC COLUMN**



**Biotic ZVI** 



#### TCE removed at week 7

Maximum daughter product at week 7 10 μM daughter products at week 10

**TCE removed immediately** 

Maximum daughter products at week 5

No contaminants at week 10



OPTIMIZATION FOR ZVI TECHNOLOGY FOR IN SITU REMEDIATION OF CHLORINATED CONTAMINANTS

## 2) **DISTRIBUTION: Mixing and Injection**

# Characteristics of colloidal iron

#### S-MicroZVI suspension



#### Low pressure sandbox demo



# Characteristics of microscale iron





OPTIMIZATION FOR ZVI TECHNOLOGY FOR IN SITU REMEDIATION OF CHLORINATED CONTAMINANTS

## 3) EASE OF USE

- A fluid suspension is provided in 200L drums
- Pumped or poured into mix tank and diluted
- Simple mixing and pumping equipment
- Safe to use
- No need for powder handling equipment
- No dust or explosion hazard
- No thick slurries to fracture into the formation

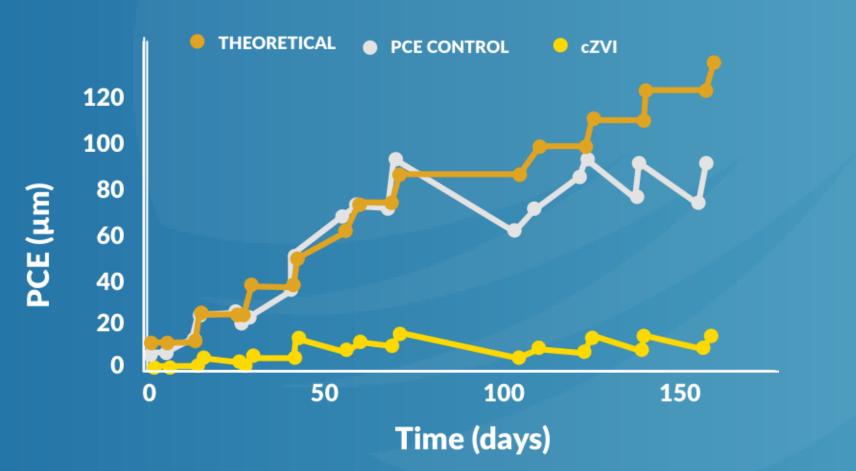






### 4) Persistence

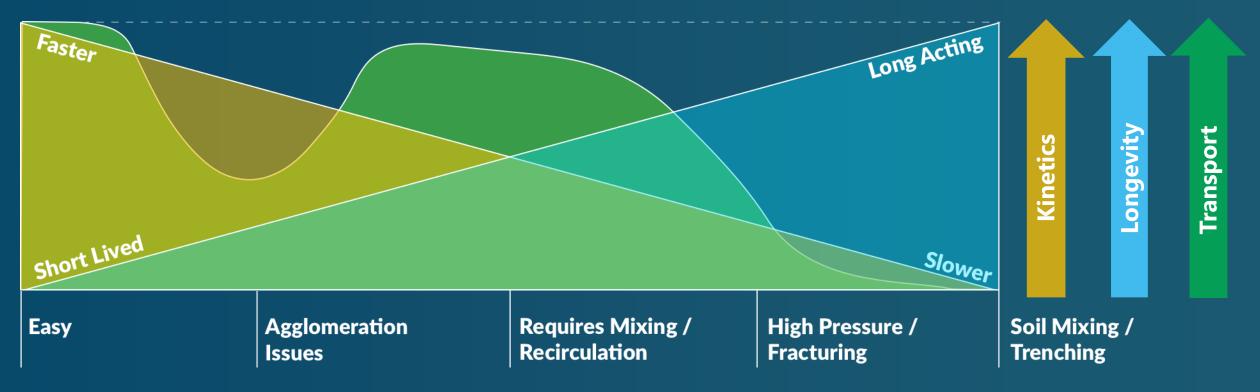
- Improved EE from sulfidation
- Reduction in passivation



#### **PCE Concentration**

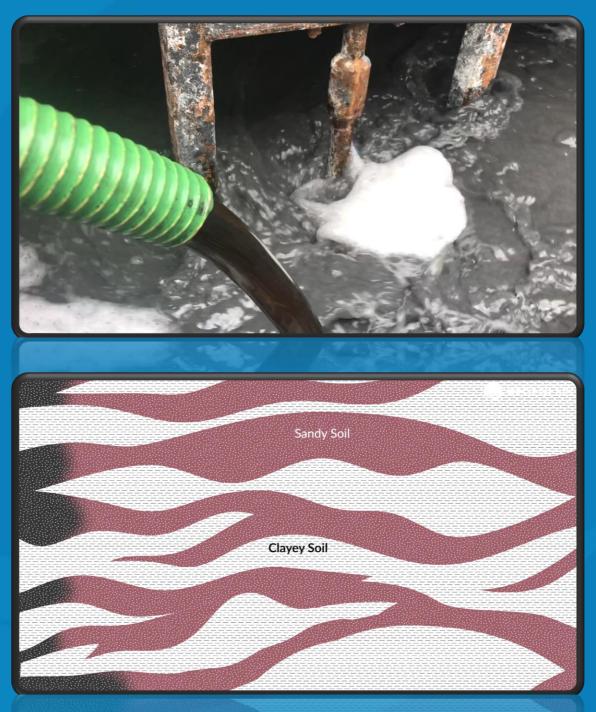
## FEATUES OF DIFFERENT PARTICLE SIZE ZVI



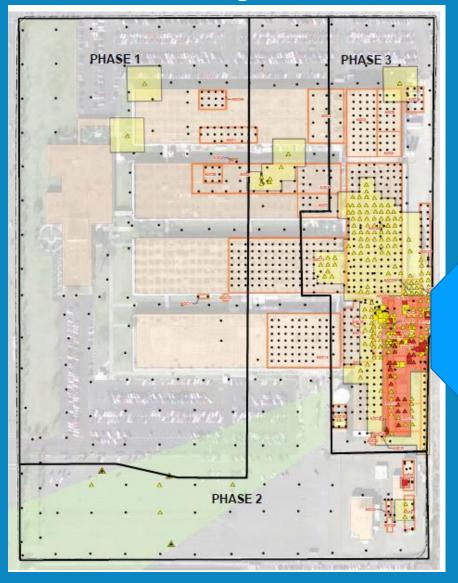


## Application





### **Case Study: Southern California Site**







### **Case Study: Results**

MW-25 Injection depth (mBGL) 3-11 11-16 16-23 23-30	Baseline TCE (μg/L) 20,000 420 26,000 2300	<mark>6 months (μg/L)</mark> 7.3 1.3 2.6 51	% Reduction 99.96% 99.71% 99.99% 97.78%	10,000     Begin ISCR injections     Complete ISCR injections       1,000     100       10     10       11/1/2018     7/1/2019       1/1/2018     1/1/2019       1/1/2019     1/1/2019       10     10       10     10       11/1/2018     1/1/2019       11/1/2019     1/1/2019       11/1/2019     1/1/2019
MW-10 Injection depth (mBGL) 3-11 11-16 16-23 23-30	<b>Baseline TCE</b> (μg/L) 320 810 5100 0.73	<mark>6 months (μg/L)</mark> 82 0.7 ND ND	% Reduction 74.38% 99.91% 100% 100%	Trichloroethene

Trichloroethene

7/1/2019

1/1/2019

▲ MW-05CR ▲ MW-08C ▲ MW-26C ● MW-PO02C ● MW-24C ● MW-25C

1/1/2020

1/1/2020

. .

100,000

1/1/2018

7/1/2018

- Site sold
- Validation will continue for a further 18 months

## Conclusions

- S-MicroZVI effective for a wide range of contaminants, particularly chlorinated solvents
- Unsurpassed combination of:
  - Reactivity
  - Persistence
  - Distribution
  - Ease of Use
- Can target high concentrations of contaminants
- Integrates with electron donor substrates and colloidal activated carbon treatment





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