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Sulfidated Zero Valent Iron: Theory, Mechanisms, and Performance Review

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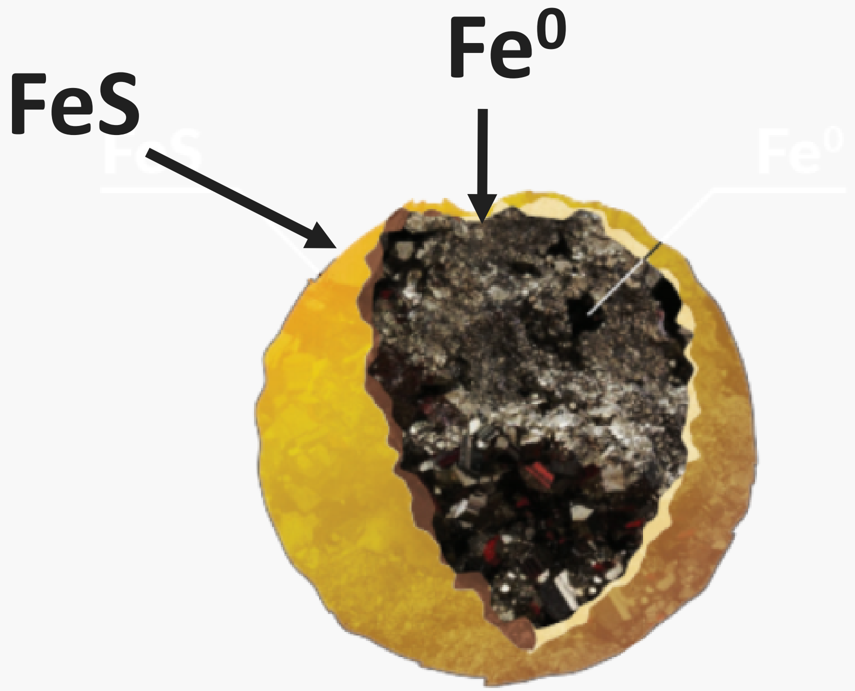
Outline

- What is Sulfidated Zero Valent Iron (SZVI)
- How to make SZVI
- SZVI Microstructure and Imaging
- SZVI Reactivity and Persistence
- Summary/Closing thoughts

What is Sulfidated Zero Valent Iron (SZVI)?

Sulfidated Iron Has an Engineered Core Shell Microstructure



- **ZVI core supplies electrons to achieve contaminant destruction**
- **FeS surface (~5 wt.%) provides unique and beneficial properties**
  - First reported 1995
  - Renewed interest 2010's
  - Commercialized 2017

What Isn’t SZVI:

- ZVI with sulfur impurities
- In-situ precipitated biogeochemical reduced minerals (BiRD)
- Chemically synthesized mackinawite
- Mixtures of mackinawite

How to Make Sulfidated Iron

React an Iron Compound With a Sulfur Compound

+

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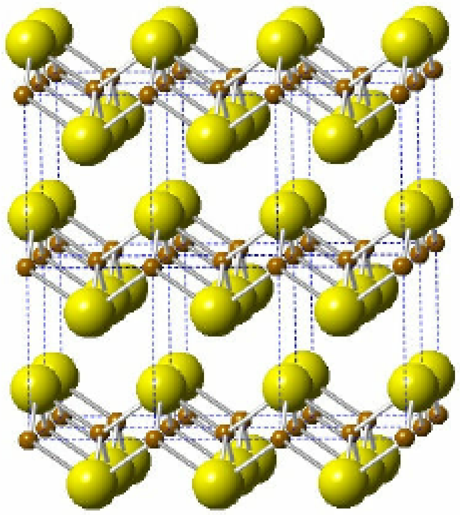

Iron Compound **Sulfur Compound** **Mackinawite**
Fe_xS_y

Candidate Sulfur Compounds

Name	Formula	Oxidation State	ΔG_0^f
Sulfate	SO_4^{-2}	+6	-745 kJ/mol
Sulfite	SO_3^{-2}	+4	-513 kJ/mol
Thiosulfate	$SO_{1.5}^{-1}$	+2	-257 kJ/mol
Iron (II) sulfide	FeS	0	-100 kJ/mol
Sulfide ion	S^{-2}	-2	-86 kJ/mol
Bisulfide ion	HS^{-}	-2	-12 kJ/mol
Elemental sulfur	S	0	0 kg/mol

More stable

Less stable

Candidate iron compounds

Zero Valent Iron Fe^0; Dissolved Iron: Fe^{+2}, Fe^{+3}

Example Reactions

Zero valent iron and sulfate

$$4\ Fe + SO_4^{-2} + 4\ H_2O \rightarrow FeS + 3\ Fe(OH)_2 + 2\ OH^- \qquad \Delta G_0^f = -169\ kJ/mol$$

- Sulfate is more stable than sulfide; reaction is not spontaneous
- Energy is supplied by the oxidation of iron
- Less oxidized compounds (e.g., dithionite) require fewer atoms of ZVI to drive the reaction

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Example Reactions

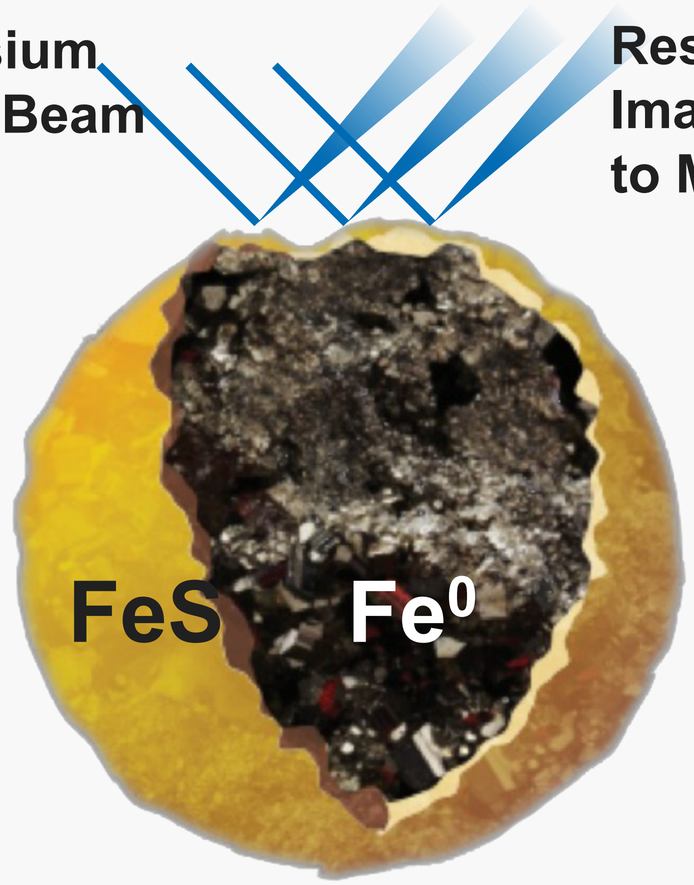
Dissolved ferrous iron and sodium bisulfide

$$Fe^{+2} + HS^{-} \rightarrow FeS + H^{+} \qquad \Delta G_0^{f} = -8 \text{ kJ/mol}$$

- Reaction is spontaneous and proceeds without added energy
- Possible health and safety concerns, odor issues
- Described as a method to make sulfidated NZVI (SNZVI)

SIMS: Secondary Ion Mass Spectrometry

Cesium
Ion Beam



Resulting Ions
Imaged According
to Mass

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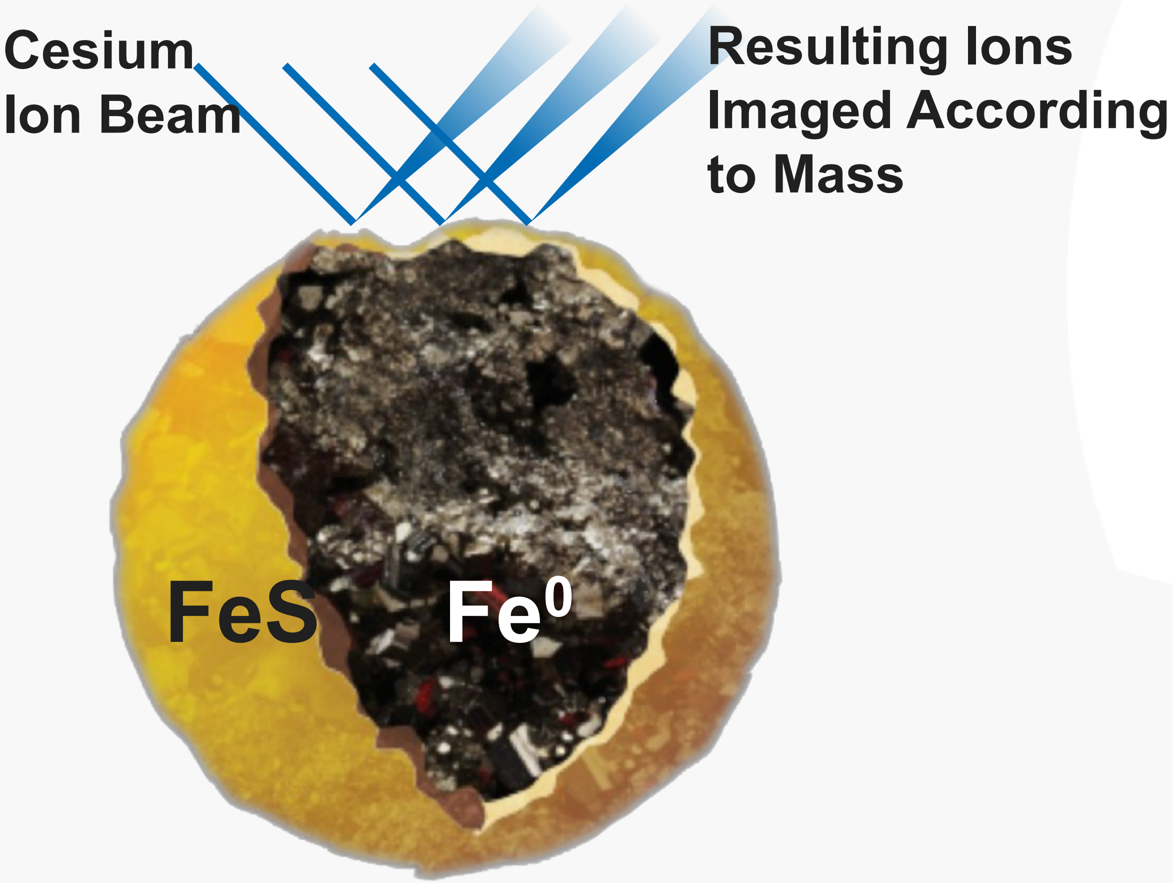
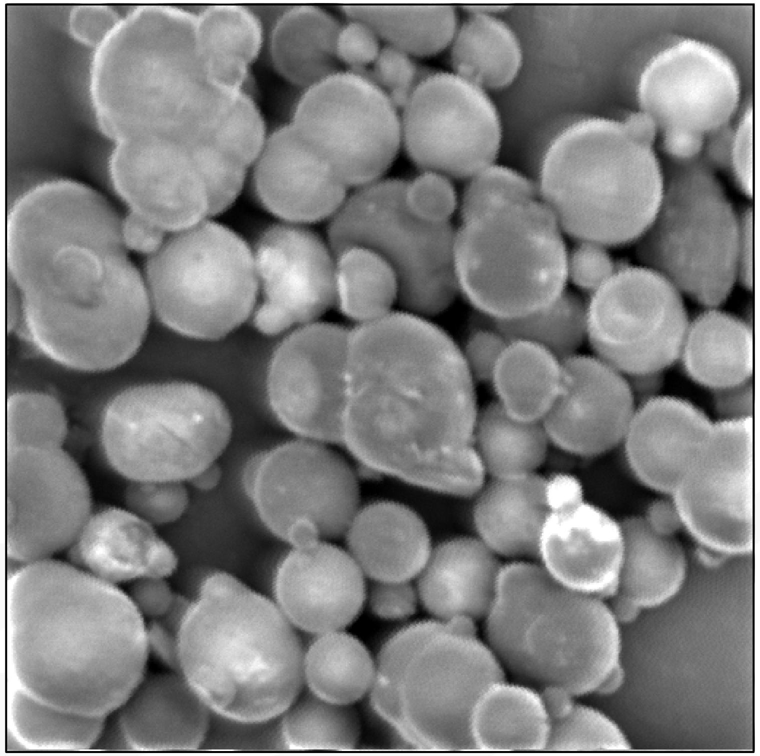
SIMS: Secondary Ion Mass Spectrometry





S-MicroZVI – SEM Image

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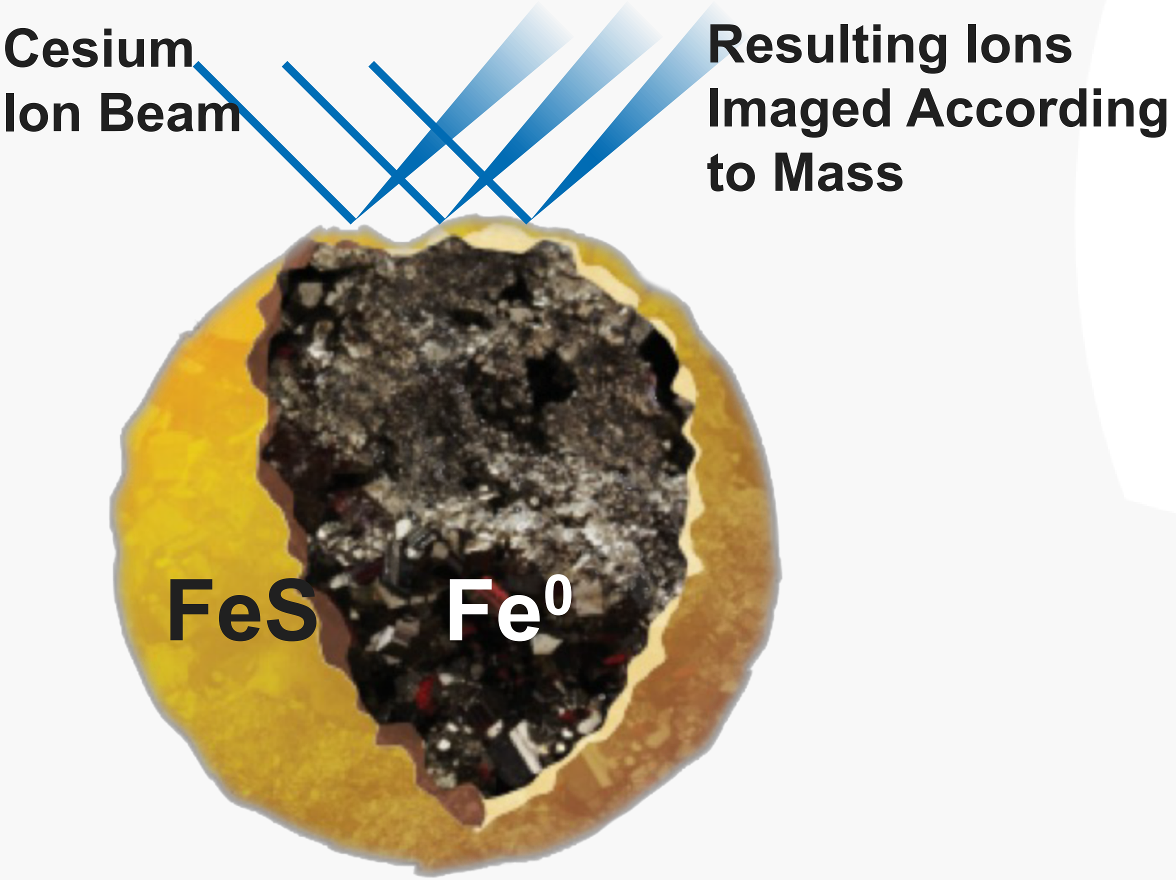
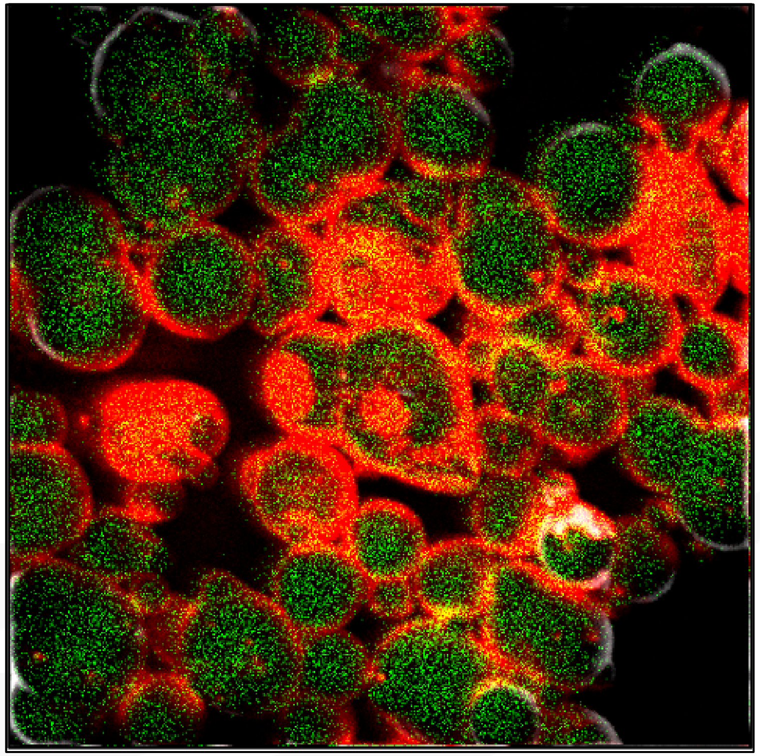
SIMS: Secondary Ion Mass Spectrometry



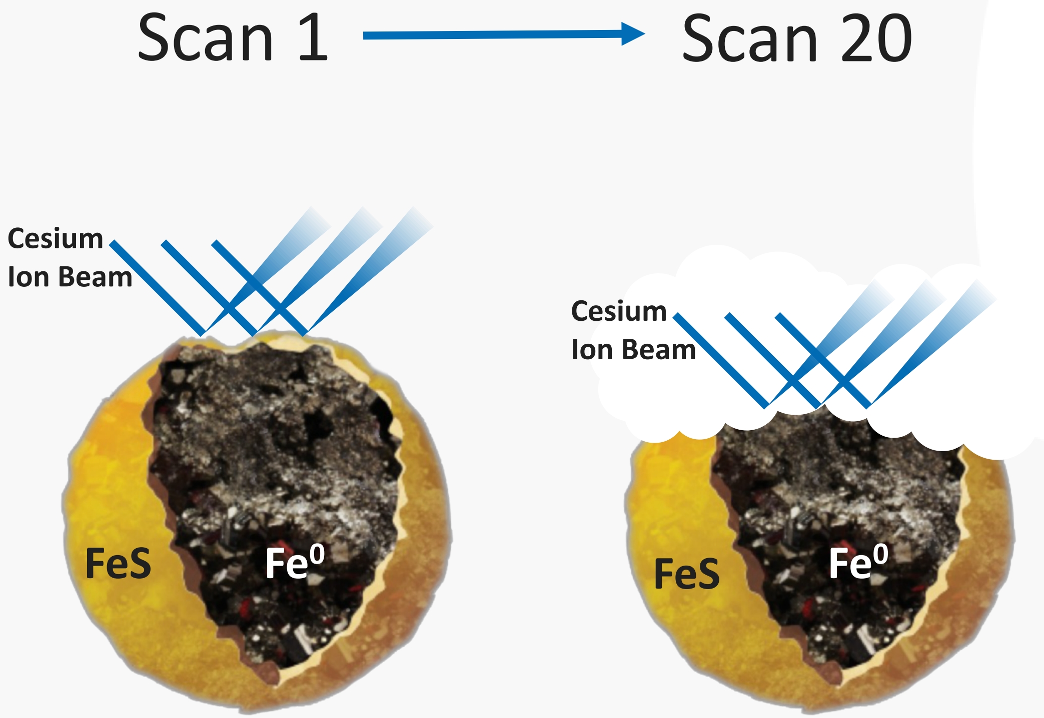
Microscope that reads mass
Etches sample surface
Lets us look inside particles



Sulfur Iron

SIMS: Secondary Ion Mass Spectrometry

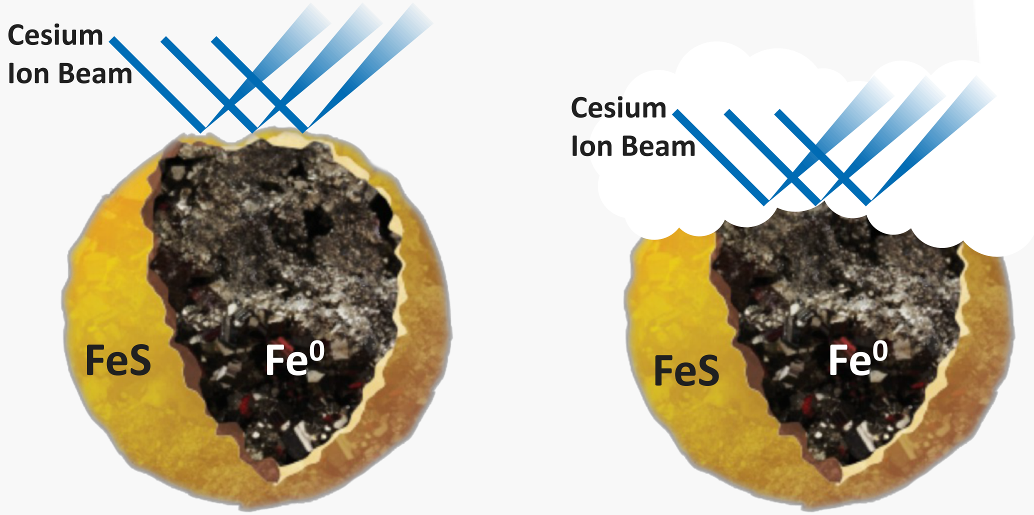
Microscope that reads mass
Etches sample surface
Lets us look inside particles

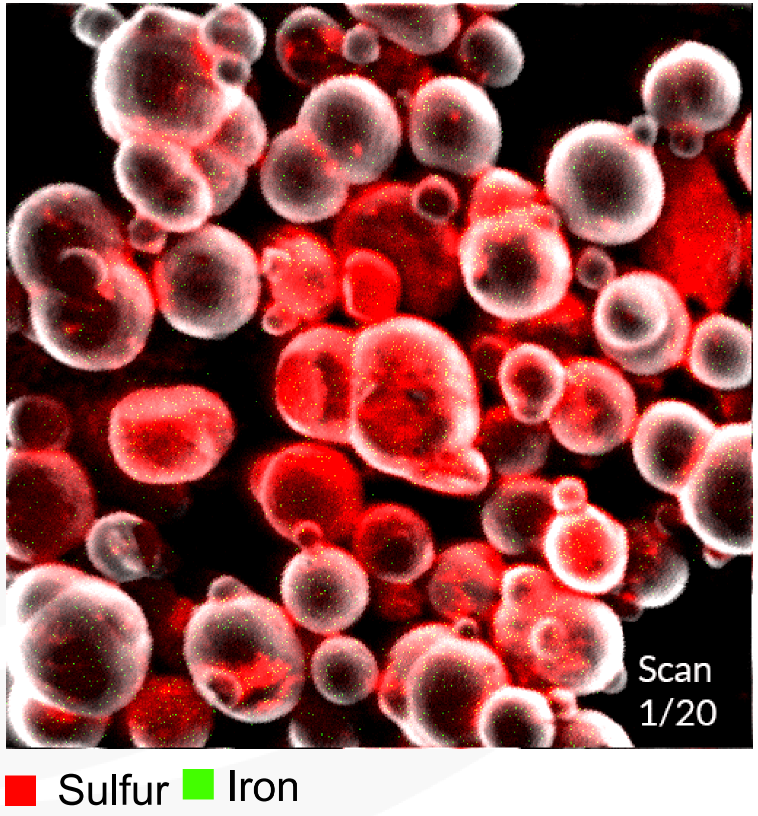


SIMS: Secondary Ion Mass Spectrometry

Microscope that reads mass
Etches sample surface
Lets us look inside particles

Scan 1 → Scan 20



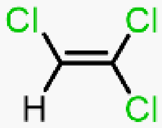


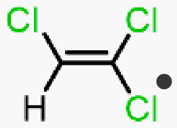
SZVI Reaction Mechanisms

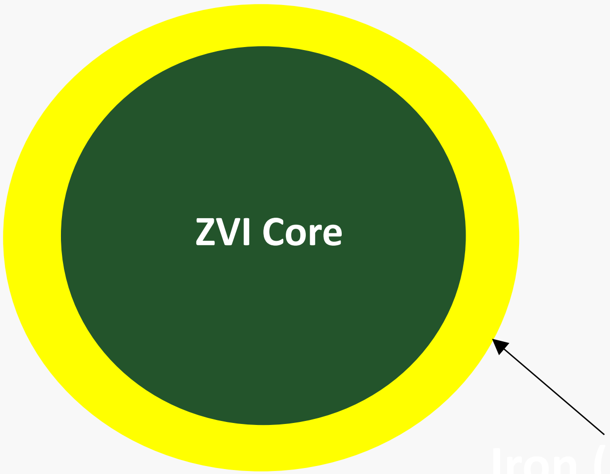
Contaminant Elimination Involves Several Steps

- Transport and Adsorption of Contaminant onto Particle Surface
- ZVI Oxidation and Electron Transport to the Adsorbed Contaminant
- Contaminant Reduction and Release of Reaction Product into Solution

SZVI: Enhanced Contaminant Sorption







- Iron (II) sulfide has more hydrophobic sites than iron oxide
- PCE/TCE adsorb preferentially to iron sulfide compared to iron oxide
- PCE/TCE are therefore more likely to take part in ISCR reactions with the ZVI
- The iron sulfide surface provides enhanced reactivity with chlorinated ethenes

Park et al., Particle Surface Hydrophobicity and the Dechlorination of Chloro-Compounds by Iron Sulfides, Water, Air, & Soil Pollution: Focus 6(1):97-110 · February 2006.

SZVI vs Bare ZVI: Batch Test

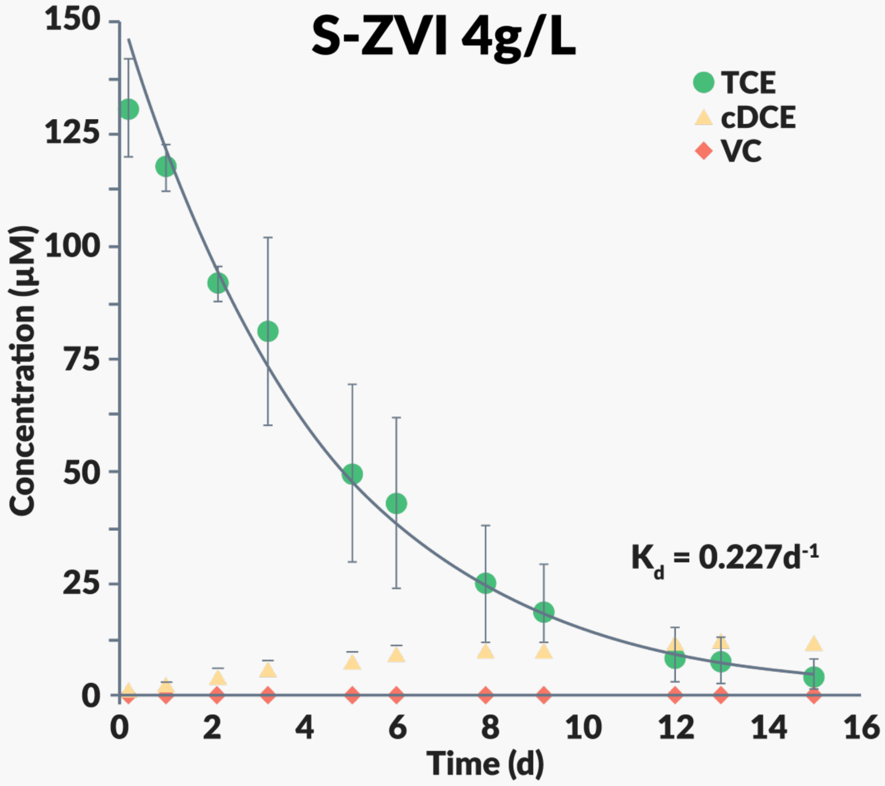
Goal: Demonstrate the effect of sulfidation on reactivity

Test Conditions:

- 240 mL anoxic bottles
- Spiked with 20 mg/L TCE
- 4 g/L ZVI (S-Micro ZVI or Bare ZVI)
- Buffered to pH =7

SZVI Reactivity: TCE

SZVI vs bare ZVI batch test



Kobs: 0.227 day^{-1}

Kmass:0.057 L g^{-1} day-1

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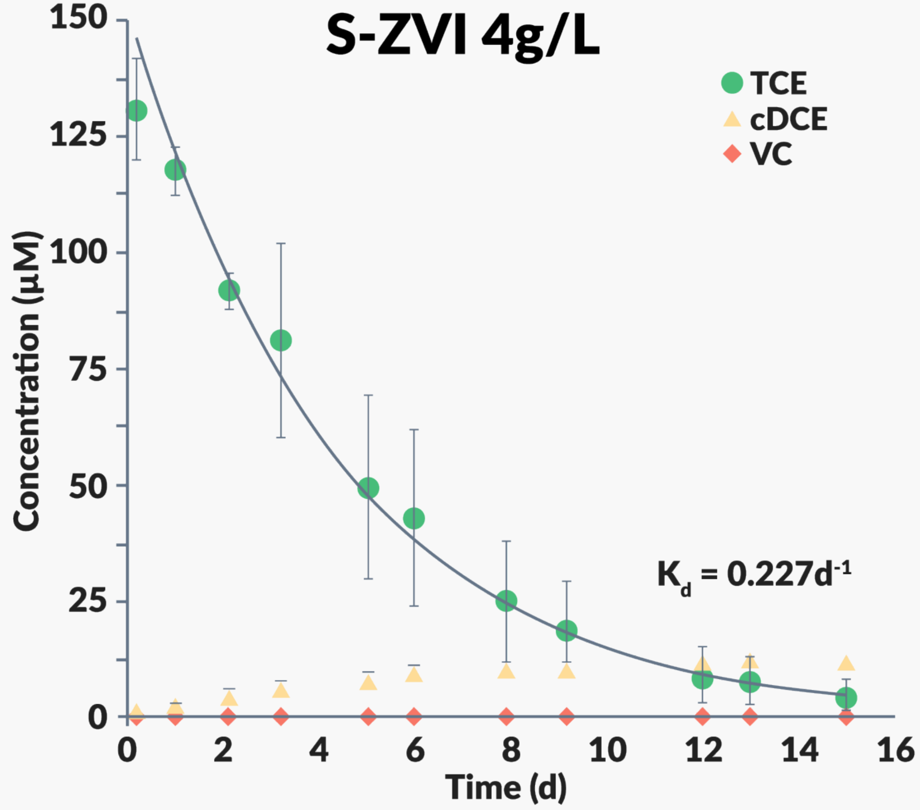
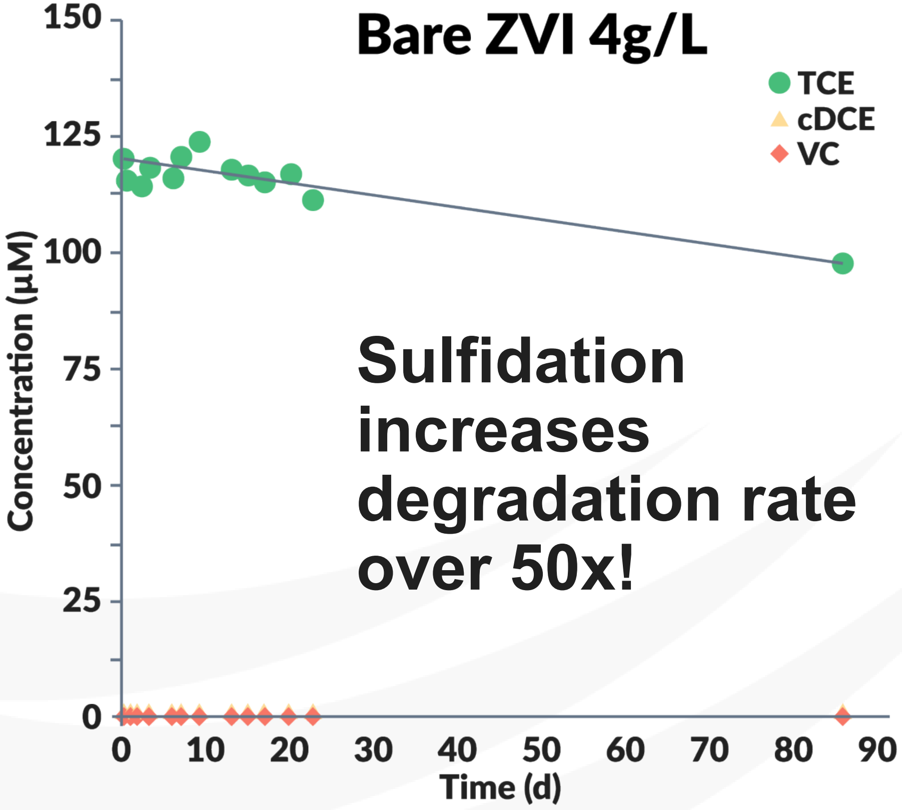
SZVI Reactivity: TCE

SZVI vs bare ZVI batch test





Sulfidation increases degradation rate over 50x!

K_{obs}: 0.227 day^{-1}

K_{mass}:0.057 L g^{-1} day-1

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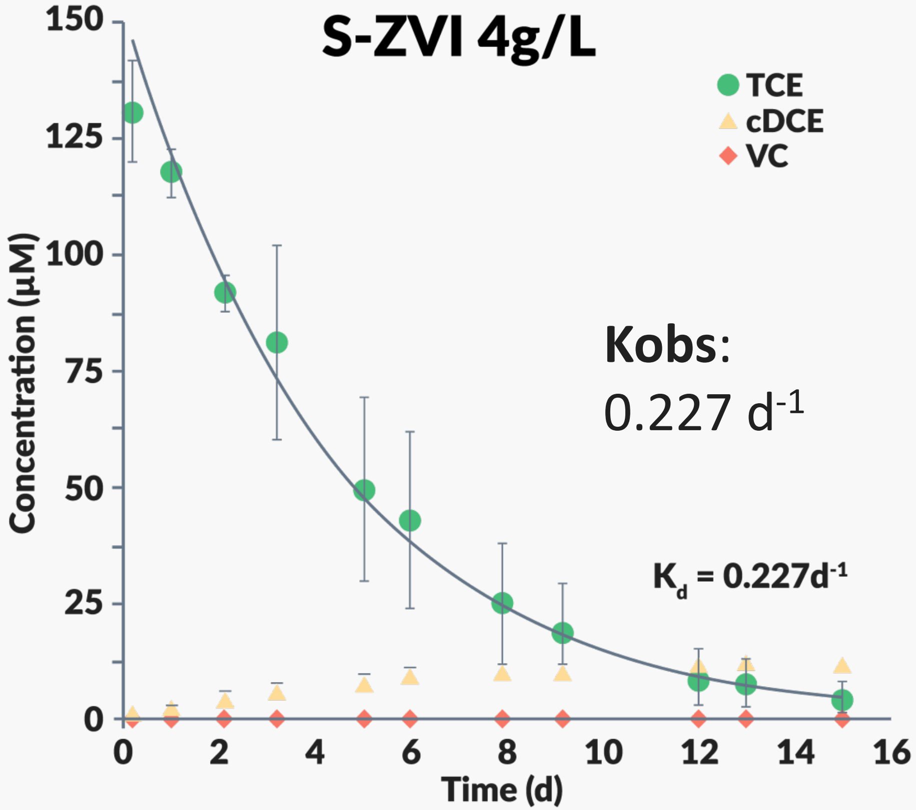
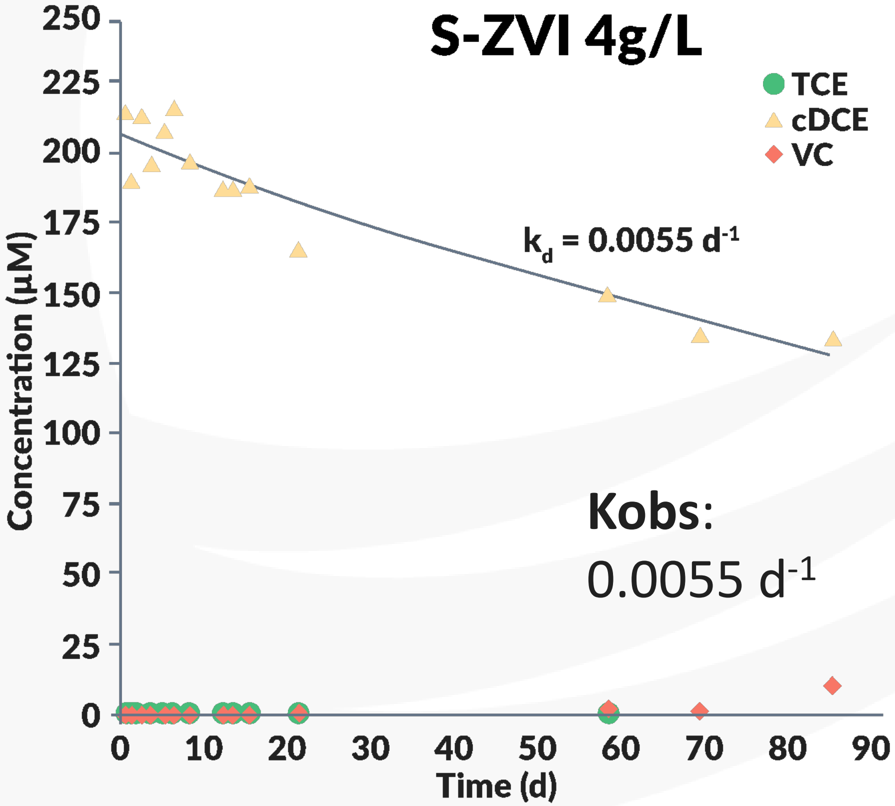
SZVI Reactivity – Daughter Products

- Abiotic TCE degradation by SZVI yields ~10% cDCE
- Abiotic cDCE degradation ~40x slower than TCE
- Biological Treatments Can Improve Outcomes for Daughters





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How long does SZVI last?

Hydrolysis Can Consume Iron

Good: $4\ Fe + C_2HCl_3 + 5\ H_2O \rightarrow 4\ Fe^{+2} + C_2H_6 + 3\ Cl^- + 5OH^-$

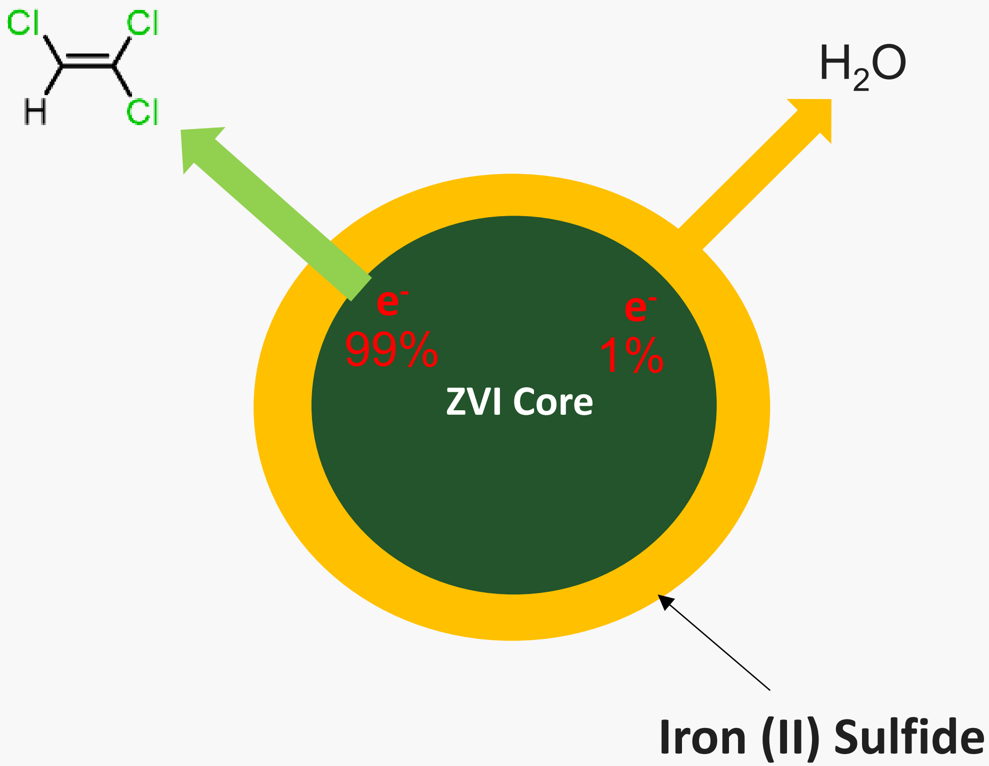
Bad: $Fe + 2\ H_2O \rightarrow Fe^{+2} + H_2 + 2\ OH^-$

Iron sulfide renders the surface of SZVI particles hydrophobic [a]

The mackinawite surface is practically hydrophobic having weak interactions with polar molecules (about - 5 kcal /mol), in contrast to the surfaces of pyrite and ZVI adsorption energies are about three times larger. Kolos et. al "A theoretical modeling of adsorption on iron sulfides toward nanoparticle modeling" Chem. Phys. Phys. Chem. (2020).

a Park et al., Particle Surface Hydrophobicity and the Dechlorination of Chloro-Compounds by Iron Sulfides, Water, Air, & Soil Pollution: Focus 6(1):97-110 · February 2006.

Sulfidated ZVI - Enhanced Electron Efficiency



- Hydrolysis of water is a competing use of electrons, resulting in:
  - Passivation
  - Low electron efficiency
- The iron sulfide layer decreases:
  - Hydrolysis
- The iron sulfide layer increases:
  - Fraction of electrons used for dechlorination [a]
  - The electron efficiency
  - Reactivity with the contaminants
  - Lifespan of effective treatment

a Fan, O'Brien et al. (2016), "Sulfidation of nZVI for Improved Selectivity during ISCR," Env. Sci. Technol:9558-9565

SMZVI Longevity: Column Study

Column Study Undertaken to Determir

How stable is the iron sulfide shell?

Iron oxides/hydroxides are more stable than FeS

FeS: ΔG_0^f -100 kJ/mol

FeO(OH): ΔG_0^f = -560 kJ/mol

What is the reactive capacity of ZVI?

TCE reduction consumes 8 electrons

Nitrate: 8 electrons

Dissolved oxygen: 4 electrons

4 Year SZVI Column Study

- 2.2 g ZVI (40 mmol) emplaced in Omnifit column
- Oxygenated TCE solution pumped upward through column

Iron/Electron Acceptor Demand

Time (months)	TCE (mg/L)	DO (mg/L)	Nitrate (mg/L)	mL solution	TCE (µmol)	DO (µmol)	Nitrate (µmol)
0-12	2	0	2	4650	71	0	150
12-19	5	4	2	2230	85	279	72
19-24	10	4	2	1620	1234	203	52
24-36	10	8	2	3630	277	908	117
36-48	20	8	2	3710	566	928	120
Total				15840	1120	2316	511

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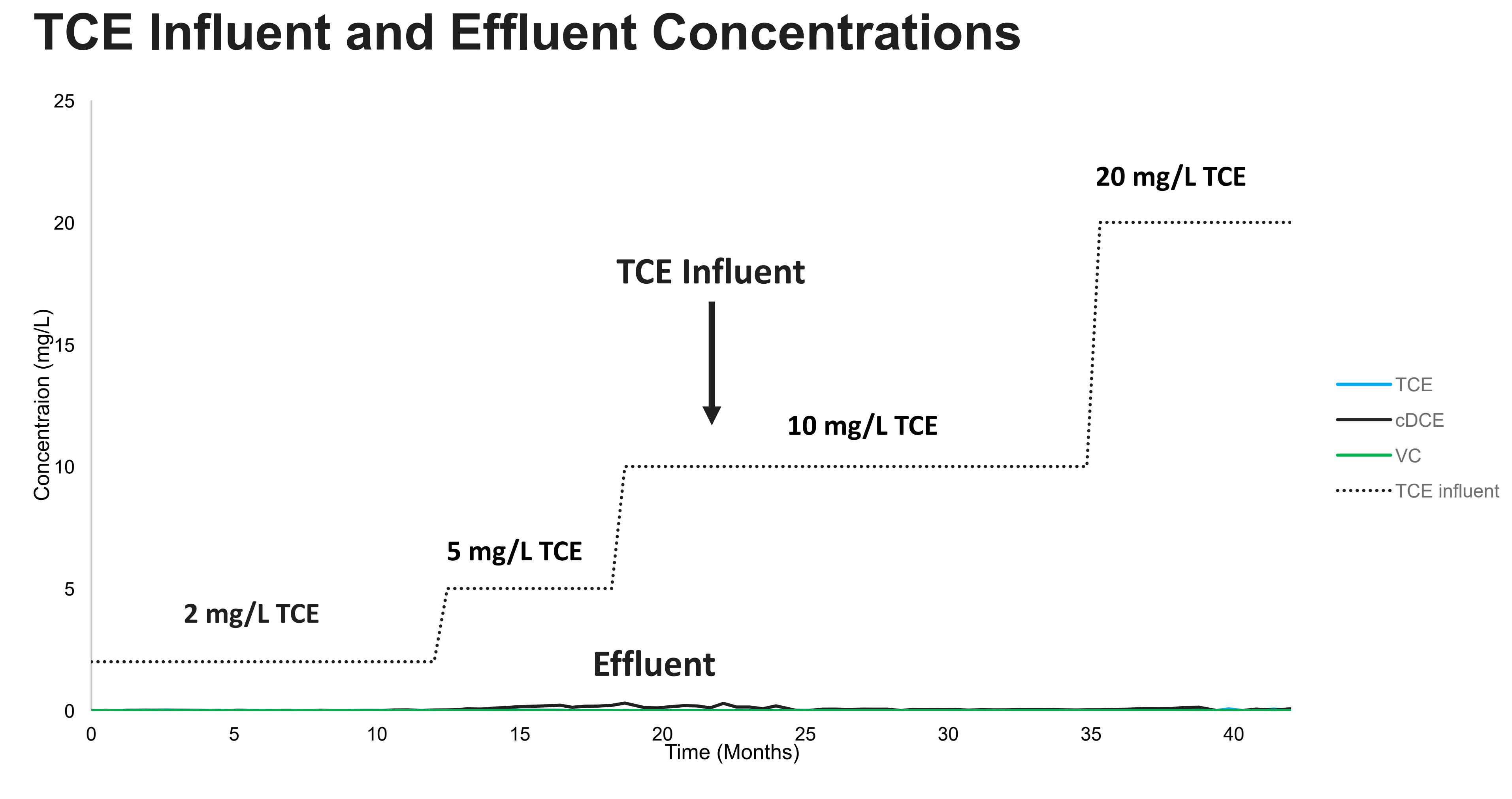
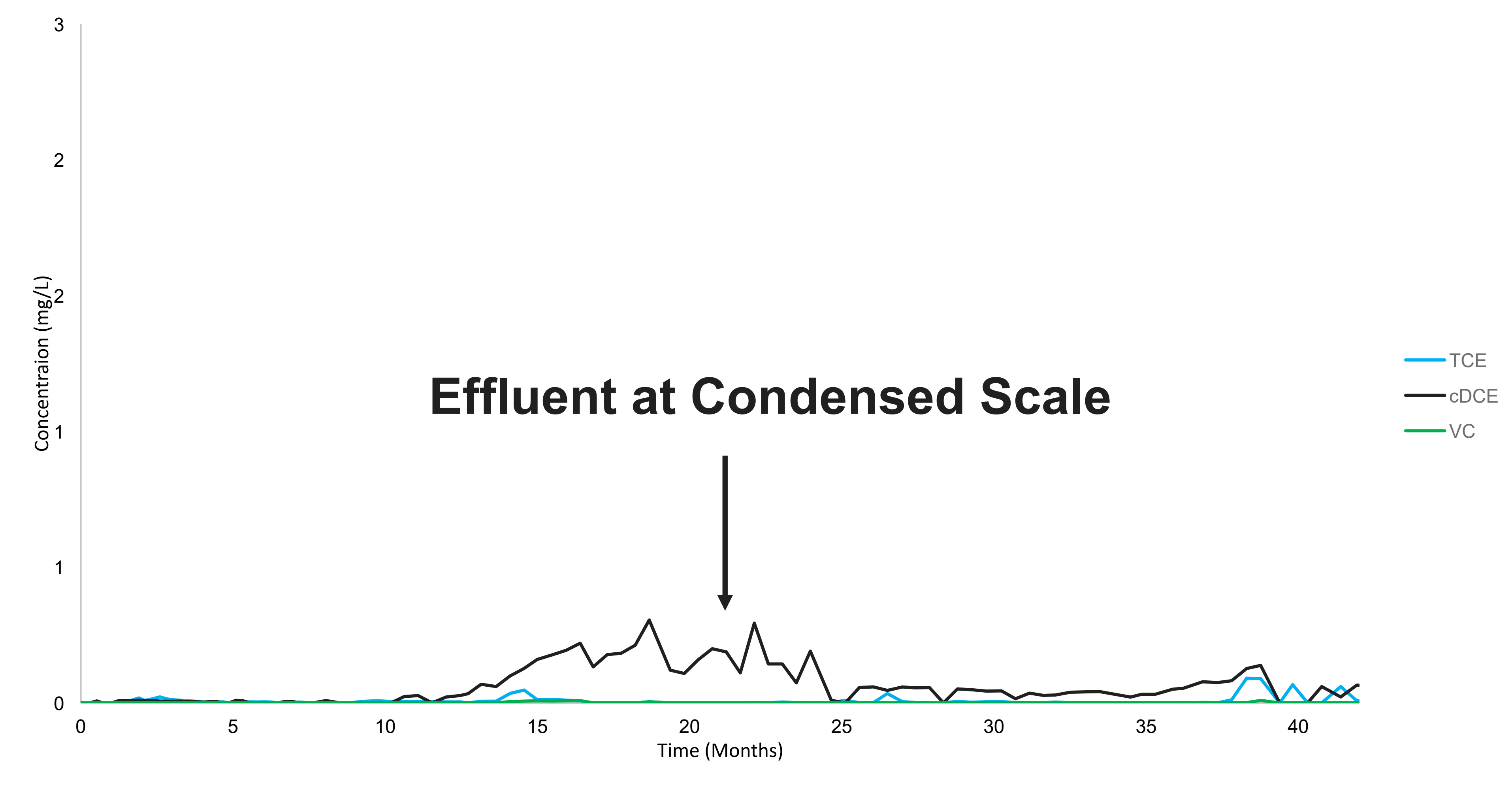
4 Year SZVI Column Study



4 Year SZVI Column Study



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4 Year SZVI Column Study

Iron/Electron Acceptor Demand in Column

TCE: 4.5 mmol Fe equivalents
DO: 4.6 mmol Fe equivalents
Nitrate: 2.0 Fe mmol Fe equivalents
Total: **11.1 mmol Fe**

Iron applied: 40 mmol

Key takeaways:

- Data suggests that the iron sulfide shell was maintained for > 4 years
- More than 27% of ZVI used to eliminate electron acceptors

Questions/Future Research

How much FeS is optimal?

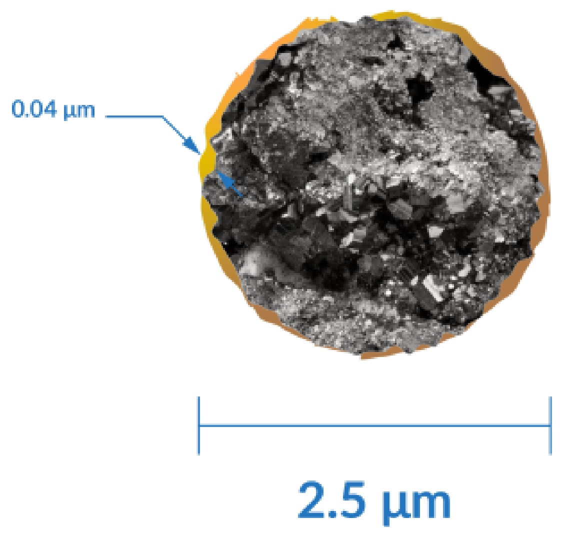
S-MicroZVI has about 4.5% FeS and 95.5 % ZVI

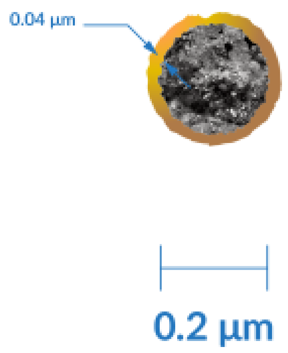
- ZVI Diameter = 2.5 µm
- Shell Thickness = 35 nm

Smaller particles need more FeS to maintain equivalent shell

- NZVI Diameter = 0.2 µm
- Shell Thickness = 35 nm
- Requires 40% FeS/60% ZVI

Inherent issues with SNZVI





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Questions/Future Research

Electron transfer mechanism

ZVI core oxidizes: $Fe \rightarrow Fe^{+2} + 2e^{-}$

How is charge neutrality maintained?

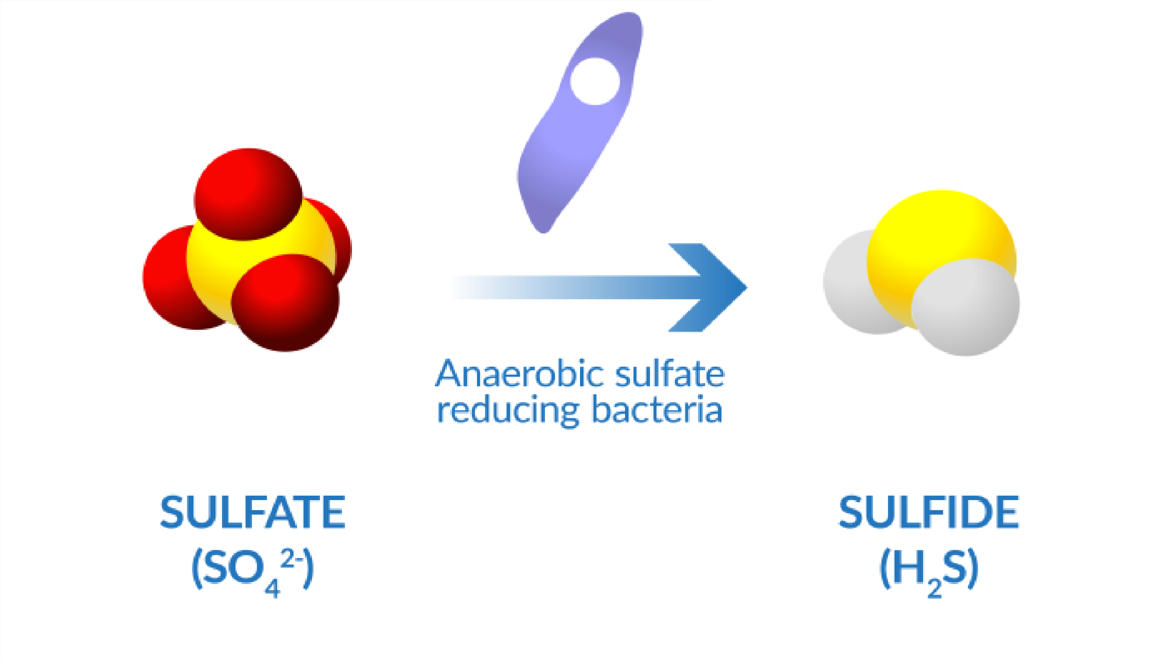
- Fe^{+2} from core into solution?
- O^{-2} from solution into core?
- S^{-2} from solution into core?

  Best case scenario

Questions/Future Research

Does the FeS shell regenerate?

- Native sulfate + microbes + organic electron donor



SZVI Best Practices

Abiotic Reactions Occur in the Aqueous Phase

- DNAPL Remediation uses combinations SZVI and Emulsified Oils

Kinetics Parents > Kinetics Daughters

- Permeable Reactive Barriers use combinations of activated carbon and SZVI

Avoid Acidic Groundwater

SZVI Best Practices

Effective Remediation Requires a Combination of:

- Reactivity
- Persistence/Longevity
- Amendment Distribution
- Safety/Ease of Use
- Design Experience
- Exploit Synergies with other Amendments

Questions?

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