REGENESIS®

Optimizing ZVI Formulations for the Degradation of Chlorinated Hydrocarbons: Effects of Composition and Particle Size

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ZVI Assisted Biodegradation:

PCE to Ethene - Simple Equation:

$$C_2Cl_4 + 4\ H^+ + 8\ e- \rightarrow C_2H_4 + 4\ Cl-$$

PCE → TCE → c-1,2-DCE → VC → ethene (Hydrogenolysis)

But…This pathway involves toxic daughter products

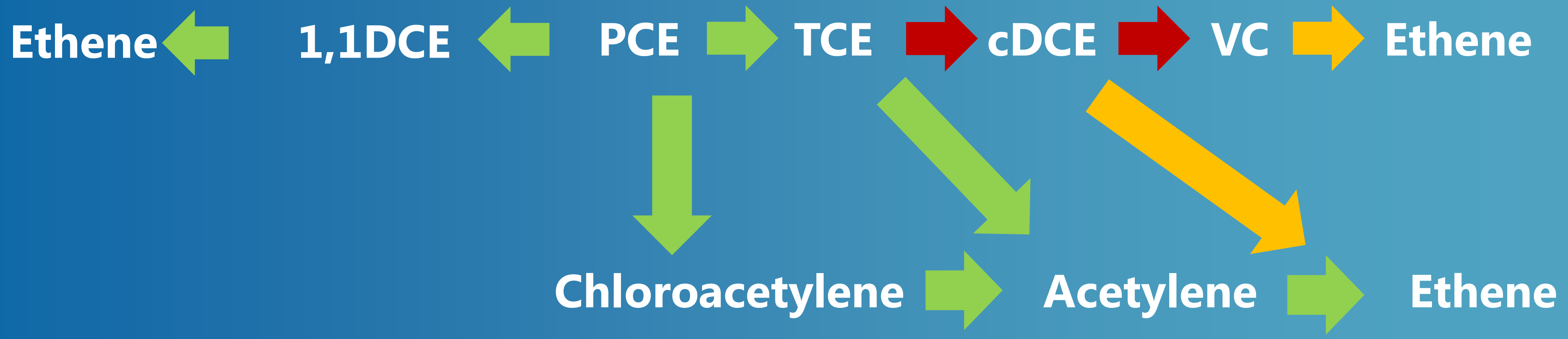
ZVI Facilitates Abiotic Degradation - TCE:

Alpha Elimination - Favorable

Avoids recalcitrant daughter products

Hydrogenolysis – Unfavorable

Involves recalcitrant daughter products



Beta Elimination / Hydrogenation - Favorable

Avoids recalcitrant daughter products

ZVI Facilitates Abiotic Degradation - TCA:

Beta / Alpha - Favorable
Avoids recalcitrant daughter products

Hydrogenolysis / Alpha – Unfavorable
Involves recalcitrant daughter products

Ethene ← **1,1-DCE** ← **1,1,1-TCA** → **1,1-DCA** → **Ethane**

↓

Ethane

Alpha- Favorable
Avoids recalcitrant daughter products

Other Reactions:

ZVI with water – Undesirable

$Fe^0 + 2\ H_2O \rightarrow Fe^{+3} + 1.5\ H_2 + 3\ OH^-$ **Wasted electons**

Then, subsequently

$Fe^{+3} + 3\ OH- \rightarrow$ **$Fe(OH)_3$** – passivating oxides / oxyhydroxides

ZVI with sulfate - Desirable

$4\ Fe + 4\ H_2O + SO_4^{-2} \rightarrow$ **FeS** $+ 8\ OH^-$

Iron sulfide is reactive

Objective:

Engineer ZVI System to Maximize Rates of Reductive Dechlorination

Catalyzed ZVI can promote accelerated reactivity and favorable reaction pathways

Precious metals (e.g. Pd):

- **Very effective** with chlorinated ethenes
- **Expensive**: 0.02% Pd = ~ $3/lb ZVI
- Subject to **catalyst poisoning** and limited persistence

Base metals (e.g. Cu, Ni):

- **Effective** in laboratory tests
- **Toxicity** concerns
- Subject to **catalyst poisoning** and limited persistence

Objective:

Engineer ZVI System to Maximize Rates of Reductive Dechlorination

Catalyzed ZVI can promote accelerated reactivity and favorable reaction pathways

IRON SULFIDE

Fe^0

Iron Sulfide:

- **Very Effective** in laboratory tests with chlorinated ethenes
- **Inhibits** reactions with water – better reactive capacity & persistence
- **Inexpensive**
- Resistant to catalyst **poisoning**
- Limited data on **persistence**

Experimental Objectives:

- Quantify TCE kinetic enhancement for sulfidated ZVI
- Quantify TCE kinetics for different sizes of sulfidated ZVI
- Explore reactivity enhancements for 1,1,1-TCA

TCE - Experimental Objectives:

TCE: Compare performance of different sulfidated materials

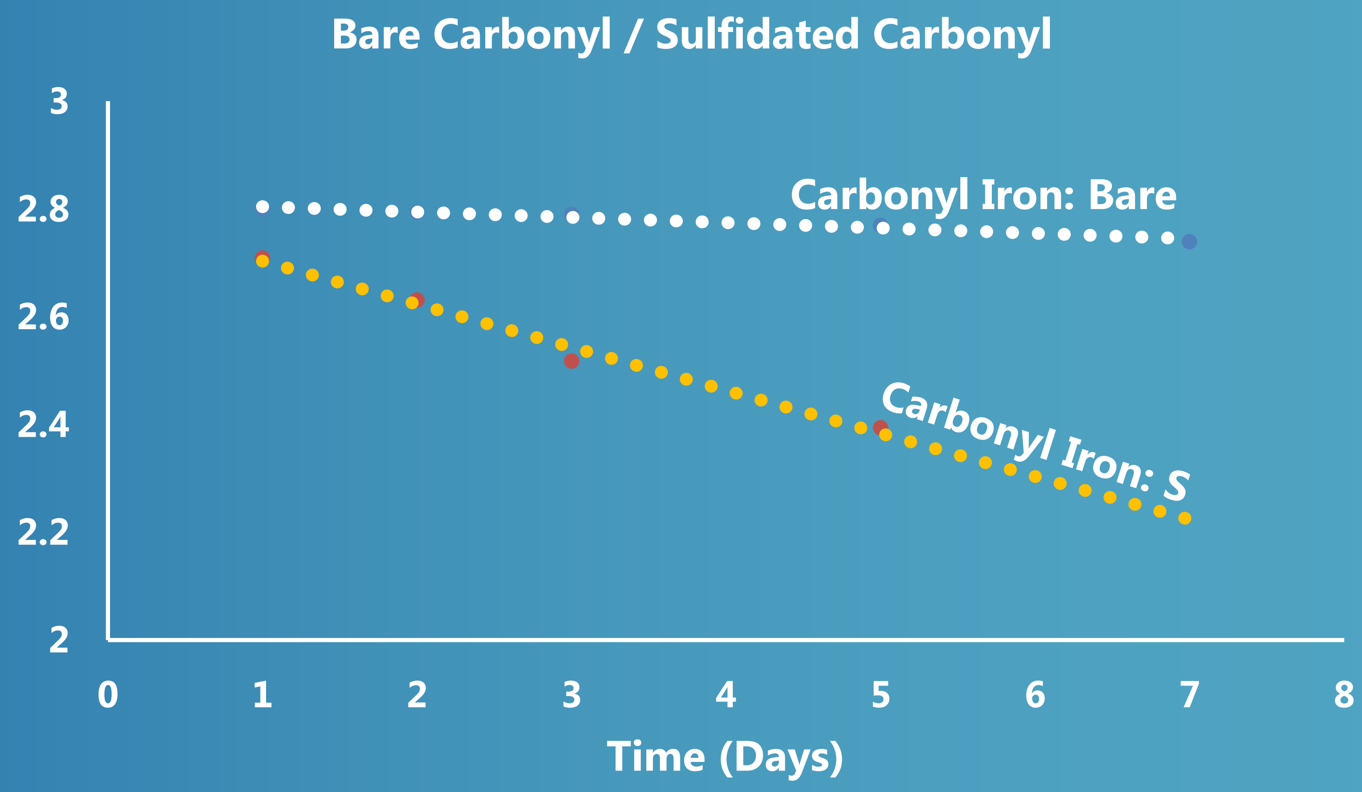
- REGENESIS AquaZVI™ : 2 µm ZVI in water-based carrier w/ sulfide
- REGENESIS MicroZVI™: 2 µm ZVI in glycerol carrier w/ sulfide
- Dry Carbonyl iron: ~4 µm ZVI (with and w/o lab-applied sulfide)
- Dry Microscale iron: Sub-100 µm (with and w/o lab-applied sulfide)
- Iron filings: Sub-350 µm (with and w/o lab-applied sulfide)

TCE - Effect of Sulfidation:

Carbonyl iron: 8x rate enhancement

Bare CIP K_m = 0.01 $(L/g^{-1}/d^{-1})$

CIP:S K_m = 0.08 $(L/g^{-1}/d^{-1})$

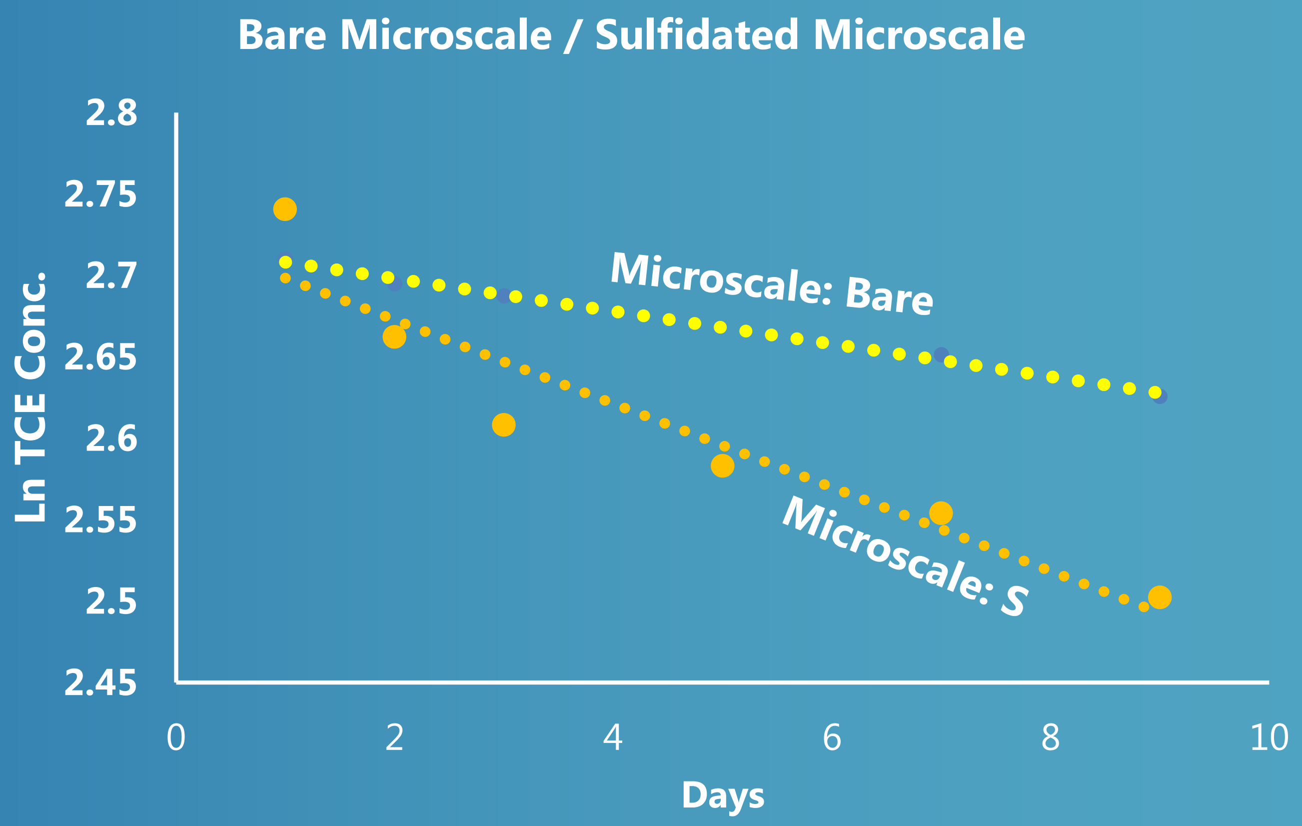


TCE - Effect of Sulfidation:

Microscale Iron: 2.6x rate enhancement

Bare Microscale K_m = 0.01 ($L/g^{-1}/d^{-1}$)

Microscale: S K_m = 0.026 ($L/g^{-1}/d^{-1}$)



TCE - Effect of Particle Size:

Sulfidated species are observed to perform better for TCE degradation – Now lets compare degradation in relation to particle size of lab-sulfidated iron materials

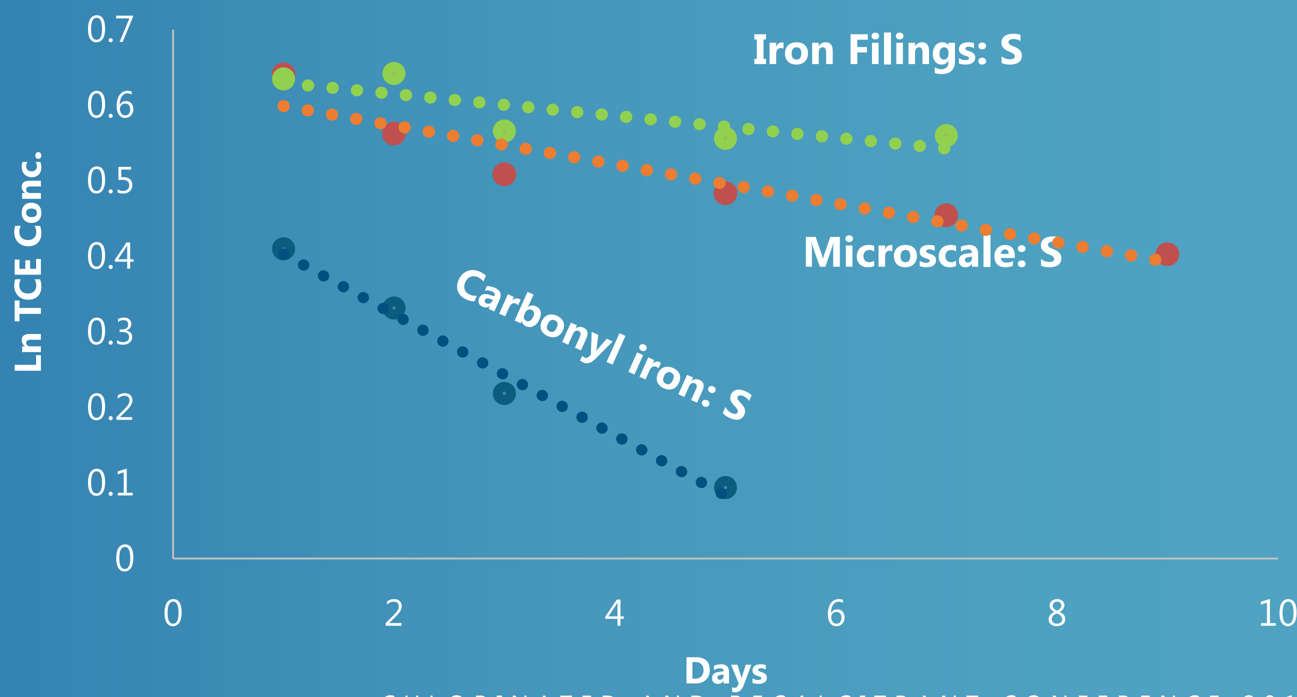
Iron filings: S K_m = 0.015 ($L/g^{-1}/d^{-1}$)

Microscale: S K_m = 0.026 ($L/g^{-1}/d^{-1}$)

Carbonyl iron K_m = 0.08 ($L/g^{-1}/d^{-1}$)

CIP 3x Microscale 1.8x Filings
4 µm sub-100 µm sub-350 µm

Relationship Between Particle Size and TCE Kinetics



TCE - Combining Benefits:

- We see that small particle size ZVI benefits TCE degradation
- Similarly, sulfidation enhances reactivity with TCE while halting competing reactions with water, carbonates, etc.

MicroZVI™ AquaZVI™

Engineered products featuring small particle size ZVI with surface preparation and sulfidation done during manufacturing.

TCE Kinetics:

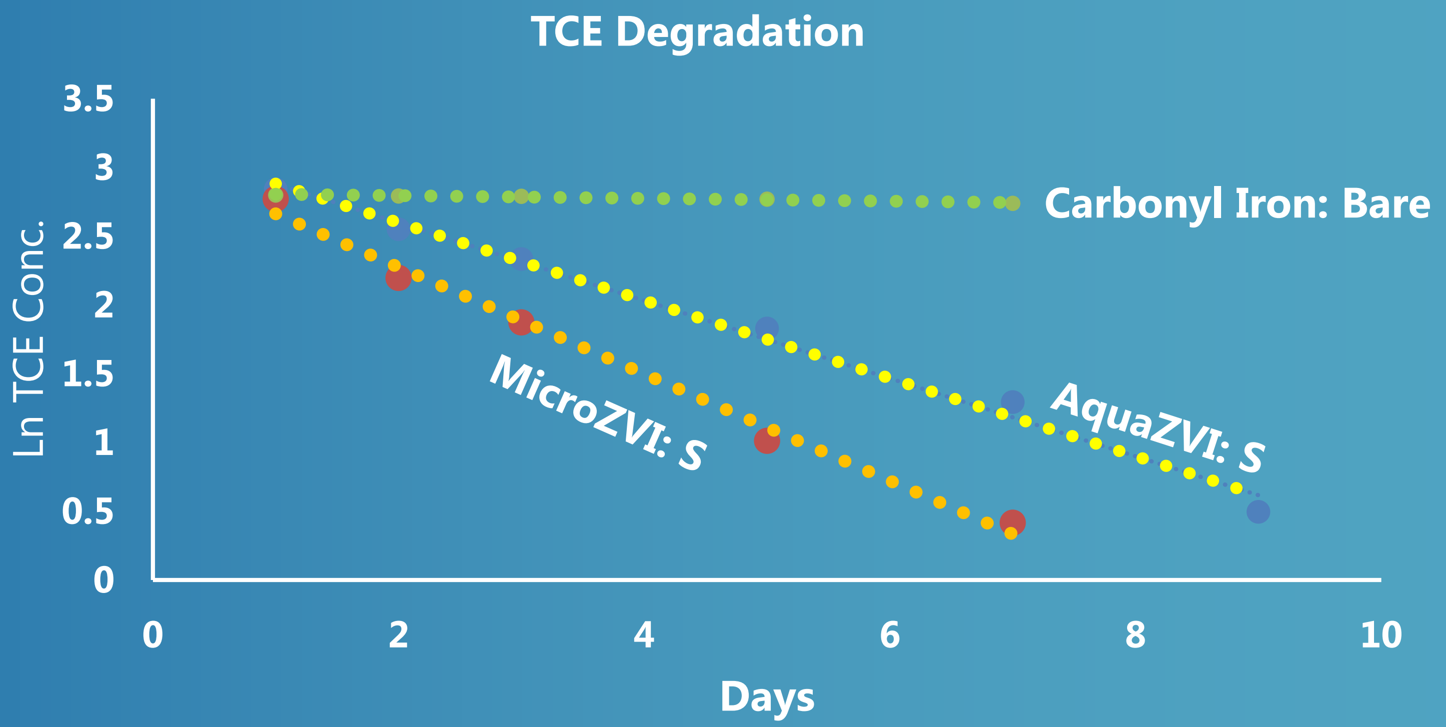
MicroZVI™ with sulfide – 38x bare Carbonyl iron

AquaZVI™ with sulfide – 28x bare Carbonyl iron

AquaZVI K_m = 0.28 ($L/g^{-1}/d^{-1}$)

MicroZVI:S K_m = 0.39 ($L/g^{-1}/d^{-1}$)

Carbonyl K_m = 0.01 ($L/g^{-1}/d^{-1}$)



TCA - Experimental Objectives:

TCA: Compare performance of sulfidated material

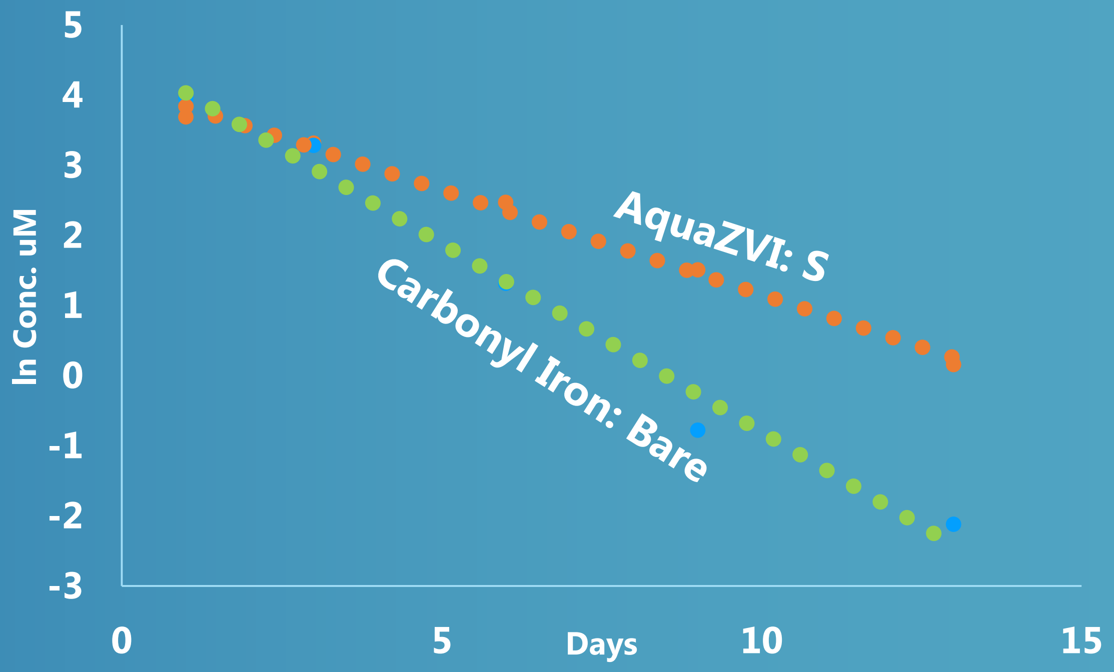
- REGENESIS AquaZVI™: 2 µm ZVI in water-based carrier w/ sulfide
- Dry Carbonyl iron: ~4 µm ZVI bare iron - no sulfide

1,1,1-TCA – Kinetics:

AquaZVI™ compared to bare carbonyl iron

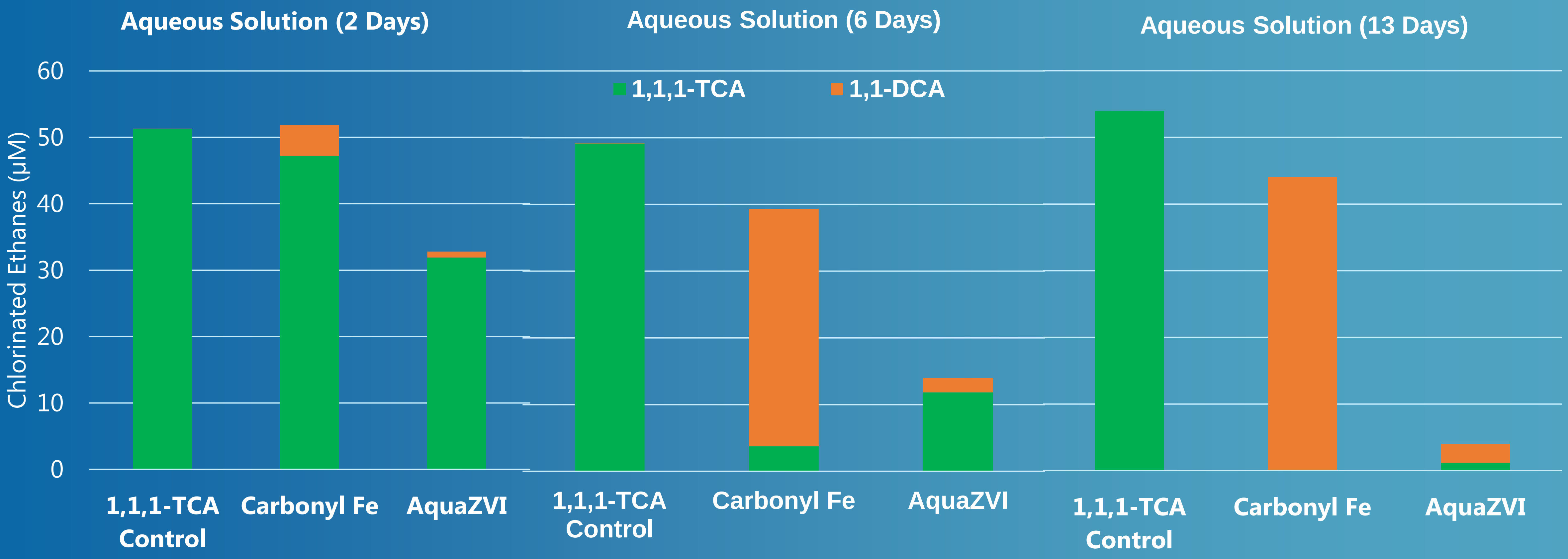
Bare Carbonyl Iron $K_m = 0.54$ (L/g^{-1}/d^{-1})

AquaZVI™ $K_m = 0.29$ (L/g^{-1}/d^{-1})



Bare iron degrades 1,1,1-TCA faster than sulfidated iron – opposite result of TCE

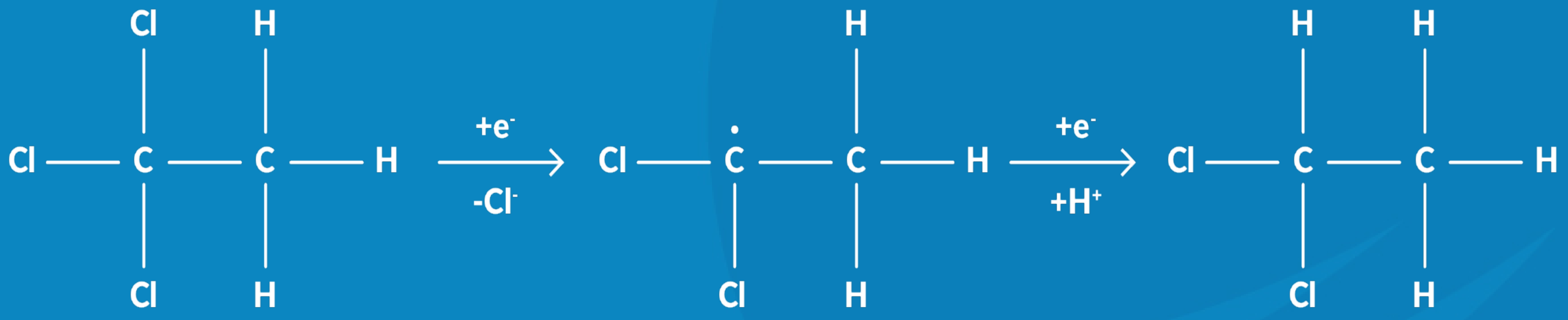
1,1,1-TCA – Degradation Products



1,1,1-TCA – Degradation Pathway

Proposed degradation pathway: Bare iron

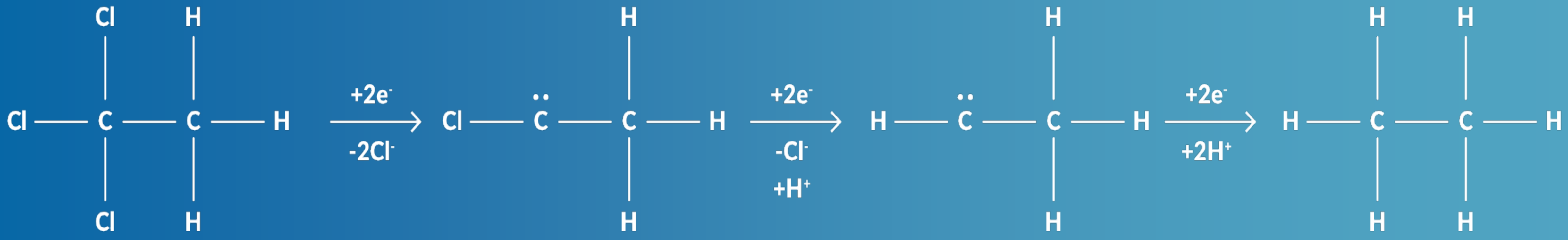
1,1,1-TCA to 1,1-DCA



1,1,1-TCA – Degradation Pathway

Proposed degradation pathway: Sulfidated iron

1,1,1-TCA to Ethane



Conclusions

TCE

- Sulfidation of commodity iron produces modest kinetic enhancement: ~ 2-8 times
- Smaller particle size products provide kinetic enhancement up to 6 times
- Engineered ZVI (AquaZVI, MicroZVI) greatly outperforms commodity iron: ~30-40 times kinetic enhancement
- No evidence of altered degradation pathway – primarily beta elimination

Conclusions

1,1,1-TCA

- Parent compound degrades rapidly, bare iron slightly faster than sulfidated iron

- Sulfidated iron beneficially alters degradation pathway using radicals

Questions?

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