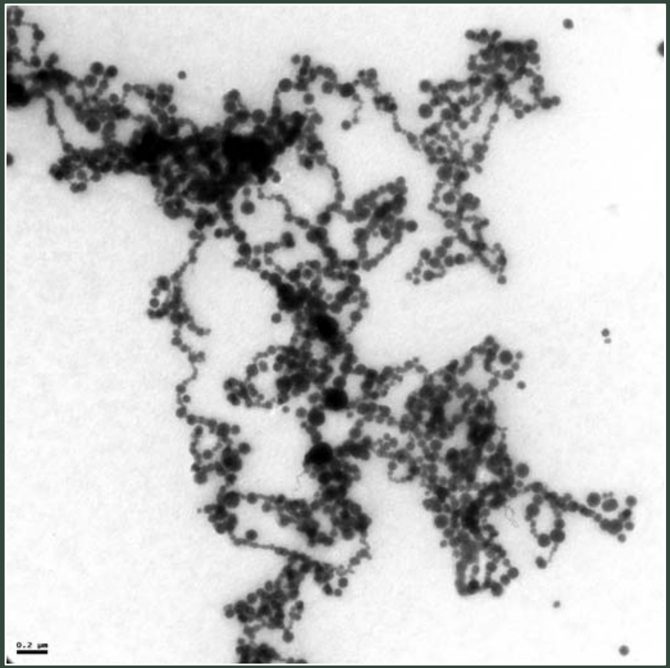
Treatment of Chlorinated Solvents by Copper-Amended Nanoscale Zero-Valent Iron Stabilized with Carboxymethylcellulose



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Outline

- Introduction
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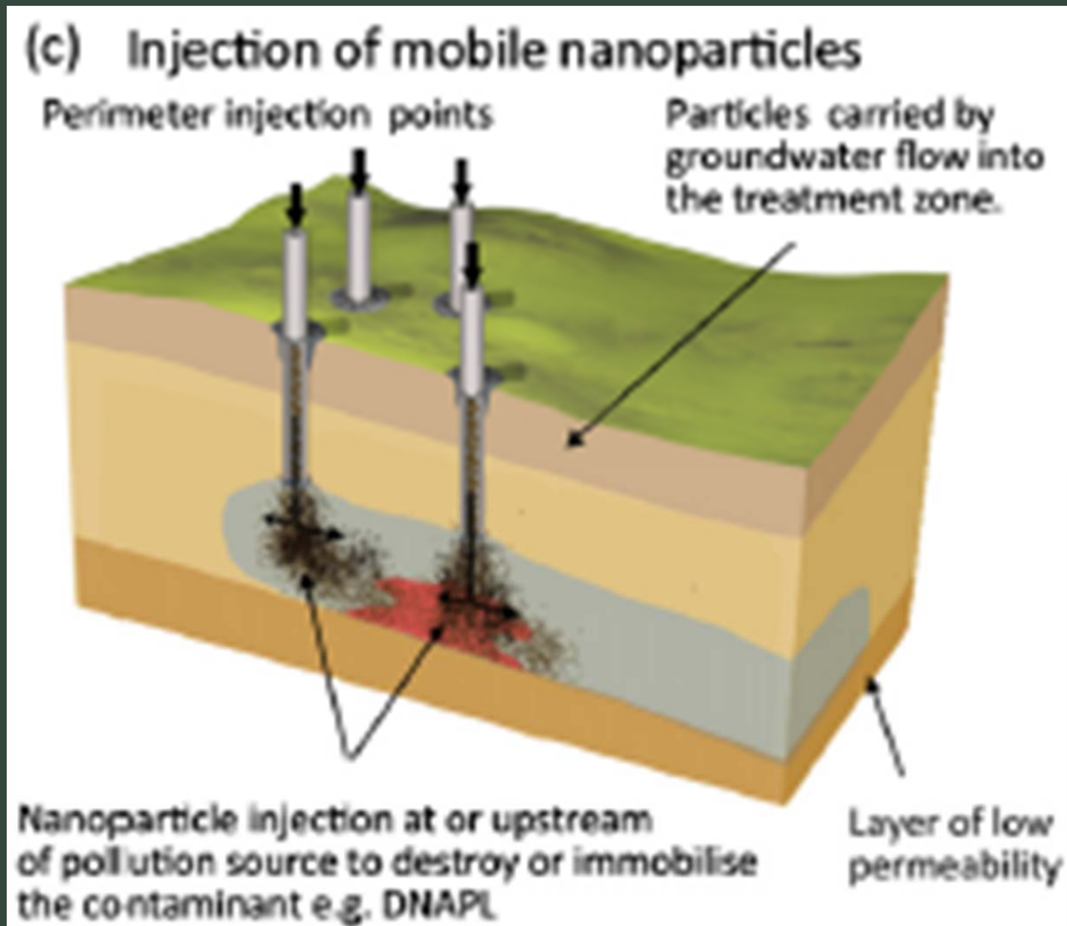
  - Degradation kinetics
  - Degradation byproducts
- Conclusions

Aquifer Remediation by nZVI Injection



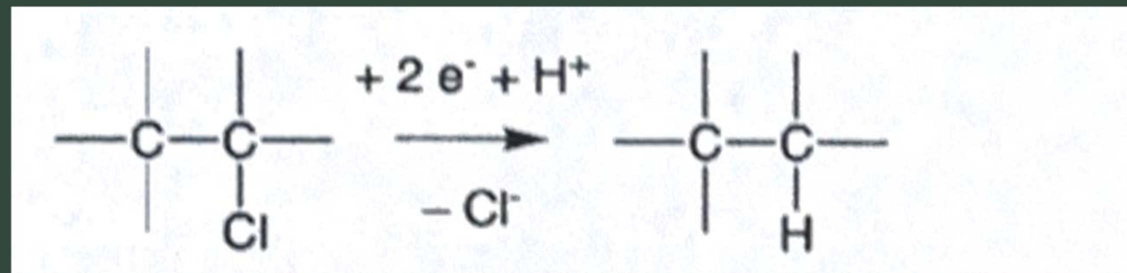
(Crane and Scott, 2012)

nZVI Enhancements

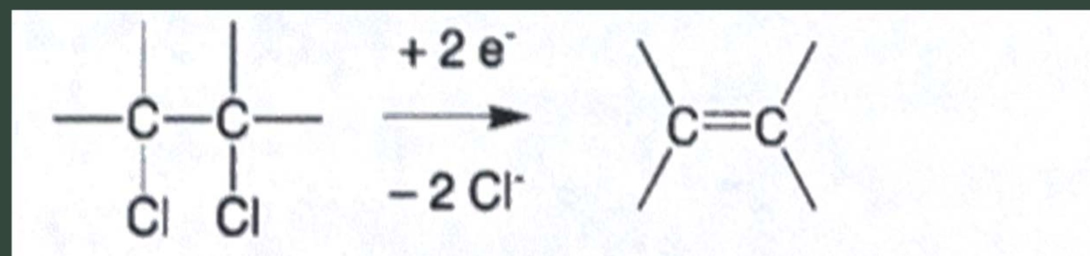
- Stabilization
  - Magnetic and van der Waals forces cause agglomeration
  - Polyelectrolyte stabilizers, such as CMC, can reduce agglomeration
- Secondary Metal Catalyst
  - Enhance degradation kinetics
  - Palladium, platinum, nickel, silver, gold, and copper
  - Copper has received little attention thus far; relatively low toxicity
- CMC stabilized Cu-nZVI is a novel formulation for faster destruction

nZVI Reactions with CHCs

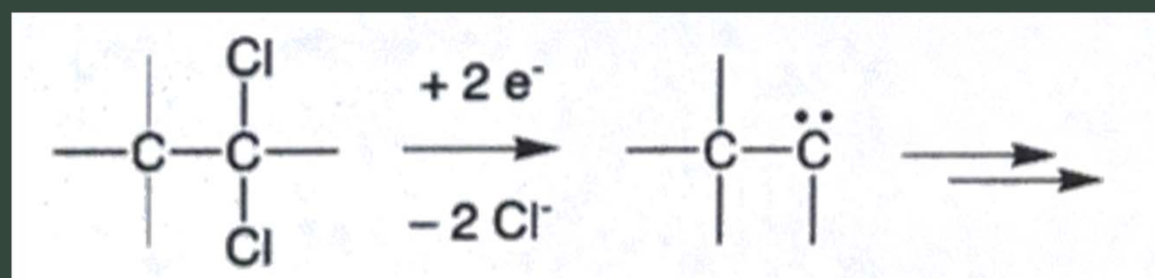
- Hydrogenolysis



- Dichloroelimination

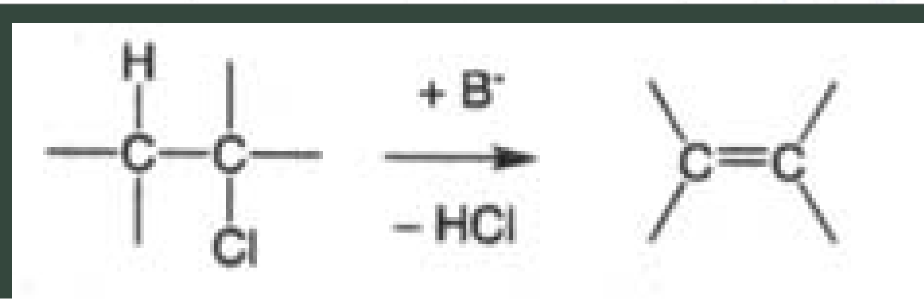


  - β-elimination



  - α-elimination

- Dehydrohalogenation



Research Objectives

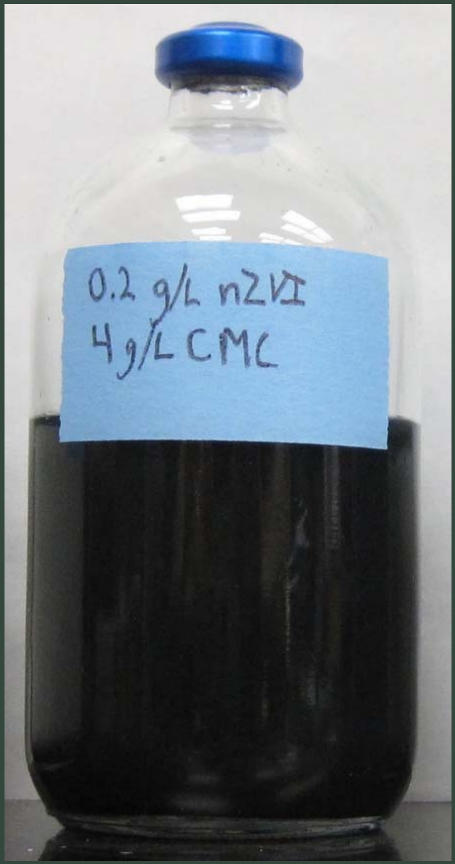
- Compare Cu-nZVI and nZVI systems
  - Evaluate the effect of Cu loading
  - Measure degradation kinetics
  - Identify degradation pathways and mechanisms

Methods: nZVI Synthesis

- Modified Borohydride Method
  (Song and Carraway, 2005)
- Reagents:
  Iron sulfate heptahydride, copper chloride, sodium borohydride, CMC (MW: 90,000), and TAPSO Buffer
- Prepared in anaerobic chamber
- Step 1: Fe^{2+}, Cu^{2+}, and CMC solutions allowed to complex for 15 minutes
- Step 2: Buffer and $NaBH_4$ added

Methods

- Batch experiments
  - Add CHC to nZVI reactor bottle
  - Measure CHC degradation with time
  - Head space analysis
  - Duplicate reactors plus a control
- Experimental conditions
  - 96 mL aqueous, 64 mL head space
  - Buffered pH 7 for all experiments
  - 0.05 or 0.2 g/L nZVI for most experiments
  - 5% Cu for most experiments
- Analytical methods
  - 7890 GC system; Agilent Technologies
- Data treatment
  - Pseudo first-order rate modeling k_{obs}
  - Dynamic kinetics k_{obs1} and k_{obs2}
  - k_M is the mass normalized rate constant

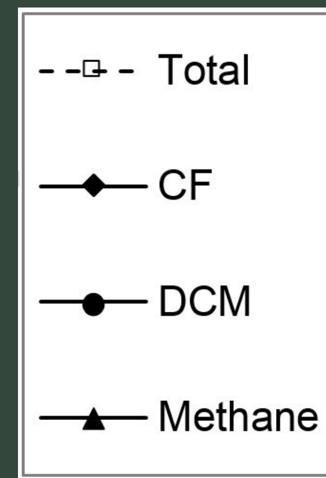


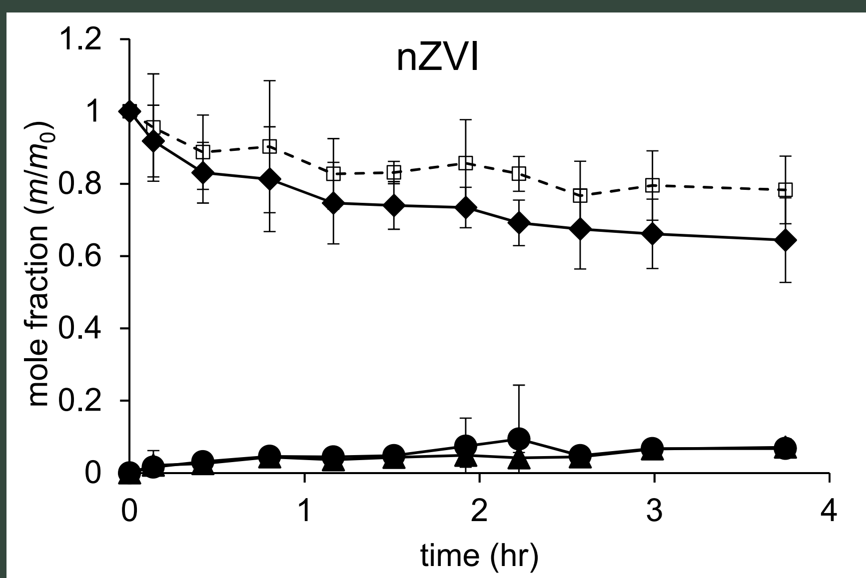
Results and Discussion

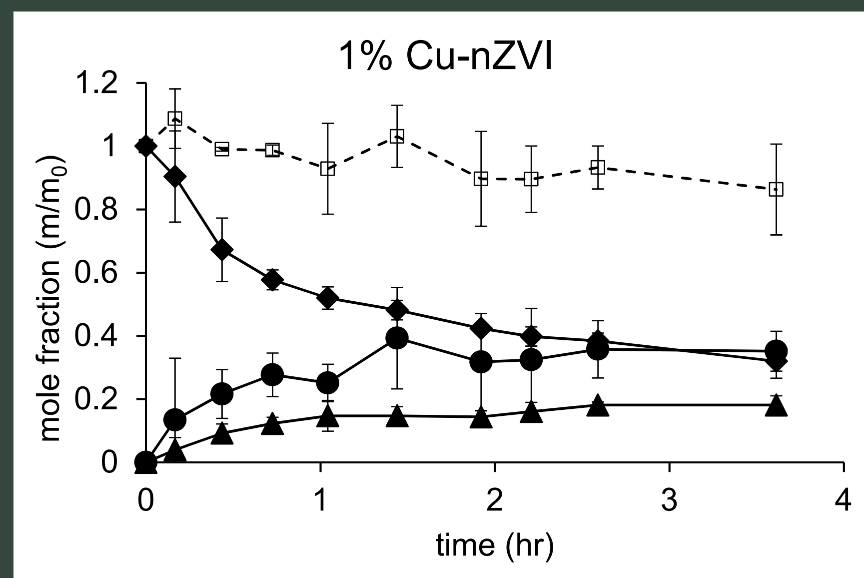
- Performance of Cu-nZVI vs. nZVI for various chlorinated solvents
- Effect of increasing Cu loading
- Particle longevity

CF degradation by nZVI and Cu-nZVI

- nZVI (k_{M1} = 8.60; k_{M2} = 0.17) (L g^{-1} hr^{-1})
- Cu-nZVI (k_{M1} = 18.6; k_{M2} = 0.47) (L g^{-1} hr^{-1})
- DCM forms via hydrogenolysis
- Methane forms via direct transformation

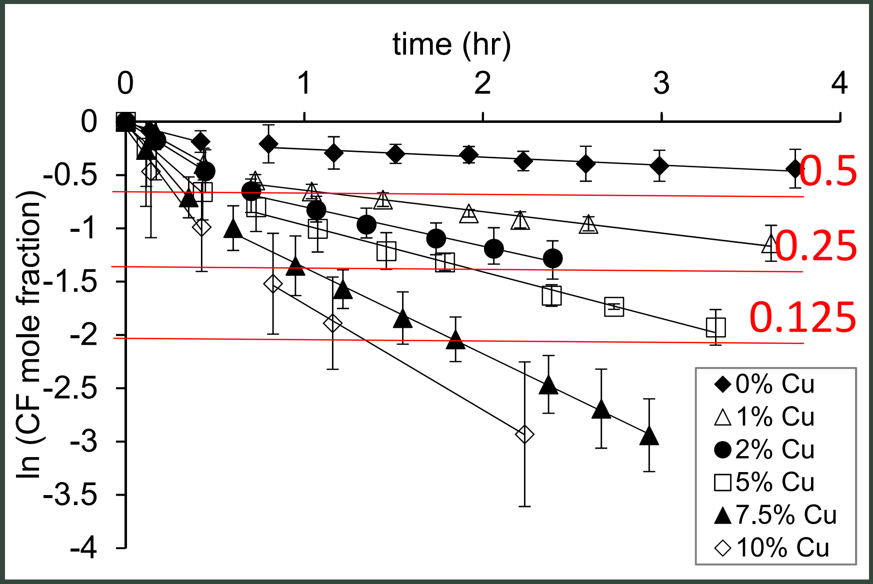


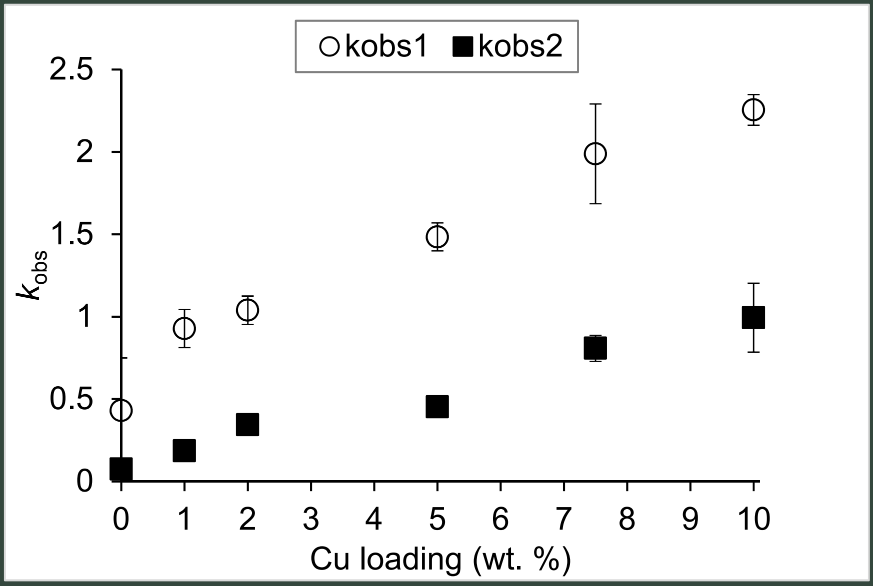




CF degradation by Cu-nZVI:
Cu loading effect on kinetics

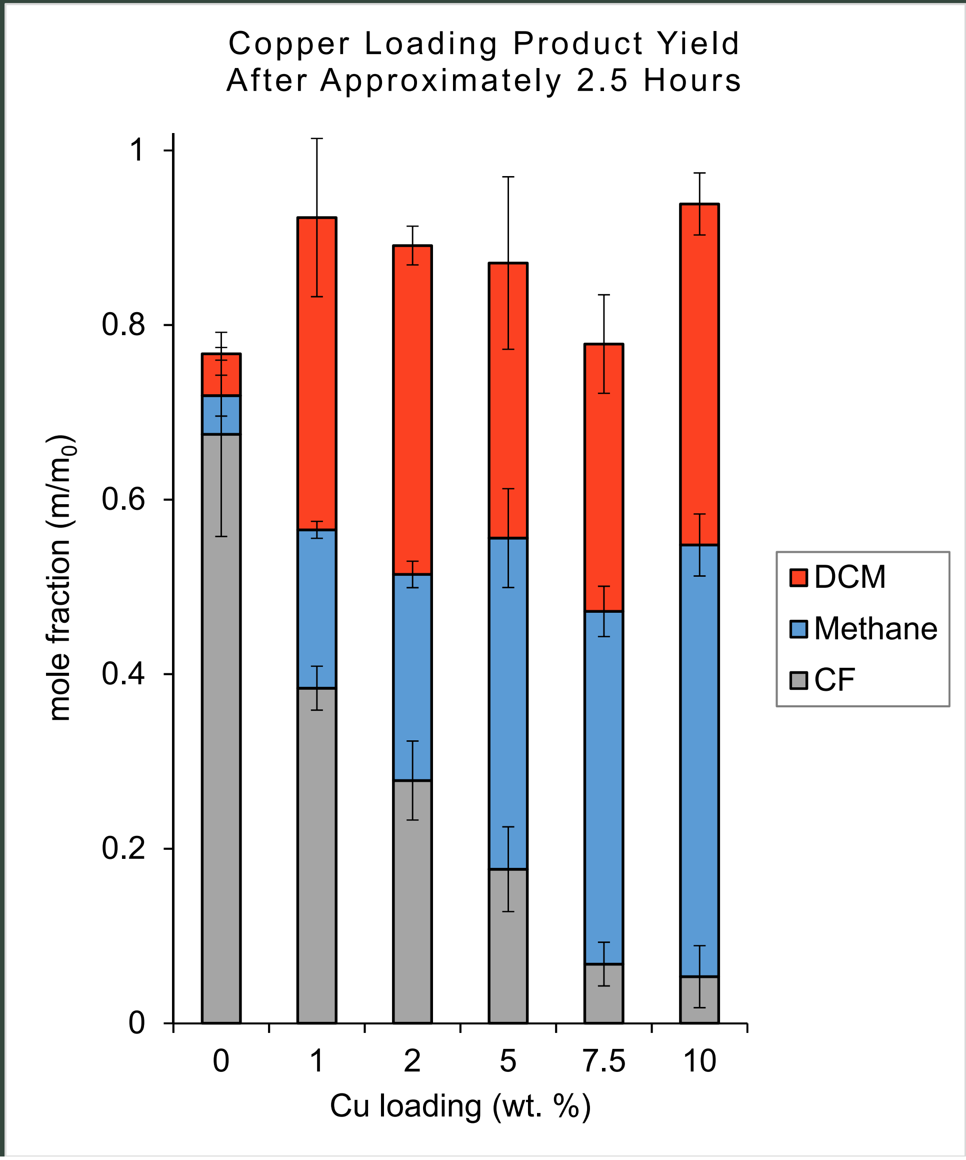
- Bimodal kinetics with nZVI and Cu-nZVI;
  - $k_{obs1} > k_{obs2}$
- Positive correlation between Cu loading and k_{obs}



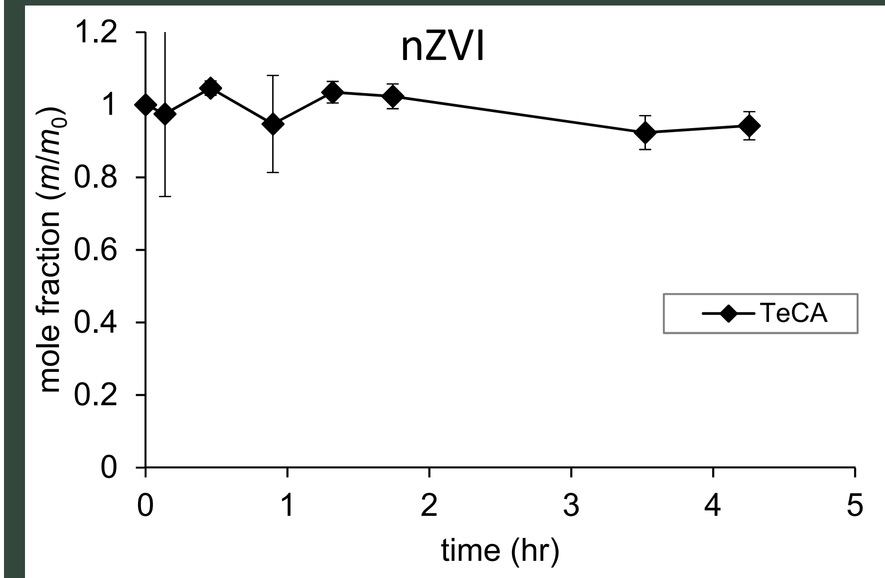


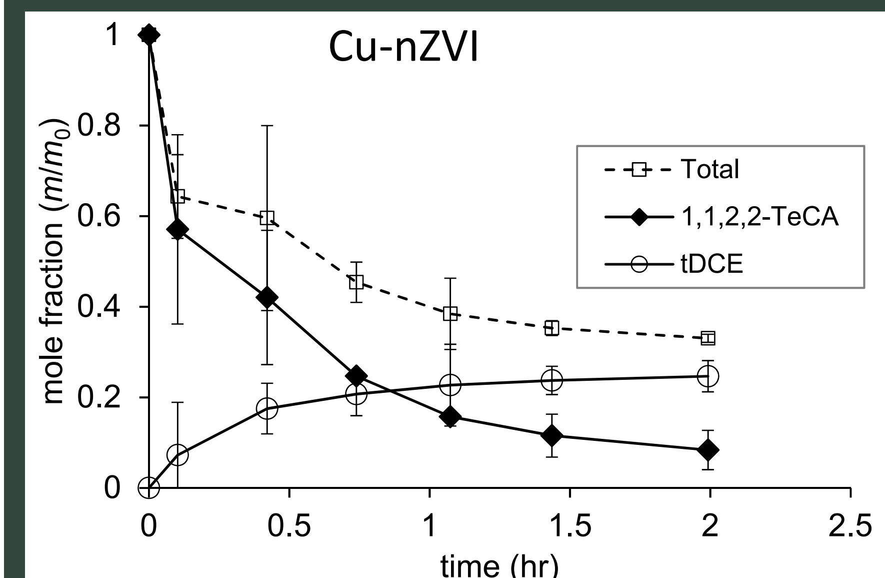
CF degradation by Cu-nZVI:
Cu loading effect on products

- Product distribution after 2.5 hrs
- C mass balance: ~85%
- DCM: ~35%
- Methane increases with increase in Cu loading
- Greater Cu loading favors the reaction pathway directly to methane



1,1,2,2-TeCA degradation by Cu-nZVI



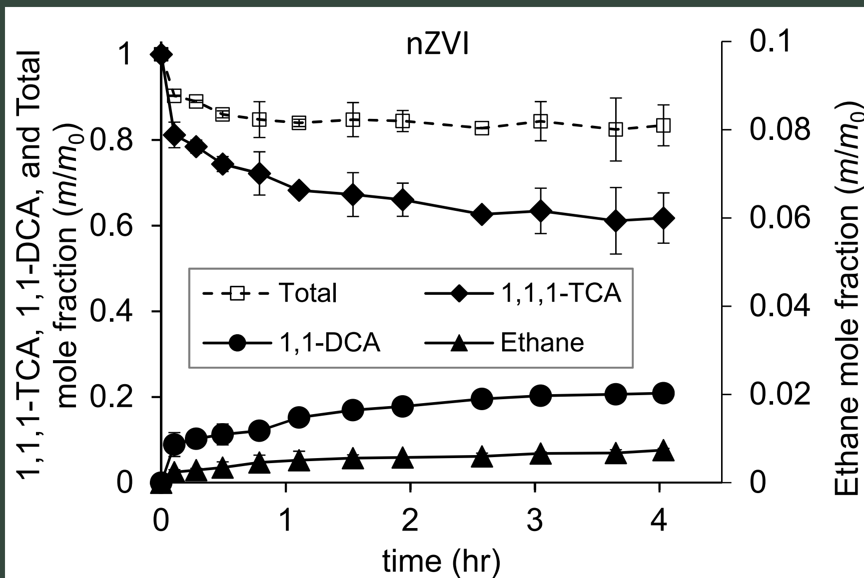


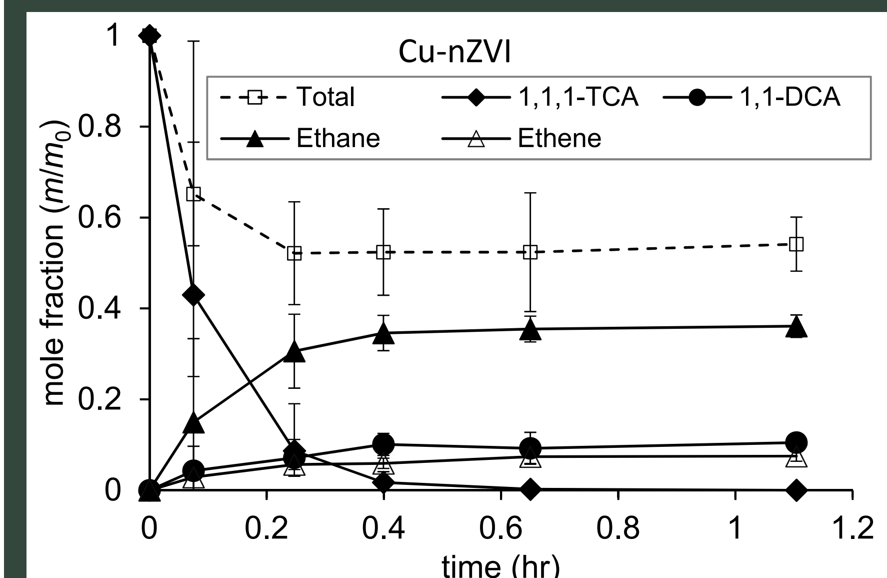
- nZVI show no significant degradation of 1,1,2,2-TeCA
- However, 1,1,2,2-TeCA degraded with Cu-nZVI
- k_{M1} = 4.80; k_{M2} = 4.21 (L g^{-1} hr^{-1})
- *trans*-DCE was the major byproduct (via β-elimination)
- Trace amounts of TCE (<1%) form via dehydrohalogenation
- Some products below detection

1,1,2,2-TeCA degradation by nZVI

- Song and Carraway (2005) studied 1,1,2,2-TeCA degradation
    - unstablized nZVI, in buffered system
    - Reported TCE and trans-DCE as products
    - k_M = 0.84 L g^{-1} hr^{-1}
- Degradation rate constant (k_M) with Cu-nZVI ~5-fold greater

1,1,1-TCA degradation by Cu-nZVI

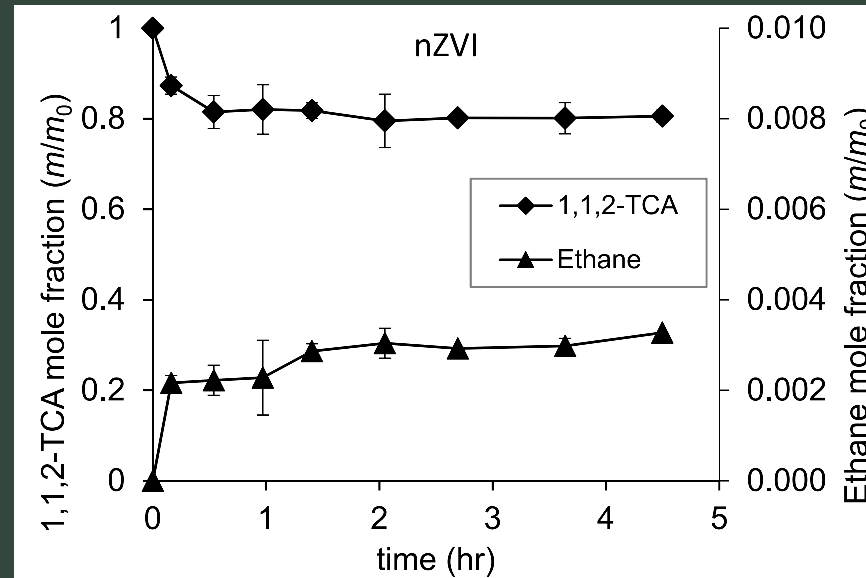


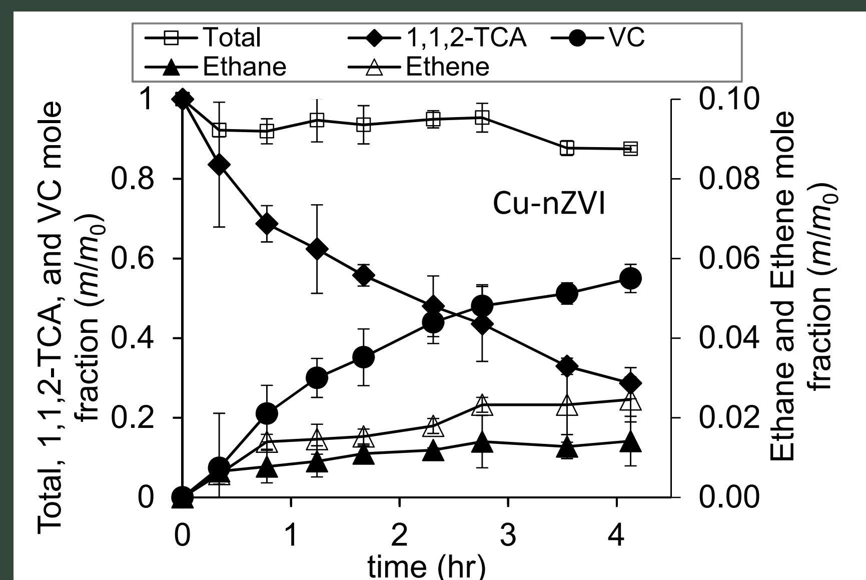


- 1,1,1-TCA degradation with Cu-nZVI was much more efficient than with nZVI
- With nZVI: k_{M1} = 3.99; k_{M2} = 2.58 (L g^{-1} hr^{-1})
- With Cu-nZVI: k_{M1} = 48.9; k_{M2} = 29.3 (L g^{-1} hr^{-1})
- Ethane was the major byproduct (36%), whereas 1,1-DCA and ethene were minor byproducts (<10%)
- Pd-nZVI (Cho and Choi, 2010) (k_M = 0.46)
  - 0.1 g/L nZVI and 0.1wt.% Pd
  - 1,1,1-TCA more difficult to degrade than PCE and TCE

1,1,2-TCA degradation by Cu-nZVI

- nZVI show no significant degradation of 1,1,2-TCA, yet it degraded with Cu-nZVI
- With nZVI: k_{M1} = 1.74; k_{M2} = 0.025 (L g^{-1} hr^{-1})
  - Trace levels of ethane via direct transformation
- With Cu-nZVI: k_{M1} = 2.41; k_{M2} = 1.37 (L g^{-1} hr^{-1})
  - VC is major product by dichloroelimination (α- or β-)
  - Ethene via direct transformation or hydrogenolysis of VC
  - Ethane via direct transformation



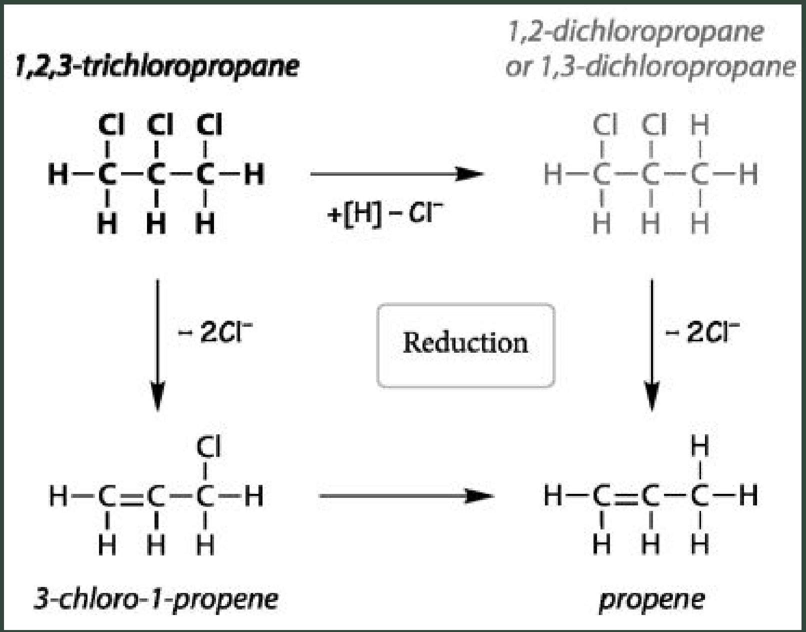


1,1,2-TCA degradation by nZVI

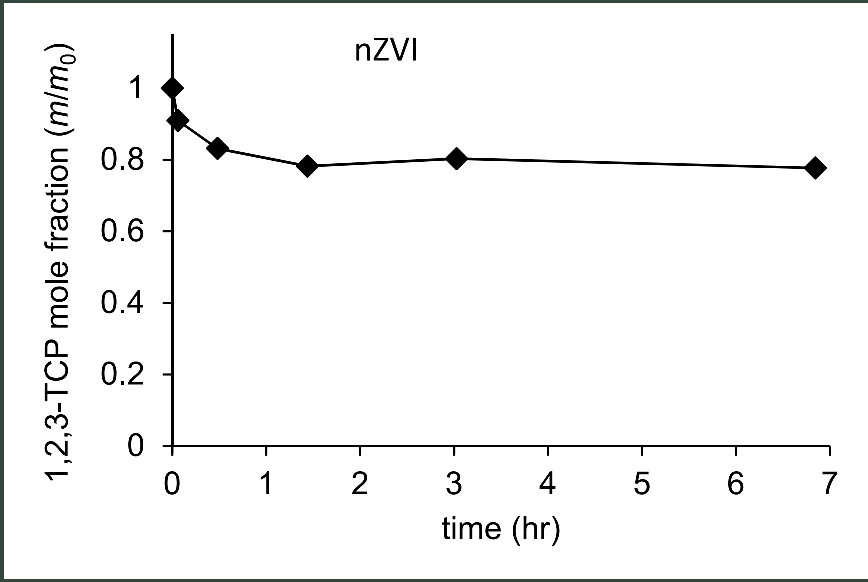
- Song and Carraway (2005) studied 1,1,2-TCA degradation
  - unstablized nZVI, in buffered system
  - Reported ethene as product
  - k_M = 0.065 L g^{-1} hr^{-1}
- Degradation rate constant with Cu-nZVI was 37-fold and 21-fold faster, for k_{M1} and k_{M2} respectively
- VC as byproduct is not desirable, but it may further degrade

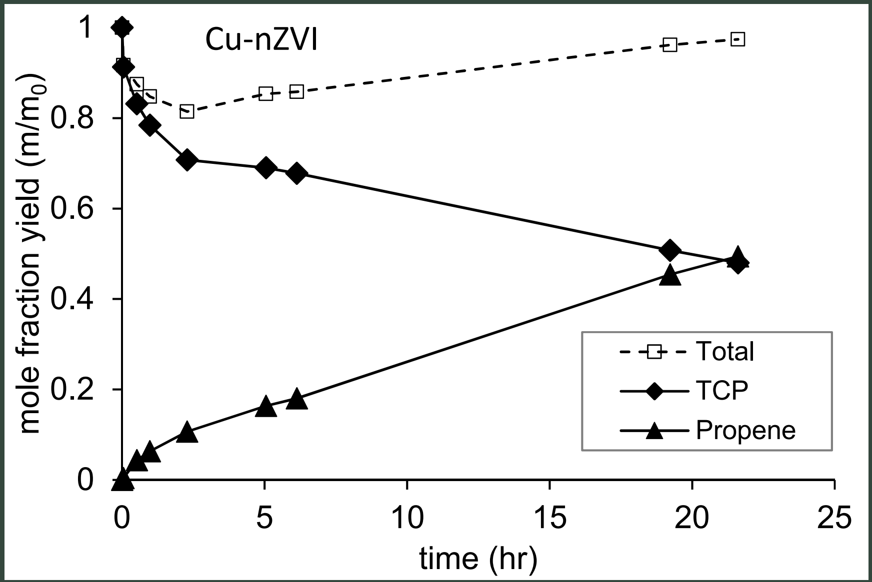
1,2,3-Trichloropropane degradation

- With nZVI: k_{M1} = 1.61; k_{M2} = 0.013 (L g^{-1} hr^{-1})
- With Cu-nZVI: k_{M1} = 1.48; k_{M2} = 0.111 (L g^{-1} hr^{-1})
- Propene forms via β-elimination followed by hydrogenolysis to propene
- Any intermediate below detection limits



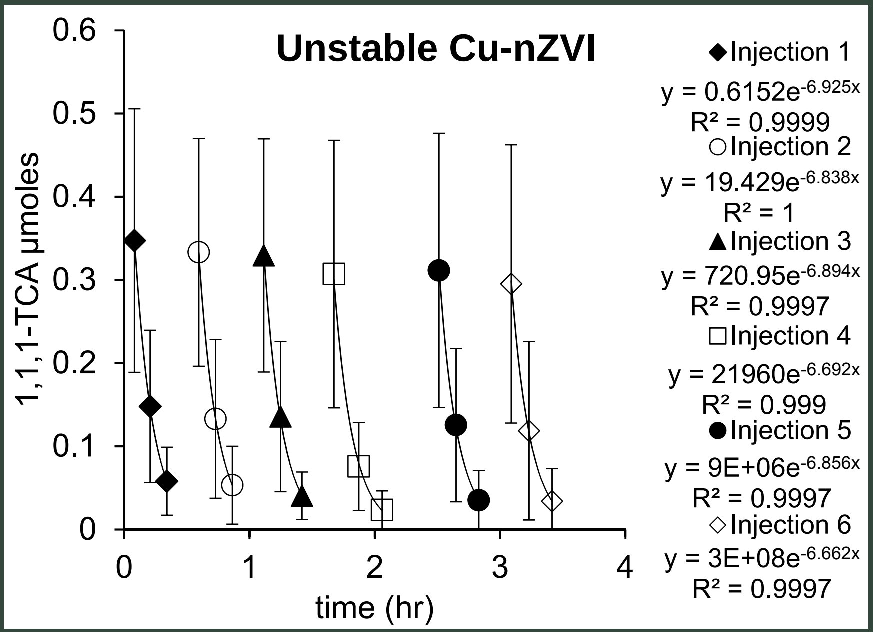
(Sarathy et al., 2010)

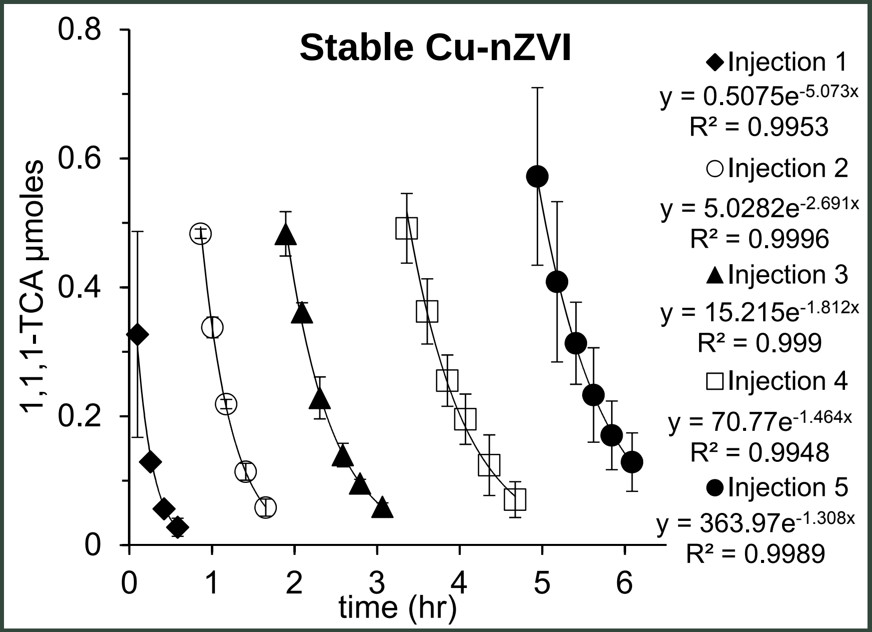




Nanoparticle longevity

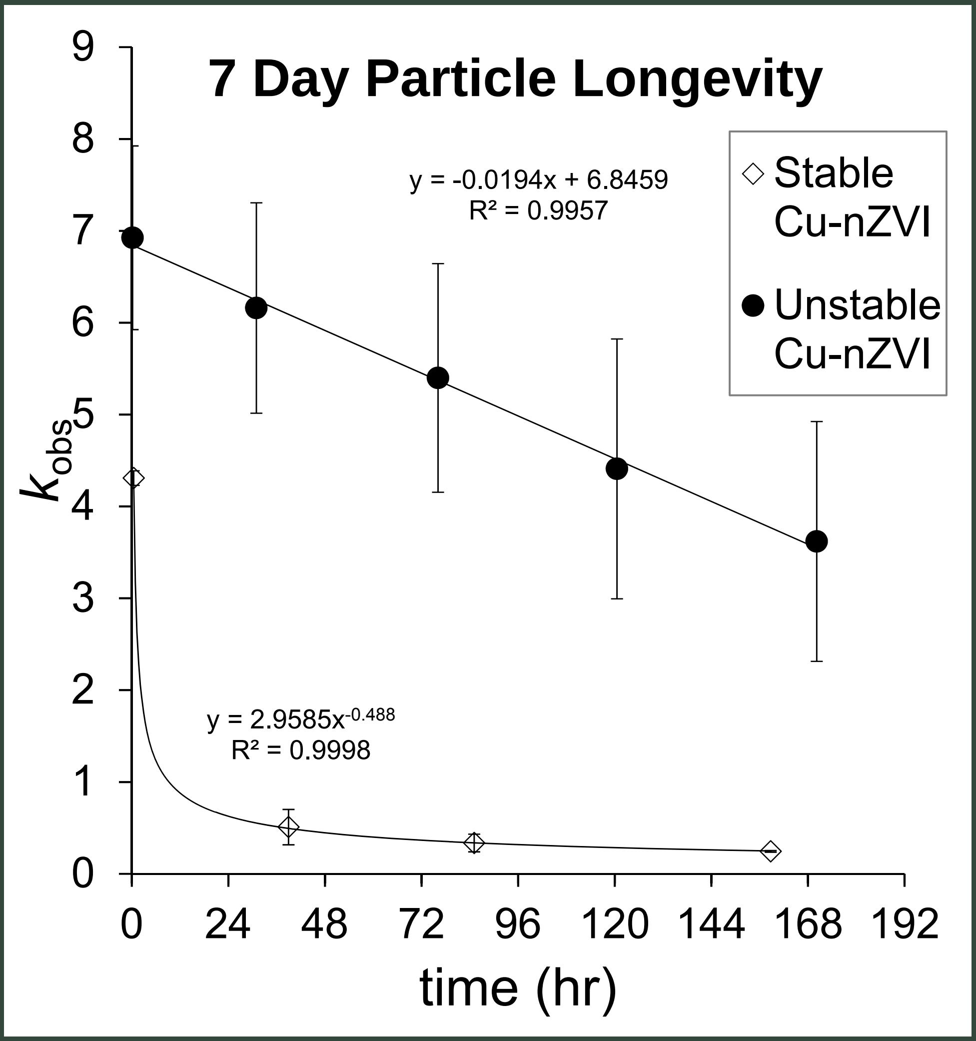
- Reinjections of 1,1,1-TCA in batch experiments with Cu-nZVI





Cu-nZVI particle longevity over 1 week

- Reinjections of 1,1,1-TCA over 1 week;
  - Unstable Cu-nZVI: linear
  - Stable Cu-nZVI: power function
- Reasons for reactivity loss
  - Oxidation of nanoparticles
  - Phenrat et al. (2009) showed a 24-fold decrease in nZVI with CMC stabilization



Conclusions

- Cu amendment improves degradation kinetics and alters byproduct distribution
- Cu-nZVI shows potential for degrading a class of compounds (chloroalkanes with 2 or 3 chlorines on 1 carbon)
- CMC may adversely effect particle reactivity, but it may be beneficial for field scale employment of technology

Acknowledgments

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