ACCELERATED DEGRADATION OF CHLORINATED SOLVENTS BY COPPER-MODIFIED NANOSCALE ZERO VALENT IRON (CU-NZVI) STABILIZED WITH CARBOXYMETHYL CELLULOSE

A thesis prepared in partial fulfillment of the requirements for the degree of Master of Science

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ABSTRACT

Franze, Andrew. M.S. Department of Earth and Environmental Sciences, Wright State University, 2015. Accelerated Degradation of Chlorinated Solvents by Copper-Modified Nanoscale Zero Valent Iron (Cu-nZVI) Stabilized with Carboxymethyl Cellulose

Nanoscale zero valent iron (nZVI) is a remediation technology that can be used to treat chlorinated hydrocarbons (CHCs) in contaminated aquifers. Nanoparticles remain mobile in water and can be transported with groundwater flow to contaminated zones. However, due to magnetic and van der Waals forces, unstabilized nZVI agglomerates. Carboxymethylcellulose (CMC) was used as a polyelectrolyte stabilizer in this study. nZVI serves as an electron donor and can dechlorinate CHCs. nZVI reactivity with CHCs can be enhanced by addition of a secondary metal catalyst. This study evaluates the potential of copper amended nZVI (Cu-nZVI) to degrade select CHCs.

The objective of this study was to characterize degradation of select CHCs in batch reactors with regard to degradation kinetics and degradation byproduct distributions. The following CHCs were studied: CF, 1,1,2,2-TeCA, 1,1,1-TCA, 1,1,2-TCA, PCE, TCE, cis-DCE, trans-DCE, and 1,2,3-TCP. Degradation kinetics were
quantified using a pseudo first-order rate constant \( (k_{obs}) \). Initial degradation of CHCs was reported separately from later degradation, which occurred after 0.5 hr. The change in reaction kinetics with time could be caused by particle aging.

The effect of Cu loading and nZVI concentration was evaluated with CF degradation. Increasing Cu loading or nZVI concentrations yielded faster degradation rates. Increasing Cu loading systematically increased methane byproduct production. The loss of reactivity with CF after 0.5 hr was greater for nZVI when compared to Cu-nZVI.

Degradation kinetics were faster and byproduct distribution was more favorable for Cu-nZVI than nZVI for all CHCs studied. Cu-nZVI outperformed most other bimetallic nZVI reductants reported in the literature for CF and chlorinated ethanes treatment. Cu-nZVI invokes \( \alpha \)-elimination of CF and 1,1,1-TCA, which produces reactive carbene intermediates capable of degrading into benign products such as methane, ethane, and ethene. Cu-nZVI also showed potential for 1,2,3-TCP remediation. However, Cu-nZVI was particularly ineffective at degrading chlorinated ethenes. Chlorinated ethene degradation pathways and mechanisms induced by Cu-nZVI were not clearly identified.

Particle longevity experiments showed that reactivity with 1,1,1-TCA decreases as particles age. Unstable Cu-nZVI particles showed a slow linear decline in reactivity with time, whereas CMC stabilized Cu-nZVI particles showed a rapid power function decline in reactivity with time. The unstable particles were 12-fold faster compared to stabilized particles 24 hr after particle synthesis. Even with declines in reactivity, 1,1,1-
TCA was rapidly degraded (over a few hours) by both stable and unstable Cu-nZVI seven days after particle synthesis. Cu-nZVI hydrogen production was minor and was limited to occurring immediately after particle synthesis. Cu-nZVI shows great potential for treating certain CHCs.
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Chapter 1

BACKGROUND

1.1 Groundwater contamination

Groundwater contamination is a serious problem that demands immediate attention. Groundwater accounts for about 50 percent of the nation’s municipal, domestic, and agricultural water supply (GAO, 2005). Consuming groundwater that contains volatile organic compounds (VOCs) can lead to disease and premature death. VOCs in groundwater and soil can reduce the quality of the natural environment in addition to negatively impacting human health. In the United States alone, there are over 126,000 sites with contaminated groundwater that require remediation. The estimated cost to remediate these sites ranges from $110 billion to $127 billion, and these figures for both the number of sites and the remediation costs are likely underestimates (National Research Council, 2013). Many contaminated sites in the United States contain chlorinated hydrocarbons (CHCs) that are particularly difficult to remediate. According to a report released by the U. S. Department of Defense (DOD), the Air Force has over 2,500 sites with contaminated groundwater; the Navy has over 2,000 sites; the Army has over 800 sites, and the Defense Logistics Agency has 16 sites. DOD has also identified an additional 500 contaminated groundwater sites on formerly used defense sites. Over
the past 10 years, DOD has invested approximately $20 billion for remediation of active, closing, and formerly used defense facilities (GAO, 2005).

CHCs are utilized in many industrial, commercial, and domestic applications. Some applications of CHCs include adhesives, aerosols, chemical intermediates, cold cleaning, dry cleaning/textile production, electronics, metal cleaning/dgreasing, paint removal/stripping, and urethane foam. CHCs can be introduced into the environment through a variety of processes. The most common sources of groundwater contamination by CHCs include the following: leaking underground or above-ground storage tanks, leaking drum storage areas, leaking buried chemical distribution pipelines, spillage at industrial facilities, spillage during highway and train accidents, and intentional disposal into the subsurface (Pankow et al., 1996). In a study that analyzed over 4,200 United States drinking water wells, the United States Geological Survey (USGS) reported that chloroform (CF) was the most frequent CHC detected in drinking water wells (Zogorski and others, 2006). CF along with many other CHCs, is recalcitrant in nature.

Many CHCs are considered dense non-aqueous phase liquids (DNAPL). DNAPLs are denser than water and have a low absolute solubility. DNAPLs tend to sink to the bottom of an aquifer and form pure phase pools on impermeable units. DNAPL pools are difficult to locate due to their distance from the ground surface. While CHCs have low absolute solubility, they have high solubility relative to drinking water standards (i.e. maximum contaminant levels) (Pankow et al., 1996). Over time, pure phase CHC pools and residual CHC sorbed to sediments will slowly dissolve forming a contaminant plume.
1.2 Degradation of CHCs

CHC degradation can occur in the environment by physical, chemical and microbiological processes, called ‘natural attenuation’. Particularly, CHCs can react and transform into other compounds due to biotic and abiotic interactions. Microorganisms can oxidize or reduce certain CHCs. However, specific conditions are necessary in order for biodegradation to occur. Natural attenuation may also occur slowly, requiring other complementary remediation technologies to be implemented. Abiotic oxidation and reduction can occur naturally or with the addition of chemicals. Reductive dechlorination occurs when there is a reducing environment (i.e. low redox potential) and oxidized species become reduced.

Permeable reactive barriers are a remediation technology that involves filling a trench with reactive media downgradient of a contaminant plume. As groundwater flows through the reactive media, contaminants are transformed into benign products. For the case of CHC contamination, zero valent metals are often used as reactive media. Iron is commonly used because it is less expensive than other metals and has a benign environmental impact (Nyer and Vance, 2001).

Nanoscale zero valent iron (nZVI) is a material that can be employed as an in situ remediation technology. nZVI particles, approximately 1 to 100 nanometers in size, can be suspended in solution as colloids that are mobile in the aqueous phase. PRBs require the contaminated groundwater to flow through the reactive material. nZVI technology is superior to PRBs because the zero-valent iron can be directly injected into the contaminated area. There is a greater surface area of iron exposed to the surroundings
when the iron particles are nanoscale, which increases the number of reaction sites. In fine-grained media, nZVI particles can be injected using hydrofracturing techniques, whereas direct injection of the particles can be implemented in media with greater permeability (Ny er and Vance, 2001). Secondary metal catalysts can enhance reactivity of nZVI (Crane and Scott, 2012). nZVI particles with the addition of a secondary metal have the potential to remediate DNAPL contamination.

1.3 Pathways of CHC degradation

The types of reactions involved in nZVI treatment are the same as those occurring with granular iron except the reaction kinetics are faster due to the increase in surface area. nZVI has the potential to remediate a wide variety of contaminants including: chlorinated solvents, pesticides, azo-dyes, flame retardants, antibiotics, nitrate, arsenic, hexavalent chromium, heavy metals, and radionuclides (Yan et al., 2013). This report will focus on nZVI application in reductive dechlorination of CHCs. nZVI serves as an electron donor and the intended electron acceptor is the CHC contaminant.

Hydrogenolysis is one reaction that is often observed in CHC reduction. A redox reaction occurs as electrons are accepted by the CHC and chlorine ions are released (Eq. 1). Anaerobic corrosion of iron is another reaction that occurs when iron is oxidized by water molecules (Eq. 2). The corrosion of iron produces hydrogen gas. Hydrogen gas can then be used to reduce the CHC as shown in Eq. 3 (Ny er and Vance, 2001).

\[
\begin{align*}
\text{Fe}^0 + \text{H}_2\text{O} + \text{R-Cl} & \rightarrow \text{Fe}^{2+} + \text{OH}^- + \text{R-H} + \text{Cl}^- & (1) \\
3\text{Fe}^0 + 2\text{H}_2\text{O} & \rightarrow 3\text{Fe}^{2+} + 2\text{OH}^- + \text{H}_2 & (2)
\end{align*}
\]
\[ \text{H}_2 + \text{R-Cl} \rightarrow \text{R-H} + \text{H}^+ + \text{Cl}^- \]  

(3)

Reactions listed above are simplified versions of actual reactions. CHCs with more than one carbon atom may exhibit dehydrohalogenation and dichloroelimination.

Dehydrohalogenation involves the removal of a chlorine and a proton from adjacent carbon atoms. Dichloroelimination involves the removal of two chlorine atoms.

Dichloroelimination can be subdivided into two different reaction mechanisms, \( \alpha \) and \( \beta \)-elimination. \( \beta \)-elimination involves the removal of two atoms or groups from adjacent carbon atoms. \( \beta \)-elimination results in the formation of a new \( \pi \) bond between the two carbon atoms for which the chlorines were removed (Smith, 2011). \( \alpha \)-elimination involves the removal of two atoms or groups from the same carbon atom. A carbene, a neutral compound that contains a carbon with a lone pair of electrons, results from \( \alpha \)-elimination (Smith, 2011). Carbene compounds are highly reactive and are considered intermediate species, not terminal products. In many cases, \( \beta \)-elimination is the preferred pathway over \( \alpha \)-elimination because a more stable product is formed.

Many reaction pathways and mechanisms have been proposed thus far for ZVI reduction of different types of CHC. Song and Carraway (2006) have described two parallel reaction pathways from carbon tetrachloride (CT) and CF to dichloromethane (DCM) and methane. Song and Carraway (2006) suggested a direct pathway from CF to methane using short-lived carbene and radical intermediate species. There are additional reactions that can occur when more than one carbon atom is present in the CHC compound. Reductive dechlorination by \( \beta \)-elimination can occur with multi carbon CHCs. Fennelly and Roberts (1998) suggested hydrogenolysis, dehydrochlorination, and to a lesser extent, coupling of radical intermediates, to be significant for 1,1,1-TCA
degradation by Ni-Fe and Cu-Fe bimetallic reductants. Cwiertny et al. (2006) found $\alpha$-elimination to play a significant role in 1,1,1-TCA degradation pathway to ethane and ethene. Possible reaction mechanisms for polychlorinated ethanes include: $\beta$-elimination, dehydrohalogenation, hydrogenolysis and $\alpha$-elimination (Arnold et al., 1999). Ethane degradation mechanisms can be extended to other, longer chain, CHCs. Some of these suggested pathways and mechanisms are based on theory; however, there is a lack of experimental data that can confirm the existence of the theorized intermediate species. Nevertheless, it is important to identify a theoretical pathway that explains the observed phenomena.

1.4 Degradation kinetics of CHCs

It is important to characterize the rate of reactions in addition to product formation. Pseudo first-order rate modeling is the most frequently used method to describe reactions involving the degradation of CHCs. When there is uncertainty regarding the pathways and mechanisms of a reaction, it is difficult to use a second-order rate model. Also, it is necessary to simultaneously measure the mass (or concentration) of both reactants in order to construct a second order reaction model. In a second-order reaction, if the amount of reactant A is high relative to reactant B, then the concentration of reactant A can be assumed a constant. This ultimately allows for the second-order reaction to be treated as a first-order reaction. A pseudo first-order observed rate constant can be determined from the exponential regression of the mass versus time plot. When mass is plotted as logarithmic on the y-axis, the function should appear linear. The observed rate constant is the product of the second-order rate constant and the zero valent
iron mass concentration. The following equation shows the pseudo first-order rate model:

$$\frac{dM}{dt} = k_{obs} \cdot M = k_M \cdot \rho_m \cdot M$$

$M$ is the amount of CHC (moles)

$k_{obs}$ is pseudo first-order degradation rate constant (hr$^{-1}$)

$k_M$ is nZVI mass normalized degradation rate constant (L$^*g^{-1}*hr^{-1}$)

$\rho_m$ is mass-concentration of nZVI (g$^*$L$^{-1}$)

The $k_{obs}$ or $k_M$ values can be used to compare kinetics among different experiments. A surface area normalized degradation rate constant can also be calculated (Johnson and others, 1996). However, particle surface area is difficult to measure with accuracy. Particles must be dry when their surface area is measured. Once the particles are in aqueous solution, their shape and size may be altered.

The degree of halogenation is a critical factor influencing reduction kinetics. Highly chlorinated compounds are in a more oxidized state and will typically undergo reduction more readily. Less chlorinated compounds are in a more reduced state and will typically be more difficult to reduce, but will become more easily oxidized. However, in certain abiotic systems driven by catalytic hydrodechlorination, the degradation rate of chlorinated ethenes is inversely proportional to the number of chlorine atoms to be removed (Song and Carraway, 2008). Enhanced degradation kinetics can also be achieved by adding a secondary metal catalyst.
1.5 Bimetallic reductants

Bimetallic iron reductants are usually more efficient at degrading contaminants than iron alone (Cwiertny et al., 2006). An additional metal in low concentrations will facilitate electron transfer from iron to the contaminant, thus increasing reaction kinetics (Keane, 2009). The primary metal serves as an electron donor, while the secondary metal serves to reduce the activation energy of the reaction, thus enhancing degradation kinetics (Zhang et al., 1998). Many secondary metals have been used in experimentation, including, but not limited to the following: palladium, aluminum, nickel, silver, zinc, and copper (Bransfield et al., 2006, Cwiertny et al., 2006, Zhou et al., 2003, Huang and Lien, 2010, Parshetti and Doong, 2012, Luo et al., 2012, Fennelly and Roberts, 1998). A secondary metal should be benign in the environment as well as efficient in facilitating electron transfer. Some studies have even evaluated trimetallic particles for catalytic dechlorination (Huang and Lien, 2010). It is generally understood that while most bimetallic mixtures increase degradation kinetics, particle longevity is decreased (Crane and Scott, 2012).

1.6 nZVI agglomeration

Agglomeration of nZVI particles is a common problem when considering employment of this technology for the treatment of contaminated sites. Due to interparticle, magnetic, and van der Waals forces, nZVI can rapidly agglomerate (He and Zhao, 2007). Various factors that can influence nZVI agglomeration include: nZVI concentration, interparticle magnetism, size distribution, pH, ionic strength, and zeta potential (Keane, 2009). Zeta potential is a critical factor when considering nZVI
agglomeration. Zeta potential, or electric potential, of a particle determines how much interparticle attraction may exist. As zeta potential approaches zero, particles tend to agglomerate, making them larger, less mobile, and of decreasing reactivity. Particles with zeta potentials greater than +30 mV and less than -30 mV are considered stable (Keane, 2009). It should be noted that employing high nZVI concentration may not be optimal for treatment of contaminants because more agglomeration may result compared to using a smaller nZVI concentration. At high concentrations, nZVI particles will have greater interparticle interactions, thus increasing agglomeration.

Stabilizing agents are often added to nZVI in order to prevent nanoparticle agglomeration so that nanoparticles particles remain dispersed, suspended, and mobile in the aqueous phase. It is important to choose a stabilizer that is benign in the environment. Carboxymethylcellulose (CMC) is a food grade additive polyelectrolyte that can be used as a stabilizer (He and Zhao, 2007). Polyelectrolytes are long, stringy, chain molecules that can bind with the nZVI particle surface and provide a negative surface charge. If steric and repulsive forces of the polyelectrolyte layer exceed the magnetic and van der Waals attraction, nZVI particles will not agglomerate. Various stabilizing coatings investigated include hydrophilic biopolymers such as starch, guar gum, alginate, and aspartame; natural organic matter such as humic acid; polyelectrolytes such as polyacrylic acid, ion-exchange resins, and block copolymers; amphiphiles including various surfactants; and various oil-based microemulsions (Keane, 2009). Such coatings can persist over a broad range of groundwater conditions for periods of several months (Crane and Scott, 2012). Carboxymethylcellulose and guar gum are commonly studied because they are cheap, non-toxic, water soluble, and biodegradable.
Clay templates may be used as an alternative to polyelectrolyte stabilization to prevent agglomeration. Phyllosilicate (clay) minerals have a sheet structure. Smectites are a class of phyllosilicate minerals that are comprised of a 2:1 structure; 2:1 clays contain repeating sequences of tetrahedral, octahedral, and tetrahedral (TOT) layers and exhibit a high cation exchange capacity upon swelling when saturated with water. Calcium or sodium ions are typically embedded in smectite TOT interlayers, and they can be exchanged with iron (Fe$^{2+}$) cations. Chemical reduction of Fe$^{2+}$ ions embedded within the clay structure to Fe$^{0}$ can yield a more stable form of nZVI. Negative charges in the clay interlayers can hold the nZVI particles in place, and clay surface charges can prevent agglomeration. This approach may produce a more reactive particle while simultaneously increasing particle longevity (Gu et al., 2010). nZVI is less susceptible to anaerobic corrosion when particles are shielded from water molecules by clay layers.

**1.7 nZVI fate**

Studies have shown that nZVI can be toxic to certain organisms. nZVI can inactivate *E. coli*, causing damage to the cell membrane and respiratory functions (Kim and others, 2011). In another study, fresh nZVI was found to be toxic to mammalian nerve cells, but the toxicity decreases once the particles become oxidized, agglomerated, coated, or aged in other ways (Phenrat et al., 2009). The oxidized forms of iron (Fe$^{2+}$ and Fe$^{3+}$) are much less toxic than nZVI (Lee et al., 2008). nZVI will eventually form iron oxides over time. Depending on the environmental conditions, nZVI will form naturally occurring minerals such as magnetite, maghemite, lepidocrocite, and goethite (Keane, 2009). As such, the release of nZVI into natural environments may not be a major concern. The human tolerance for oxidized forms of iron (Fe$^{2+}$ and Fe$^{3+}$) is relatively
high compared to other metals. There is some potential for nZVI to be used as a drinking water treatment method for removal of trihalomethanes (Xiao et al., 2014). The U.S. Environmental Protection Agency (EPA, 2013) considers iron to be a secondary contaminant in drinking water and it does not enforce a maximum contaminant level for dissolved Fe\(^{2+}\) in drinking water. The side effects of iron consumption are generally limited to cosmetic (skin or tooth discoloration) and aesthetics effects (taste or color) (EPA, 2013).

1.8. Research objectives

This study evaluates the ability of copper modified nZVI (Cu-nZVI) in comparison to nZVI in degrading select CHCs. Bench-scale experiments were conducted to determine the distribution of reaction products, degradation kinetics, and carbon mass balance. The focus of this research is to characterize Cu amended nZVI performance in destroying pollutants. The goal of the research is to develop an innovative technology that can be implemented at sites contaminated with CHCs. This study aims to expand on the current nZVI remediation literature. Many other studies investigated various secondary metals as catalysts (section 1.5), but Cu has received little attention. Literature studies do not indicate any systemic toxicity associated with dietary exposures to Cu (EPA, 2008). Cu is commonly present in tap water due to the use of copper plumbing fixtures and water pipes. The use of Cu has advantages over palladium, nickel and other metals due to its relative low toxicity.

i. Evaluate the effect of Cu loading and nZVI loading on degradation of CHCs.
ii. Measure degradation kinetics of select CHCs using a pseudo first-order modeling. Compare the performance of Cu-nZVI to nZVI. Evaluate the potential of Cu-nZVI compared to other bimetallic reductants studied in literature.

iii. Determine the degradation product distribution and identify degradation pathways/ mechanisms resulting from reactions involving Cu-nZVI and various CHCs. The product distribution is a critical component when evaluating a remediation technology. If unfavorable toxic products result, the technology may not be acceptable for remediation. A desirable remediation technology should demonstrate fast degradation of the contaminants and yield benign products.
Chapter 2

MAT MATERIALS AND METHOD

2.1 Materials

The following chemicals were used as received: Chloroform (CF, Fisher Scientific, 99.8%), dichloromethane (DCM, Fisher Scientific, 99.9%), 1,1,2,2-tetrachloroethane (1,1,2,2-TeCA, Acros Organics, 98.5%), 1,1,2-trichloroethane (1,1,2-TCA, Sigma-Aldrich, 97%), 1,1,1-trichloroethane (1,1,1-TCA, Sigma-Aldrich, 99%), 1,2-dichloroethane (1,2-DCA, Sigma-Aldrich, 99%), 1,1-dichloroethane (1,1-DCA, Pfaltz & Bauer, 99%), tetrachloroethene (PCE, Sigma-Aldrich, 99.9%), trichloroethene (TCE, Acros Organics, 99%), cis-1,2-dichloroethene (cis-DCE, Acros Organics, 97%), trans-1,2-dichloroethene (trans-DCE, Acros Organics, 99%), 1,2,3-trichloropropane (1,2,3-TCP, Acros Organics, 98%), 1,2-dichloropropane (1,2-DCP, Acros Organics, 98%) and vinyl chloride (VC, Air Liquide, 1,000 mg/L VC by volume with nitrogen balance). Other chemicals used included ferrous sulfate (FeSO₄·7H₂O; MP Biomedicals), copper (II) chloride (CuCl₂·2H₂O; Acros, 99+%), sodium borohydride (NaBH₄; Sigma-Aldrich, >98%), TAPSO (2-hydroxy-3-[tris(hydroxymethyl)methylamino]-1-propanesulfonic acid, N-[tris(hydroxymethyl)methyl]-3-amino-2-hydroxypropanesulfonic acid; Sigma-Aldrich, 99%), sodium hydroxide (NaOH. Fisher Scientific), carboxymethyl cellulose sodium salt (CMC-Na, Sigma-Aldrich, molecular
weight 90,000 amu), and high purity gases (He, N₂, H₂, air; Weiler Welding, Dayton, OH).

2.2 nZVI synthesis

Ferrous sulfate was used to prepare nZVI (Fe⁰) particles, and copper (II) chloride was used as a catalyst. Sodium borohydride was used as a reductant. Experimental reactors were filled with deoxygenated 30 mM (typically 96 mL; 2.88 mmoles) TAPSO titrated to pH 7 by 1 M NaOH. Carboxymethyl cellulose sodium salt was used as a polyelectrolyte for stabilizing nanoparticles. Fresh nZVI particles were used immediately after synthesis without rinsing or drying.

A bottom up synthesis approach was used in this study to prepare nZVI and bimetallic Cu-nZVI. Batch reactors (160 mL serum bottles, Wheaton) were prepared in an anaerobic chamber (Coy Lab, MI) to simulate conditions in an anaerobic aquifer. All reagent solutions used in nZVI synthesis were de-oxygenated in advance by sparging with high-purity N₂ gas for at least 40 min prior to their use in the anaerobic chamber. Ferrous sulfate (0.860–12.04 mL of 100 mM), with or without copper (II) chloride (0.030–0.525 mL of 100 mM), was added to reactor bottles first. CMC reagent solution (0–19.2 mL of 20 g/L) was then added and allowed to complex with Fe (II) with or without Cu (II) for 15 min. CMC is a food grade additive that can assist in dispersing and stabilizing nZVI and Cu-nZVI particles during synthesis, thus reducing their agglomeration. TAPSO buffer (25 mL of 30 mM; pH of 7) was added to reactor bottles to minimize pH fluctuation during experiments. Freshly prepared sodium borohydride reagent (500 mM; 0.472 g dissolved in 25 mL water) was then added to the batch reactors.
drop wise to chemically reduce the Fe (II) to nanoscale Fe\(^0\) (nZVI) (Eq. 4 below). The actual molar ratio of borohydride (BH\(_4^-\)) added to Fe (II) used in nZVI synthesis was 3:1. While a 2:1 BH\(_4^-\) to Fe (II) stoichiometric ratio is required for Fe (II) reduction, excess borohydride was used to compensate for borohydride reaction with water during nanoparticle synthesis (Eq. 5) and ensure complete Fe (II) reduction.

\[
\text{Fe(H}_2\text{O)}\text{)_6}^{2+} + 2\text{BH}_4^- \rightarrow \text{Fe}^0 \text{ (solid)} + 2\text{B(OH)}_3 + 7\text{H}_2 (\text{gas}) \quad (4)
\]

\[
\text{BH}_4^- + 2\text{H}_2\text{O} \rightarrow \text{BO}_2^- + 4\text{H}_2 (\text{gas}) \quad (5)
\]

\[
\text{Fe}^0 \text{ (solid)} + 2\text{H}_2\text{O} \rightarrow \text{H}_2 \text{ (gas)} + 2\text{OH}^- + \text{Fe}^{2+} \quad (6)
\]

### 2.3 Batch experiments

Following nZVI synthesis, additional water was added to the reactors in order to achieve 96 mL aqueous solution and 64 mL of headspace (i.e., 60:40 water headspace ratio). Reactors were gently swirled for 10 seconds, and then sealed with a Teflon-lined rubber stopper and aluminum crimp. Injection of a CHC and headspace sampling began immediately after reactor setup was complete. nZVI particles are most reactive immediately after synthesis because they can oxidize in water over time (Eq. 6). Reactors were prepared in duplicate along with a control bottle. All bottles were placed on an end-over-end rotator for the duration of sampling. This general batch experiment procedure was applied for experiments described in sections 3.1-3.4 of the results and discussion portion of this document.

Longevity experiments were performed to evaluate the effect of particle aging on reactivity. The general conditions regarding batch reactor set-up for longevity
experiments was the same as for experiments described above. However, reactors were on end-over-end rotator only during sampling, they were unmixed between sampling times. Both stable and unstable (i.e. with and without 4 g/L CMC) nanoparticles with and without Cu amendment were evaluated. Stable and unstable Cu-nZVI reactivity with 1,1,1-TCA was monitored over 7 days. Reactors were reinjected with 1,1,1-TCA multiple times throughout the experiment. The longevity experiments are contained in section 3.5 of the results and discussion portion of this document.

2.4 Analytical methods

The amount of CHCs and byproducts in reactor bottles was quantified by gas chromatography, (7890 GC system; Agilent Technologies) electron capture (ECD) and flame ionization (FID) detectors. CHCs were separated on a HP-624 column (30 m x 0.32 mm x 0.25 μm, Agilent Technologies) connected to ECD, whereas other hydrocarbons were separated on a HP-624 column (30 m x 0.32 mm x 0.25 μm, Agilent Technologies) connected to the FID, and Helium served as the carrier gas at constant flow of 2.5 mL min\(^{-1}\). GC method was as follows: split/splitless inlet = 250 °C, and oven temperature = 150 °C (isothermal). The make-up gas for the GC 7890 was N\(_2\) with a flow rate of 25 mL min\(^{-1}\) for the ECD. The flow rate for gases to FID was 30 mL min\(^{-1}\) H\(_2\) and 450 mL min\(^{-1}\) of air.

Sampling consisted of 50 μL injections of reactor headspace into the GC inlet using 250 μL gastight syringe (Hamilton, Reno, NV). Sampling interval varied depending on retention time and degradation kinetics of different compounds. Most
experiments were conducted over the course of one day. Certain experiments were conducted with 1,1,1-TCA to evaluate particle longevity over a one week time period.

2.5 Data treatment

CHC stock solutions were prepared by adding 25 μL of pure organic liquid into a 160 mL serum bottle containing 160 mL Milli-Q water (no headspace). Serum bottles were sealed using a Teflon-lined rubber stopper and aluminum crimp. Stock solution bottles were wrapped in aluminum foil and placed on an end-over-end rotator (setting at 70; 45 rpm) for at least 48 hr to allow for CHC dissolution. Five standards were prepared similar to batch reactors by injecting different amounts of CHC stocks and gases to generate a calibration curve for each compound. Standard bottles contained the compound of interest in 96 mL of water with 64 mL of headspace. Standards were wrapped in aluminum foil to prevent potential photodegradation. Standards were placed on a rotator for end-over-end mixing at 45 rpm for at least 4 hr prior to analysis to ensure equilibration. The amount of the compound was plotted on the ordinate (y-axis) and their corresponding peak areas from GC chromatograms on the abscissa (x-axis). The linear regression equation of the data points on the x-y scatter plot could then be used to transform GC peak areas into compound amounts in batch reactors.

For degradation experiments, the natural logarithm of CHC amount was plotted on y-axis as a function of time (hr) on x-axis. The slope of the linear fit to the natural logarithm amount vs. time plot is reported as the pseudo first-order observed rate constant ($k_{obs}$). It was determined that degradation kinetics were changing through time, reactivity decreased over time. A distinction was made between the initial pseudo first-order
observed rate constant ($k_{\text{obs1}}$) and the later pseudo first-order observed rate constant ($k_{\text{obs2}}$). $k_{\text{obs1}}$ was calculated from the first three data points collected, approximately during the first 30 minutes after particle synthesis. $k_{\text{obs2}}$ was calculated from all data points collected more than 30 minutes after particle synthesis. Xiao et al. (2014) also reported $k_{\text{obs1}}$ and $k_{\text{obs2}}$ kinetics for CHC degradation by nZVI stabilized with activated carbon.

Error bars located on figures represent a 95% confidence interval (two standard deviations). However, due to instrumentation limitations, only two duplicate reactors were prepared for each experiment. Calculating standard deviations with only two samples can exaggerate error bars. Furthermore, an assumption that samples from both duplicate reactors were analyzed simultaneously must be made in order to calculate error bars. This assumption is invalid when degradation kinetics are fast. Therefore, large error bars early in experiments do not necessarily mean data quality is poor. Error bars are not always a good indication of data quality in this study.
3.1 Chlorinated Methanes

3.1.1: CF degradation by nZVI

CF degradation ($k_{obs1} = 0.430 \text{ hr}^{-1}; k_M1 = 8.60 \text{ L g}^{-1} \text{ hr}^{-1}; k_{obs2} = 0.0754 \text{ hr}^{-1}; k_M2 = 1.50 \text{ L g}^{-1} \text{ hr}^{-1}$) with stabilized 0.05 g/L nZVI was observed (Fig. 3.1). DCM and methane formed as products. After 4 hr, CF remaining ($m/m_0$) was 0.64, DCM and methane yields ($m/m_0$) were 0.07 each, and the carbon mass balance ($m/m_0$) was 0.78. DCM appeared to be a stable product, as no further degradation was observed.

In a similar study (Song and Carraway, 2006), CF degradation by 0.16 g/L unstabilized nZVI (0.02 g nZVI in 124 mL buffered water) was comparable ($k_{obs} = 0.189 \text{ hr}^{-1}; k_M = 1.18 \text{ L g}^{-1} \text{ hr}^{-1}$). The reactivity of unstabilized nZVI particles towards CF (Song and Carraway, 2006) were 7.3-fold slower for $k_M1$ and 6.9-fold faster for $k_M2$ reported in this study. In the present study, the use of CMC polyelectrolyte during synthesis acted as a particle stabilizer and prevented agglomeration. CMC sorbs to particle surfaces and provides a surface charge that encourages repulsion of particles. CMC can also decrease nanoparticle reactivity to a certain degree (Phenrat et al., 2009). However, the application of CMC may provide significant benefits and improved feasibility of this
technology at field scale. The effect of CMC on reactivity of particles was evaluated using 1,1,1-TCA and is discussed later in section 3.5. Differences in nZVI synthesis could also lead to differences in reactivity.

3.1.2: CF degradation by nanoscale zero valent copper (nZVC)

nZVC was prepared the same way nZVI was prepared except Cu was used in place of Fe. CF degradation ($k_{obs1} = 0.309 \text{ hr}^{-1}; \quad k_{M1} = 6.18 \text{ L g}^{-1} \text{ hr}^{-1}; \quad k_{obs2} = 0.0102 \text{ hr}^{-1}; \quad k_{M2} = 0.204 \text{ L g}^{-1} \text{ hr}^{-1}$) with 0.05 g/L stabilized nZVC was observed (Fig. 3.2). DCM and methane formed as products. After 3 hr, CF remaining ($m/m_0$) was 0.82, DCM and methane yields ($m/m_0$) were 0.15 and 0.03 respectively, and the carbon mass balance ($m/m_0$) was ~1.0. However, DCM degradation was not observed. There were no unidentified products in the nZVC system as indicated by a complete carbon mass balance. Studies involving nZVC have not been reported much in literature. Huang et al. (2011) reported that nZVC is superior to nZVI for 1,2-DCA degradation. However, in this study nZVI was more effective than nZVC at degrading CF. There was a significant loss in nZVC particle reactivity after ~0.5 hr, as $k_{obs1}$ is ~30-fold faster than $k_{obs2}$. In comparison, $k_{obs1}$ for CF degradation with nZVI particles was only 6-fold faster than $k_{obs2}$. It is possible that residual sodium borohydride remaining from particle synthesis is responsible for the higher $k_{obs1}$ in the case of nZVC. The effect of residual sodium borohydride is discussed later (section 3.3.3).

3.1.3: CF degradation by Cu-nZVI

Degradation of CF ($k_{obs1} = 0.928 \text{ hr}^{-1}; \quad k_{M1} = 18.6 \text{ L g}^{-1} \text{ hr}^{-1}; \quad k_{obs2} = 0.186 \text{ hr}^{-1}; \quad k_{M2} = 3.72 \text{ L g}^{-1} \text{ hr}^{-1}$) occurred with 0.05 g/L stabilized nZVI and 1 wt% Cu (Fig. 3.3). After
4 hr, CF remaining ($ml/m_0$) was 0.29, while DCM and methane yields ($ml/m_0$) were 0.34 and 0.20 respectively, and a carbon mass balance ($ml/m_0$) of 0.84 was observed. No evidence of DCM degradation was observed for any experiments involving Cu-nZVI. Cu-nZVI showed greater effectiveness at degrading CF compared to nZVI alone. Additional studies were conducted to evaluate Cu-nZVI furthermore. When compared to unstabilized nZVI (Song and Carraway, 2005) Cu-nZVI (1 wt.% Cu) was 16-fold faster for $k_{M1}$ and 2.5-fold slower for $k_{M2}$.

3.1.4: Effect of Cu loading on CF degradation

CF degradation by Cu-nZVI was evaluated with 0.05 g/L nZVI and a range of Cu loadings (1-10 wt% Cu). Pseudo first-order degradation rate constant, $k_{obs1}$, was higher than $k_{obs2}$ ($k_{obs1} = 0.928-2.26$ hr$^{-1}$; $k_{M1} = 18.6-45.1$ L g$^{-1}$ hr$^{-1}$; $k_{obs2} = 0.201-0.994$ hr$^{-1}$; $k_{M2} = 4.02-19.9$ L g$^{-1}$ hr$^{-1}$) (Fig. 3.3-3.9 and table 3.1). DCM and methane were observed as degradation products (Fig. 3.3-3.7 and 3.10). After 2.5 hr from the start of experiments, CF remaining ($ml/m_0$) varied from 0.36-0.053, while DCM and methane yields ($ml/m_0$) varied from 0.31 to 0.39 and from 0.18 to 0.50, respectively. The carbon mass balance ($ml/m_0$) varied from 0.77 to 0.95 at various Cu loadings. DCM was a stable byproduct of CF degradation with Cu-nZVI. Trace amounts of ethane ($ml/m_0 \approx 0.01$) were produced in all Cu-nZVI experiments. Degradation kinetics of CF increased with increasing Cu loading (Fig 3.8). The $k_{obs}$ as a function of Cu loading plot shows a positive linear correlation for both $k_{obs1}$ and $k_{obs2}$ kinetics. Bransfield et al. (2006) showed a similar trend in their 1,1,1-TCA degradation study with granular iron modified with various Cu loadings.
The initial degradation that occurs over the first 0.5 hours is faster than the later degradation after 0.5 hours. Xiao et al. (2014) reported an analogous $k_{\text{obs}1}$ and $k_{\text{obs}2}$ for CHC degradation by nZVI stabilized with activated carbon, and noted a 4-fold decrease in reactivity during the experiment ($k_{\text{obs}1} = 1.24 \text{ hr}^{-1}$ declined to $k_{\text{obs}2} = 0.30 \text{ hr}^{-1}$). In that study, Xiao et al. (2014) reported $k_{\text{obs}1}$ as the degradation rate constant for the first 15 min of reaction and $k_{\text{obs}2}$ as the degradation rate constant from the data after 15 min. In this study with nZVI and Cu-nZVI, a decrease in reactivity was noted after the first half hour; however, the decline in degradation kinetics was greater for nZVI than Cu-nZVI (Fig 3.9). As Cu loading was increased, the difference between $k_{\text{obs}1}$ and $k_{\text{obs}2}$ became less pronounced. The initial degradation could be faster for a variety of reasons. Residual sodium borohydride could interact with nZVI to form a complex capable of faster reduction. Sodium borohydride could also reduce CF directly. The outer layer of nZVI particles oxidize over time in water (Liu et al., 2015). Oxidation of the outer nZVI particle will hinder electron transfer from the inner core of the particle to CF. It is also possible that the nZVI particles are completely spent, even the inner core has been oxidized. Dissolved Fe (II) formation in the system may also play a role in degradation. A more detailed discussion of particle longevity will occur later (section 3.5).

Hydrogenolysis and reductive elimination mechanisms must be considered for CF degradation to DCM and methane. The production of DCM was evidence of hydrogenolysis. Further sequential hydrogenolysis of DCM would produce chloromethane and methane. However, DCM was a stable product, and it did not show degradation at various Cu loadings. This suggests that the pathway for direct transformation of CF into methane may involve removal of multiple chlorines.
simultaneously. Further, since methane production began immediately after CF was introduced into the system, it suggests a direct transformation pathway similar to reductive elimination. Chloromethane, as a product of DCM hydrogenolysis or CF dichloroelimination was not detected. It is likely that hydrogenation of certain reactive intermediate radicals/species, which remained adsorbed to the nanoparticle surface, led to the formation of methane. Song and Carraway (2006) have suggested a direct CF transformation pathway to methane. Other potential byproducts include carbon monoxide, formate, and C2-dimers involving chlorocarbene and carbanion radicals (Feng and Lim, 2005).

Product distributions were evaluated for each Cu loading experiment after 2.5 hr. Cu loading significantly influenced product distribution (Fig 3.10). The carbon mass balance \( \frac{m}{m_0} \) was between 0.77 and 0.95 for all Cu loading experiments. Formate and carbon monoxide products were below detection limits and likely account for remaining carbon mass balance. Increasing Cu loading degraded more CF for a given time interval. DCM yields did not change much due to increase in Cu loading from 1-10 wt%. Methane yields increased systematically with increasing Cu loading. Methane was the desired outcome, and its production suggested that CF was completely dechlorinated by Cu-nZVI. This study suggests that increasing Cu loading favors direct transformation of CF to methane. The addition of Cu to nZVI has the potential to yield more favorable degradation products. Huang and Lien (2010) studied CT degradation with a Fe-Pd-Al microscale particle mixture. Degradation kinetics \( k_M = 0.649 \text{ hr}^{-1} \) (Huang and Lien, 2010) were slower than the Cu-nZVI system in this study even though CT typically degrades faster than CF. Huang and Lien (2010) also had an undesirable, highly toxic,
product distribution (100% DCM). The objective of the present study, with Cu-nZVI, aims to increase the reaction kinetics, in addition to promoting more desirable, less toxic, byproducts.

3.1.5: Effect of Cu-nZVI concentration on CF degradation

CF degradation by Cu-nZVI was evaluated for a range of nZVI concentrations (0.05 – 0.7 g/L) with 5 wt% Cu. Pseudo first-order degradation, $k_{obs1}$ was faster than $k_{obs2}$ ($k_{obs1} = 1.40-7.53 \text{ hr}^{-1}$; $k_{M1} = 10.5-28.0 \text{ L g}^{-1} \text{ hr}^{-1}$; $k_{obs2} = 0.546-2.41 \text{ hr}^{-1}$; $k_{M2} = 3.44-10.9 \text{ L g}^{-1} \text{ hr}^{-1}$) (Fig. 3.11-3.19 and table 3.2). DCM and methane were observed as degradation products (Fig. 3.11-3.18, 3.20 and table 3.2). After ~2.5 hr from the start of experiments, CF remaining ($m/m_0$) varied from 0.0040-0.184, while DCM and methane yields ($m/m_0$) varied from 0.23-0.31 and 0.34-0.50 respectively. A carbon mass balance varied from 0.67-0.78 for nZVI loading experiments. No evidence of DCM degradation was observed for any experiments involving Cu-nZVI. Trace amounts of ethane ($m/m_0 \approx 0.01-0.03$) were produced in all Cu-nZVI experiments.

Figure 3.19 A shows that increasing nZVI loading causes $k_{obs}$ to increase. This trend was expected because increase in nZVI loading increases the nZVI surface area that participates in reaction with CF. This reaction is likely second-order with respect to nZVI surface area and CF. Song and Carraway (2005) observed a similar relationship when studying 1,1,1-TCA degradation by various nZVI concentrations. Figure 3.19 B shows that $k_M$ is higher at lower nZVI loadings. Higher $k_M$ at low nZVI loadings suggests greater reactivity of nZVI per unit mass. Mass normalized reactivity may be greater at low nZVI loadings due to minimal agglomeration, as a larger surface area per
unit mass can participate in reaction with CF. At higher nZVI loadings, the system appears to be progressively less effective as nZVI surface area per unit mass may actually decrease, thus decreasing $k_M$.

There are a couple of recognizable trends in product distribution at increasing nZVI concentrations. The CF remaining ($m/m_0$) shows a progressive decline from 0.18 at 0.05 g/L Cu-nZVI to 0.01 at 0.4 g/L nZVI at ~2.5 hr, and it becomes non-detectable at higher nZVI loading. Further, a systematic increase in total methane yield at ~2.5 hr is evident at increasing nZVI concentration. Higher nZVI loading can create stronger reducing conditions and facilitate larger total nZVI surface area, which favors greater methane production. It seems likely that increase in nZVI surface area (at higher nanoparticle loading) may reduce competition among chloromethane species and thus facilitate more complete reduction of adsorbed species.

3.2 Chlorinated Ethanes

3.2.1: 1,1,2,2-TeCA degradation by nZVI and Cu-nZVI

1,1,2,2-TeCA degradation with 0.2 g/L stabilized nZVI was minimal (Fig. 3.21) with no identifiable degradation products. After ~4 hr, 1,1,2,2-TeCA remaining ($m/m_0$) was 0.94. The pseudo first-order degradation rate constants, $k_{obs1}$ and $k_{obs2}$, were grouped together and reported as one value ($k_{obs} = 0.0173 \text{ hr}^{-1}; k_M = 0.00865 \text{ g}^{-1} \text{ hr}^{-1}$) because little degradation was observed in the first 0.5 hr. Further, the coefficient of determination ($R^2$) was poor (0.336). The poor fit line coupled with marginal degradation suggests that degradation may not have been statistically significant for the time interval monitored.
In comparison, 1,1,2,2-TeCA degradation with 0.2 g/L stabilized Cu-nZVI (5 wt% Cu) was more effective (Fig. 3.22), where TCE and trans-1,2 DCE were the only products identified. After ~2 hr, 1,1,2,2-TeCA remaining (m/m₀) was 0.08, while the TCE and trans-DCE yields (m/m₀) were 0.02 and 0.25 respectively. A carbon mass balance of 0.33 suggests that 0.67 of the original 1,1,2,2-TeCA was degraded into an unidentified product. k_{obs1} was about 2-fold faster than k_{obs2} (k_{obs1} = 1.80 hr⁻¹; k_{M₁} = 8.98 L g⁻¹ hr⁻¹; k_{obs2} = 0.842 hr⁻¹; k_{M₂} = 4.21 L g⁻¹ hr⁻¹).

The Cu-nZVI system was much more effective at degrading 1,1,2,2-TeCA compared to the nZVI system. In a similar study (Song and Carraway, 2005), 1,1,2,2-TeCA degradation by 0.081 g/L unstabilized nZVI (0.01 g nZVI in 124 mL buffered water) was comparable (k_{obs} = 0.0682 hr⁻¹; k_{M} = 0.842 L g⁻¹ hr⁻¹). The unstabilized nZVI particles (Song and Carraway, 2005) were almost 100-fold faster than k_{M} reported in this study for the nZVI system, which may be attributed to 4 g/L CMC polyelectrolyte causing decreased kinetics (Phenrat et al., 2009). However, the Cu-nZVI experiment in this study were ~10-fold and 5-fold faster, for k_{M₁} and k_{M₂} respectively, than k_{M} reported by Song and Carraway (2005) for unstabilized nZVI. Cu clearly plays a role as a catalyst in facilitating electron transfer from Cu-nZVI particles to 1,1,2,2-TeCA.

The degradation of 1,1,2,2-TeCA by β-elimination yields trans-DCE, which was the major product observed in this study. Dehydrohalogenation of 1,1,2,2-TeCA yields TCE, but it was only a minor product. Both products were also observed by Song and Carraway (2005); however they reported, ethane, ethene, and cis-DCE as well. This study observed a carbon mass balance of 0.33 after ~2 hr for the Cu-nZVI experiments. Unidentified products account for ~0.66 of the original 1,1,2,2-TeCA. It is possible that
chloroacetylene and acetylene compounds account for remaining mass. Chloroacetylene and acetylene compounds can form when there is dehydrochlorination or β-elimination of TCE or DCEs. Arnold and Roberts (2000) have suggested pathways for acetylene formation in their studies of 1,1,2,2 TeCA degradation by zero-valent metals (Zn and Fe). No evidence of 1,1,2,2 TeCA degradation by hydrogenolysis pathway was observed in this study.

3.2.2: 1,1,1-TCA degradation by nZVI and Cu nZVI

The degradation of 1,1,1-TCA with 0.2 g/L stabilized nZVI was significant (Fig. 3.23). 1,1-DCA and trace amounts of ethane were produced. After ~4 hr, 1,1,1-TCA remaining ($m/m_0$) was 0.62, 1,1-DCA yield ($m/m_0$) was 0.21, and the carbon mass balance ($m/m_0$) was 0.83. Most of the degradation occurred during the first hour. $k_{obs1}$ was about 15-fold faster than $k_{obs2}$ ($k_{obs1} = 0.797 \text{ hr}^{-1}; k_M1 = 3.99 \text{ L g}^{-1} \text{ hr}^{-1}; k_{obs2} = 0.0515 \text{ hr}^{-1}; k_M2 = 0.258 \text{ L g}^{-1} \text{ hr}^{-1}$). 1,1,1-TCA is prone to dehydrohalogenation in water, but the control bottle showed no significant degradation over the sampling period.

In comparison, the degradation of 1,1,1-TCA with Cu-nZVI (0.2 g/L stabilized nZVI and 5 wt% Cu) was rapid (Fig. 3.24). 1,1-DCA, ethane, and ethene were identified as degradation byproducts. After ~0.5 hr, 1,1,1-TCA remaining ($m/m_0$) was 0.002, while the 1,1-DCA, ethane, and ethene yields ($m/m_0$) were 0.09, 0.35, and 0.07 respectively. A carbon mass balance of 0.54 suggests that 0.46 of the original 1,1,1-TeCA was degraded into unidentified products. $k_{obs1}$ was about 1.7-fold faster than $k_{obs2}$ ($k_{obs1} = 9.77 \text{ hr}^{-1}; k_M1 = 48.9 \text{ L g}^{-1} \text{ hr}^{-1}; k_{obs2} = 5.86 \text{ hr}^{-1}; k_M2 = 29.3 \text{ L g}^{-1} \text{ hr}^{-1}$). The Cu-nZVI system was much more effective at degrading 1,1,1-TCA compared to the nZVI system (12-fold and 114-
fold faster for \( k_{\text{obs}1} \) and \( k_{\text{obs}2} \) respectively). Furthermore, the Cu-nZVI system was more effective at degrading 1,1,1-TCA than any other CHC in this study. More 1,1,1-TCA degradation experiments were conducted to evaluate particle longevity (section 3.5.1).

Ethane was the primary reaction byproduct \( (m/m_0 = 0.35) \) observed during 1,1,1-TCA degradation with Cu-nZVI. The reaction pathway from 1,1,1-TCA to ethane may involve sequential removal of chlorine atoms by hydrogenolysis \( (1,1,1\text{-TCA} \rightarrow 1,1\text{-DCA} \rightarrow \text{chloroethane (CA)} \rightarrow \text{ethane}) \). However, it is unlikely because 1,1-DCA degrades too slow for it to exist as an intermediate species in the formation of ethene or ethane (Fennelly and Roberts, 1998). The presence of ethene \( (m/m_0 = 0.07) \) may suggest degradation via dehydrohalogenation of 1,1,1-TCA followed by hydrogenolysis of 1,1-DCE and VC \( (1,1,1\text{-TCA} \rightarrow 1,1\text{-DCE} \rightarrow \text{VC} \rightarrow \text{ethene}) \) (Fennelly and Roberts, 1998). 1,1-DCE may have been a key intermediate, which was below detection limits. A carbene intermediate can form as a result of \( \alpha \)-elimination of 1,1-DCE then the carbene can hydrogenate to ethene and ethane. It is also plausible that \( \alpha \)-elimination has a role in a more direct transformation of 1,1,1-TCA into ethene and ethene (Cwiertny et al., 2006). Song and Carraway (2006) suggested a CF degradation pathway involving \( \alpha \)-elimination also. CF and 1,1,1-TCA are structurally similar, each containing three chlorine atoms bonded to one carbon atom, and their degradation mechanisms could be similar as well.

In a similar study (Fennelly and Roberts, 1998), the reaction of granular iron with and without Cu\(^0\) plating was studied in 1,1,1-TCA degradation. The reaction of granular iron \( (\text{Fe}^0) \) alone with 1,1,1-TCA (Fennelly and Roberts, 1998) yielded 1,1-DCA and ethene byproducts suggesting degradation by hydrogenolysis pathway. However, granular iron and Cu\(^0\) plating with 1,1,1-TCA yielded 1,1-DCE and ethene in addition to
1,1-DCA and ethane byproducts, which suggests degradation by dehydrohalogenation pathway. Furthermore, the Cu plated granular iron (Fennelly and Roberts, 1998) degraded 1,1,1-TCA faster and produced a higher proportion of ethane and a lesser proportion of 1,1-DCA compared to the granular iron alone. Cwiertny et al. (2006) evaluated Ni, Pd, Cu, Co, Au, and Pt in combination with granular iron and found that all the bimetallic reductants favored ethene and ethane production over 1,1-DCA. The present study with Cu-nZVI shows similar results regarding product distribution changes induced by the addition of Cu to nZVI.

In another study (Song and Carraway, 2005), 1,1,1-TCA degradation by 0.081 g/L unstabilized nZVI (0.01 g nZVI in 124 mL buffered water) was comparable ($k_{obs} = 0.340$ hr$^{-1}$; $k_M = 4.20$ L g$^{-1}$ hr$^{-1}$). In a comparison with unstable nZVI particles (Song and Carraway, 2005), the degradation kinetics of 1,1,1-TCA with stabilized Cu-nZVI was much faster; 12-fold and 7-fold faster for $k_{M1}$ and $k_{M2}$ respectively. Furthermore, Song and Carraway (2005) reported that 1,1,1-TCA degradation by unstabilized nZVI yielded 1,1-DCA as the major product ($m/m_0 \sim 0.5$) followed by ethane as a secondary product ($m/m_0 \sim 0.2$) after 5 hr. Degradation of 1,1,1-TCA with stabilized Cu-nZVI in ~2 hrs showed more complete dechlorination and produced less 1,1-DCA, which was a desirable outcome.

1,1,1-TCA is a recalcitrant CHC commonly found at contaminated sites. The biotransformation of 1,1,1-TCA often occurs under strongly reducing (methanogenic and sulfate-reducing) conditions (Fam et al., 2012). However, the ability of Cu-nZVI to completely degrade 1,1,1-TCA abiotically is of major significance. Cho and Choi (2010) studied PCE, TCE and 1,1,1-TCA degradation by CMC stabilized Pd-nZVI, and reported
that 1,1,1-TCA was the most difficult to degrade among the three compounds \((k_{\text{obs}} = 0.0546 \text{ hr}^{-1}; k_M = 0.546 \text{ L g}^{-1} \text{ hr}^{-1})\); they suggested that the difficulty in 1,1,1-TCA degradation may be due to the arrangement of three chlorines on one carbon atom. The present study, however, found that Cu-nZVI was able to degrade 1,1,1-TCA more rapidly than Pd-nZVI (Cho and Choi, 2010), but degraded TCE much slower (section 3.4.1). Overall, Cu-nZVI was particularly efficient at degrading 1,1,1-TCA compared to other metallic systems reported in literature. Various secondary metals with nZVI may produce dramatically different results regarding CHC degradation kinetics and byproduct distributions.

### 3.2.3: 1,1,2-TCA degradation by nZVI and Cu-nZVI

The degradation of 1,1,2-TCA with 0.2 g/L stabilized nZVI was small (Fig. 3.25). After ~4.5 hr, only trace amounts of ethane (~0.03) was identified, and 1,1,2-TCA remaining \((m/m_0)\) was 0.81 with the carbon mass balance at ~0.84. Most of the degradation occurred during the first 0.5 hr. \(k_{\text{obs1}}\) was about 68-fold faster than \(k_{\text{obs2}}\) \((k_{\text{obs1}} = 0.347 \text{ hr}^{-1}; k_{M_1} = 1.74 \text{ L g}^{-1} \text{ hr}^{-1}; k_{\text{obs2}} = 0.00510 \text{ hr}^{-1}; k_{M_2} = 0.0255 \text{ L g}^{-1} \text{ hr}^{-1})\).

In comparison, 1,1,2-TCA degradation with stabilized Cu-nZVI (0.2 g/L nZVI and 5 wt% Cu) was considerable (Fig. 3.26). VC, ethene, and ethane were identified as degradation products. After ~4 hr, 1,1,2-TCA remaining \((m/m_0)\) was 0.29, while the VC, ethene and ethane yields \((m/m_0)\) were 0.55, 0.02, and 0.01 respectively. A carbon mass balance \((m/m_0)\) of 0.88 suggests that most of the original 1,1,2-TCA was identified in the observed byproducts. The \(k_{\text{obs1}}\) of 1,1,2-TCA degradation was about 1.8-fold faster than \(k_{\text{obs2}}\) \((k_{\text{obs1}} = 0.481 \text{ hr}^{-1}; k_{M_1} = 2.41 \text{ L g}^{-1} \text{ hr}^{-1}; k_{\text{obs2}} = 0.273 \text{ hr}^{-1}; k_{M_2} = 1.37 \text{ L g}^{-1} \text{ hr}^{-1})\).
The Cu-nZVI system was much more effective at degrading 1,1,2-TCA compared to the nZVI system (1.4-fold and 54-fold faster for \( k_{M1} \) and \( k_{M2} \) respectively). The nZVI system showed substantial degradation in the first 0.5 hr, but a major loss in reactivity toward 1,1,2-TCA after 0.5 hr. Conversely, the Cu-nZVI system experienced only minor loss in reactivity after 0.5 hr. Furthermore, data collected 20 hr after the start of the experiment (not shown in Fig 3.26), indicates no loss in reactivity of the Cu-nZVI particles occurred after 0.5 hr. After 20 hr, the 1,1,2 TCA remaining \((m/m_0)\) was ~ 0.05 and it also showed continued buildup of VC, ethane, and ethene yields \((m/m_0)\) at 0.76, 0.03, and 0.08 respectively.

Song and Carraway (2005) studied 1,1,2-TCA degradation \((k_{obs} = 0.00520 \text{ hr}^{-1}, k_M = 0.0645 \text{ L g}^{-1} \text{ hr}^{-1})\) by 0.081 g/L unstabilized nZVI (0.01 g nZVI in 124 mL buffered water). In comparison with the unstable nZVI particles (Song and Carraway, 2005), 1,1,2-TCA degradation by stabilized Cu-nZVI was 37-fold and 21-fold faster for \( k_{M1} \) and \( k_{M2} \), respectively. Further, Song and Carraway (2005) reported a near complete carbon mass balance and ethane as the only degradation product. Ethane is more favorable than VC, which formed as the major product in the Cu-nZVI system. However, over a longer time interval VC may degrade to ethene in the Cu-nZVI system.

A majority of products were identified as indicated by a near complete carbon mass balance. VC could form via \( \alpha \) or \( \beta \)-dichloroelimination of 1,1,2-TCA. VC appears to form as a terminal product in the Cu-nZVI system at the experimental conditions in this study. VC is not a desirable product due to its high toxicity. However, VC may degrade rapidly via oxidative processes in the natural environment. If there is an aerobic zone downgradient of a source zone where nZVI injection is implemented, then any VC
produced should mineralize to carbon dioxide by direct and co-metabolic microbial oxidation (Bradley, 2000). Many contaminated sites often require the utilization of multiple remediation technologies. This study suggests that Cu-nZVI alone may not be enough to completely remEDIATE a 1,1,2-TCA contaminated site. However, if Cu-nZVI source treatment was coupled with another technology such as monitored natural attenuation in a downgradient aerobic zone to treat VC, the remediation would be effective.

Ethane and ethene also formed in the Cu-nZVI system and are benign products. Both ethane and ethene were observed in trace amounts. Ethane could form from sequential hydrogenolysis of 1,1,2-TCA, hydrogenation of ethene, or via a direct pathway with short-lived intermediate species. Ethene could form from hydrogenolysis of 1,1,2-TCA followed by dichloroelimination of 1,1-DCA or 1,2-DCA. No evidence of DCA species were observed. However, low levels of DCA as an intermediate or product may have been below detection limits.

3.3 Chlorinated Ethenes

3.3.1: PCE degradation by Cu nZVI

PCE degradation with Cu-nZVI (0.2 g/L stabilized nZVI and 5 wt% Cu) was small (Fig. 3.27). After ~5 hr, TCE, 1,1-DCE, cis-DCE, trans-DCE, ethane, and ethene yields were observed in trace amounts (totaling <0.01). PCE remaining ($m/m_0$) was 0.81. A carbon mass balance ($m/m_0$) of 0.82 suggests that other product(s) may have been produced, but could not be identified. Another possibility for unaccounted mass is sorption to particle surfaces (Burris et al., 1995). $k_{obs1}$ was about 49-fold faster than $k_{obs2}$.
\[ k_{\text{obs1}} = 0.338 \, \text{hr}^{-1}; k_{M1} = 1.69 \, \text{L g}^{-1} \text{hr}^{-1}; k_{\text{obs2}} = 0.0069 \, \text{hr}^{-1}; k_{M2} = 0.0345 \, \text{L g}^{-1} \text{hr}^{-1}. \] The \( k_{\text{obs2}} \) degradation may not be statistically significant. Due to poor PCE degradation with Cu-nZVI, the ability of nZVI alone to degrade PCE was not evaluated.

Song and Carraway (2008) reported that PCE degradation was slower than any other chlorinated ethenes with unstable nZVI. Conversely, microbial processes could degrade PCE more rapidly than other chlorinated ethenes because PCE is highly oxidized and reducing it is more energy yielding (Bradley, 2000). The present study with Cu-nZVI does not show much potential for PCE remediation. Chiu et al. (2012), however, showed that bioaugmentation with a certain bacteria drastically increased degradation of PCE in the presence of ZVI. It appears that a strictly abiotic approach, using CMC stabilized Cu-nZVI, to remediate PCE is much less effective than microbially mediated PCE degradation.

### 3.3.2: TCE degradation by Cu nZVI

TCE degradation with Cu-nZVI (0.2 g/L stabilized nZVI and 5 wt% Cu) was minor (Fig. 3.28). After ~2.7 hr, ethane and ethene yields were observed in trace amounts \((m/m_0) \sim 0.02 \) and 0.02 respectively). 1,1-DCE, cis-DCE, trans-DCE were also observed in trace amounts \((m/m_0 \) total <0.01). TCE remaining \((m/m_0) \) was 0.82. A carbon mass balance \((m/m_0) \) of 0.85 suggests that other product(s) may have been produced, but could not be identified. Another possibility for unaccounted mass is sorption to particle surfaces (Burris et al., 1995). \( k_{\text{obs1}} \) of TCE degradation was ~11-fold faster than \( k_{\text{obs2}} \) \((k_{\text{obs1}} = 0.348 \, \text{hr}^{-1}; k_{M1} = 1.74 \, \text{L g}^{-1} \text{hr}^{-1}; k_{\text{obs2}} = 0.0327 \, \text{hr}^{-1}; k_{M2} = 0.164 \, \text{L} \)
Due to poor TCE degradation with Cu-nZVI, an experiment with higher nZVI loading was conducted.

TCE degradation by Cu-nZVI with increased nZVI concentration (0.5 g/L stabilized nZVI and 5 wt% Cu) was greater than the previous experiment with a lesser nZVI concentration (Fig. 3.29). After ~6 hr, ethane, and ethene yields (m/m₀) were in trace amounts (0.02 and 0.04, respectively). Further, 1,1-DCE, cis-DCE, and trans-DCE were also observed in trace amounts (m/m₀ < 0.01). TCE remaining (m/m₀) was 0.72 and the carbon mass balance (m/m₀) was 0.78. k_{obs1} was about 11-fold faster than k_{obs2} (k_{obs1} = 0.432 hr⁻¹; k_{M1} = 0.0183 L g⁻¹ hr⁻¹; k_{obs2} = 0.864 hr⁻¹; k_{M2} = 0.0366 L g⁻¹ hr⁻¹). The higher iron loading had higher k_{obs}, but lower k_{M}.

In a similar study (Song and Carraway, 2008), TCE degradation by 0.16 g/L unstabilized nZVI (0.02 g nZVI in 124 mL buffered water) was much faster when comparing kₐ₅ᵗ (k_{obs} = 0.495 hr⁻¹; k_{M} = 3.09 L g⁻¹ hr⁻¹). TCE degradation in the Cu-nZVI system was 1.8-fold and 19-fold slower than unstabilized nZVI (Song and Carraway, 2008) with regard to k_{M1} and k_{M2} respectively. Higher Cu-nZVI concentrations may be necessary to achieve substantial degradation. While lower k_{M} kinetics typically result when increasing nZVI loading, the increase in k_{obs} can be more beneficial. Degradation pathways of TCE include many of the pathways and mechanisms described for PCE degradation (Arnold and Roberts, 2000).

Schrick et al. (2002) studied TCE degradation by Ni-nZVI and they reported faster kinetics than TCE degradation by Cu-nZVI in the present study. Chlorinated ethene degradation is driven by hydrogen gas (Scott and Crane, 2012). The CMC
stabilized Cu-nZVI particles do not produce much hydrogen, which may explain why slow degradation resulted (section 3.5.2).

3.3.3: *Cis*-DCE and *trans*-DCE degradation by Cu nZVI

The degradation of *cis*-1,2 DCE with 0.2 g/L stabilized nZVI and 5 wt% was modest (Fig. 3.30). After ~2 hr, ethane and ethene yields were observed in trace amounts (totaling 0.01); DCE remaining ($m/m_0$) was 0.57 and the carbon mass balance was 0.58. $k_{obs1}$ was about 30-fold faster than $k_{obs2}$ ($k_{obs1} = 0.985 \text{ hr}^{-1}$; $k_{M1} = 4.93 \text{ L g}^{-1} \text{ hr}^{-1}$; $k_{obs2} = 0.0324 \text{ hr}^{-1}$; $k_{M2} = 0.162 \text{ L g}^{-1} \text{ hr}^{-1}$). Due to the fast $k_{obs1}$ paired with slow $k_{obs2}$, an experiment to evaluate the effect of NaBH$_4$ on *cis*-DCE degradation was conducted.

*Cis*-DCE degradation by 0.13 mM NaBH$_4$ was similar to Cu-nZVI (0.2 g/L stabilized nZVI and 5 wt% Cu) (Fig. 3.). 0.13 mM NaBH$_4$ is the concentration needed to reduce 0.2 g/L nZVI during particle synthesis. Both *cis*-DCE degradation experiments exhibited rapid initial degradation followed by slow or negligible degradation. Both experiments also had trace ethane and ethene formation (totaling 0.01). For the NaBH$_4$ only system, $k_{obs1}$ ($k_{obs1} = 2.51 \text{ hr}^{-1}$) was ~86-fold faster than $k_{obs2}$ ($k_{obs2} = 0.0293 \text{ hr}^{-1}$). The NaBH$_4$ only system had 2.5-fold greater $k_{obs1}$, but a 10% smaller $k_{obs2}$ than the Cu-nZVI system. These experiments suggest that NaBH$_4$ is reacting with *cis*-DCE. NaBH$_4$ is highly reactive in water, and will quickly become depleted in the reactor. In the Cu-nZVI system, there should be some residual NaBH$_4$ that is leftover from nanoparticle synthesis. The residual NaBH$_4$ can react with the *cis*-DCE causing a high $k_{obs1}$, while a much lower $k_{obs2}$ follows after NaBH$_4$ is be depleted. In the NaBH$_4$ system, minimal or negligible degradation occurs after initial NaBH$_4$ is depleted because no other capable
reductants exist in the system. Residual NaBH₄ likely plays a role in enhancing $k_{\text{obs1}}$ for degradation of other CHCs.

Trans-DCE degradation with Cu-nZVI (0.2 g/L stabilized nZVI and 5 wt% Cu) was modest (Fig. 3.31). After ~3 hr, ethane and ethene yields were observed (0.02 and 0.04 respectively); trans-DCE remaining ($m/m₀$) was 0.75 and the carbon mass balance was 0.81. Initial degradation kinetics ($k_{\text{obs1}} = 0.492 \text{ hr}^{-1}; k_{M1} = 2.46 \text{ L g}^{-1} \text{ hr}^{-1}$) were ~30-fold faster than later kinetics ($k_{\text{obs2}} = 0.0206 \text{ hr}^{-1}; k_{M2} = 0.105 \text{ L g}^{-1} \text{ hr}^{-1}$). Trans-DCE degradation was similar to other chlorinated ethenes. Rapid initial degradation was followed by minimal or negligible degradation later.

3.4 Chlorinated Propanes

3.4.1: 1,2,3-TCP degradation by nZVI and Cu-nZVI

1,2,3-TCP degradation with 0.2 g/L nZVI was small (Fig. 3.32). After ~7 hr, no products were identified and 1,2,3-TCP remaining ($m/m₀$) was 0.78. $k_{\text{obs1}}$ was ~123-fold faster than $k_{\text{obs2}}$ ($k_{\text{obs1}} = 0.321 \text{ hr}^{-1}; k_{M1} = 1.61 \text{ L g}^{-1} \text{ hr}^{-1}; k_{\text{obs2}} = 0.0026 \text{ hr}^{-1}; k_{M2} = 0.013 \text{ L g}^{-1} \text{ hr}^{-1}$). Little or no 1,2,3-TCP degradation was observed after 0.5 hr. An experiment lasting several days may be needed to verify mass removal and reaction products.

In comparison, the degradation of 1,2,3-TCP with Cu-nZVI (0.2 g/L stabilized nZVI and 5 wt% Cu) was much faster than nZVI alone (Fig. 3.33). After ~22 hr, propene was the only identified product ($m/m₀ = 0.49$) and 1,2,3-TCP remaining ($m/m₀$) was 0.48. A carbon mass balance ($m/m₀$) of 0.97 suggests that any unidentified product was in trace amount. The carbon mass balance ($m/m₀$) was 0.81 at ~2.3 hr, which suggests formation
of an intermediate/adsobed species before propene. The $k_{\text{obs1}}$ was ~13-fold faster than $k_{\text{obs2}}$ ($k_{\text{obs1}} = 0.295 \text{ hr}^{-1}; k_M = 1.48 \text{ L g}^{-1} \text{ hr}^{-1}; k_{\text{obs2}} = 0.0221 \text{ hr}^{-1}; k_M = 0.111 \text{ L g}^{-1} \text{ hr}^{-1}$).

Degradation of 1,2,3-TCP with Cu-nZVI may involve β-elimination and hydrogenolysis. Sarathy et al. (2010) suggested that 1,2,3-TCP degradation may begin with β-elimination to produce 3-chloro-1-propene, which further degraded by hydrogenolysis to form propene. 3-chloro-1-propene was below detection limits. However, the decrease and increase in the carbon mass balance (Fig. 3.33) is interpreted as the formation and degradation of 3-chloro-1-propene. It is also possible for 1,2,3-TCP to undergo hydrogenolysis first and then β-elimination, however this is only a minor pathway (Sarathy et al., 2010). No evidence of sequential hydrogenolysis or dehydrohalogenation was observed.

### 3.5 nZVI Particle longevity

#### 3.5.1: 1,1,1-TCA degradation by unstable and stable Cu-nZVI over extended period

1,1,1-TCA degraded more rapidly than any other compound evaluated in this study. Over a 1 day time period, unstable Cu-nZVI maintained higher reactivity compared to stable Cu-nZVI as particles aged. Unstable Cu-nZVI showed a linear decline in reactivity with time. Stable Cu-nZVI showed a power function decline in reactivity with time. These data suggest that stabilization with CMC decreases particle reactivity. However, in order for the nZVI technology to be implemented at field scale, the use of a stabilizer to ensure particle mobility in water is essential.
A longer experiment evaluated stable Cu-nZVI, unstable Cu-nZVI, stable nZVI, and unstable nZVI over the course of 7 days (Fig 3.35). The unstable Cu-nZVI continued to show a linear decline in reactivity with time; the unstable Cu-nZVI showed a 2-fold decrease in $k_{\text{obs}}$ over 7 days. In comparison, 0.2 g/L Cu-nZVI stabilized with 4 g/L CMC showed a fast non-linear decline in reactivity with time. The $k_{\text{obs}}$ of the stabilized Cu-nZVI reactivity declined 8.6-fold over 1 day, followed by another 2-fold decline in $k_{\text{obs}}$ from day 2 to day 7. The $k_{\text{obs}}$ of the unstable Cu-nZVI was ~14-fold greater than stabilized Cu-nZVI after 7 days.

In comparison to Cu-nZVI systems, both stable and unstable nZVI showed drastically lower reactivity (~140-fold smaller $k_{\text{obs}}$). In addition, both stable and unstable nZVI degradation was difficult to measure with confidence after the first day due to slow degradation. Due to slow degradation of the stable and unstable nZVI systems, one degradation rate was calculated for the later six days (stable nZVI $k_{\text{obs}}^2 = 0.00102$; unstable nZVI $k_{\text{obs}}^2 = 0.00216$) and was used to compare with the degradation kinetics collected on the first day (stable nZVI $k_{\text{obs}}^1 = 0.838$, $k_{\text{obs}}^2 = 0.0460$; unstable nZVI $k_{\text{obs}}^1 = 0.0515$, $k_{\text{obs}}^2 = 0.00216$).

There are a wide variety of reasons for losses in particle reactivity with time. Residual NaBH$_4$ could interact with nZVI producing complexes capable of enhancing CHC degradation (Koehne et al., 2014). The influence of residual borohydride would be limited to the first few minutes of the reactions though. Borohydride reacts vigorously in water and would become depleted in a short time period. As nZVI ages in water, the outer layers become oxidized. nZVI will anaerobically corrode in water (Nyer and Vance, 2001). Liu et al. (2015) studied nZVI particle (using borohydride synthesis)
aging in static water. After 5 days in static water, particle shells were composed of magnetite (Fe₃O₄), maghemite (γ-Fe₂O₃), and lepidocrocite (γ-FeOOH); after 10 days the particle shell was composed of ferrihydrite and lepidocrocite. While the outer shell of the particles is oxidizing, the inner core remains zero-valent for a longer period of time because it is shielded from reactions to a certain extent. Also, CMC is known to adversely affect reaction kinetics. Phenrat et al. (2009) showed that CMC stabilization can cause up to a 24-fold decrease in reactivity when treating TCE with nZVI. There are a variety of causes for particle reactivity loss and there may be multiple processes occurring simultaneously that can lead to particle reactivity loss.

3.5.2: Hydrogen production by nZVI and Cu-nZVI in water

Experiments evaluating hydrogen evolution through nZVI and Cu-nZVI reactions in water were conducted. As previously mentioned, anaerobic corrosion of nZVI produces hydrogen gas (Nyer and Vance, 2001). Three different stabilized particle systems were evaluated; 0.2 g/L nZVI, 0.2 g/L nZVI with 5 wt% Cu, and 0.2 g/L nZVI with 10 wt% Cu (Fig 3.36). The total amount of hydrogen in the reactor bottles can vary to a minor degree for the following reasons. 1) The hydrogen in the anaerobic chamber, where particle synthesis took place, fluctuates between 1-2% of total atmosphere. 2) The synthesis of nZVI requires adding NaBH₄ to the reactor bottles before bottles are sealed. Hydrogen production is greatest immediately after reduction of Fe (II) and because this is done before reactor bottles are sealed, some hydrogen escapes the reactor bottles. Sealing of the reactor bottles was done approximately 30 seconds after Fe (II) reduction. Reactor bottles could not be sealed prior to NaBH₄ addition because pressure build up would create over pressurized bottles. 3) Lastly, there may be more hydrogen in a given
reactor because the particles in that reactor are producing more hydrogen. Due to the reasons stated above, total hydrogen in reactor bottles is not meaningful for comparison among the different systems studied. The significance of this series of experiments is related to the rate of hydrogen production and not the total amount of hydrogen produced.

The linear rate of hydrogen production for the three systems studied in order of greatest to least is as follows: nZVI, 5% Cu-nZVI, and 10% Cu-nZVI. It should be noted that due to the low hydrogen production rates for all systems, it was difficult to measure hydrogen production rates with accuracy. It was unexpected that 10% Cu-nZVI would have the lowest rate of hydrogen production and that nZVI would have the highest rate of hydrogen production (Fig 3.36). It is likely that there is no significant difference in the hydrogen production rates for all the systems studied. Chen et al. (2011) report conflicting results, showing that unstabilized Cu-nZVI produces 18% more hydrogen than unstabilized nZVI.

A more meaningful observation extracted from the series of hydrogen experiments was that hydrogen production was low for all systems and production plateaued after a few hours. Hydrogen production data collected 24 hr after particle synthesis showed that only ~0.1 mmole of hydrogen was produced in between 4 and 20 hr after particle synthesis for all particle systems. The outer layer of nZVI particles oxidizes and becomes less reactive over time (Liu et al., 2015). While the particles are much less reactive in water after one day, particles are still highly reactive with certain CHCs, such as 1,1,1-TCA seven days after particle synthesis. Furthermore, CMC stabilization has been shown to reduce nZVI reactivity with CHCs (Phenrat et al., 2009). It is therefore reasonable to suggest that CMC stabilization also reduces nZVI reactivity
with water. Chen et al. (2011) reported continuous hydrogen production from unstable nZVI for over 200 hr after particle synthesis.

In summary, Cu-nZVI and nZVI stabilized with CMC did not show much hydrogen production. The only significant hydrogen production occurred immediately after particle synthesis. Furthermore, it is possible that the hydrogen production was derived from NaBH₄ directly, not nZVI or Cu-nZVI. While particles are not reactive with water, they remain reactive with certain CHCs, such as 1,1,1-TCA, for multiple days.

3.5.2: Agglomeration of unstable nZVI and Cu-nZVI in static water

An experiment was conducted to evaluate the degree of nanoparticle agglomeration. This experiment consisted of synthesizing four different types of particles: unstable nZVI, stable nZVI, unstable Cu-nZVI, and stable Cu-nZVI. After synthesis, the four bottles were placed on a rotator for five minutes and then placed on a countertop for 3 hr. Pictures were taken of the bottles to document any visual agglomeration. It was also noted that stabilized particles were dark black in color and unstabilized particles were gray in color immediately after synthesis. Agglomeration was visibly occurring in the unstable particles one hr after synthesis. After 3 hr most of the unstable nZVI had settled to the bottom of the bottles. On the other hand, CMC-stabilized particles did not agglomerate and remained suspended in water, even after multiple days of monitoring. There was no visual difference between nZVI particles and Cu-nZVI particles.
Chapter 4

CONCLUSIONS

- Cu-nZVI proved to be superior to nZVI for CF degradation. The addition of Cu to the nZVI system increased reaction kinetics and produced more favorable byproducts. Cu loading experiments showed that increasing the Cu loading (0 – 10 wt%) caused a linear increase in $k_{obs}$. nZVI concentration experiments with 5 wt% Cu showed that increasing nZVI concentrations increased $k_{obs}$ but decreased $k_M$.

For field scale implementation of this technology, site characteristics need to be carefully considered when selecting concentrations of Cu and nZVI. Using higher Cu loadings will cause the particles to be more reactive and will likely decrease their longevity. Using high nZVI concentrations will decrease $k_M$. Implementing this technology with a high nZVI concentration (lower $k_M$) is less efficient and will increase cost.

- 1,1,2,2-TeCA, 1,1,1-TCA, and 1,1,2-TCA all degraded more rapidly in the Cu-nZVI system compared to the nZVI alone system. Cu clearly has a favorable effect on degradation kinetics and byproduct distributions with regard to chlorinated ethenes. It is worth mentioning that 1,1,1-TCA and CF were the most effectively degraded CHCs by Cu-nZVI evaluated in this study. It appears that the arrangement of multiple chlorines bonded to a single carbon in 1,1,1-TCA and in CF make them
more susceptible to dechlorination (α-elimination) by Cu-nZVI. Cho and Choi (2010) reported that 1,1,1-TCA was more difficult to degrade than chlorinated ethenes with Pd-nZVI due to the chlorine atom arrangement. However, the present study suggests that the opposite may be true for Cu-nZVI, which is more effective at degrading compounds with multiple chlorines a single carbon atom. Furthermore, Cu-nZVI is more effective at degrading compounds with single bonds than double bonds.

- In general, the performance of Cu-nZVI was poor for degradation of chlorinated ethenes. Song and Carraway (2008) have shown that unstabilized nZVI can potentially serve as a legitimate chlorinated ethenes remediation technology. The present study with Cu-nZVI did not show significant advantages for remediation of chlorinated ethenes. In many cases, Cu-nZVI showed negligible degradation of chlorinated ethenes after 0.5 hr of initiating the experiment. As shown with the NaBH₄ and cis-DCE experiments, the initial degradation may not even be caused by the Cu-nZVI particles. Initial degradation is likely caused by interactions with NaBH₄. Other secondary metals, beside Cu, show more potential for chlorinated ethene degradation. Chlorinated ethene degradation is driven by hydrogen gas (Scott and Crane, 2012). The lack of hydrogen production by CMC stabilized Cu-nZVI particles may explain why chlorinated ethene degradation is poor.

- 1,2,3-TCP degradation was significantly enhanced by the addition of Cu to the nZVI system. Propene was identified as the major byproduct of 1,2,3-TCP degradation; accounting for nearly all original 1,2,3-TCP one day after initiating the experiment. Propene is an ideal product and it was not detected in the nZVI system.
The longevity experiments confirmed that Cu-nZVI particles remain highly reactive with 1,1,1-TCA seven days after particle synthesis. As nZVI particles age, the outer layer may become oxidized, that decreases its reactivity to a certain degree. The hydrogen production data show that only marginal hydrogen production occurs from stabilized nZVI and stabilized Cu-nZVI particles in water. It is likely that stabilization (by CMC) causes decreased reactivity of particles in water. Stabilization is necessary in order for this technology to be implemented at field scale. Particles injected at contaminated sites need to remain suspended in solution in order to be transported to DNAPL sources and mix with dissolved DNAPL. Furthermore, decreased reactivity of particles in water can be viewed as a favorable effect of CMC stabilization. The intended electron acceptors are CHCs and not water.

The present study shows that Cu-nZVI has potential for remediation of chlorinated methanes, ethanes and propanes; however, more research is needed. Future work could focus on the effect that pH or CMC concentration has on degradation kinetics of various CHCs. Batch, column, and pilot-scale field studies should be done to evaluate the longer-term performance of Cu-nZVI. There are also additional CHCs that should be evaluated for degradation by Cu-nZVI. Since CMC showed a negative effect on particle reactivity the effect of other stabilization techniques could be investigated.
References


Parshetti, G. K. and Doong, R., Dechlorination of chlorinated hydrocarbons by mimetallic Ni/Fe immobilized on polyethylene glycol-grafted microfiltration membranes under anoxic conditions. Chemosphere. 86, 392-399.


Figure 3.1: CF degradation and product formation with 0.05 g/L nZVI prepared in 4 g/L CMC and 30 mM TAPSO buffer at pH 7. Initial CF = 0.28 μmoles (~100 μL of 233 mg/L CF stock solution). (A) Degradation and byproducts (mole fraction). (B) CF degradation rate constants, $k_{obs1}$ and $k_{obs2}$, plotted on semi-log scale.
Figure 3.2: CF degradation and product formation with 0.05 g/L nZVC prepared in 4 g/L CMC and 30 mM TAPSO buffer at pH 7. Initial CF = 0.53 μmoles (≈200 μL of 233 mg/L CF stock solution). (A) Degradation and byproducts (mole fraction). (B) CF degradation rate constants, $k_{obs1}$ and $k_{obs2}$, plotted on semi-log scale.
Figure 3.3: CF degradation and product formation with 0.05 g/L nZVI and 1 wt% Cu. Reactors were prepared in 4 g/L CMC and 30 mM TAPSO buffer at pH 7. Initial CF = 0.27 μmoles (~100 μL of 233 mg/L CF stock solution). (A) Degradation and byproducts (mole fraction). (B) CF degradation rate constants, \( k_{\text{obs1}} \) and \( k_{\text{obs2}} \), plotted on semi-log scale.
Figure 3.4
CF degradation and product formation with 0.05 g/L nZVI and 2 wt% Cu. Reactors were prepared in 4 g/L CMC and 30 mM TAPSO buffer at pH 7. Initial CF = 0.35 μmoles (~125 μL of 233 mg/L CF stock solution). (A) Degradation and byproducts (mole fraction). (B) CF degradation rate constants, $k_{obs1}$ and $k_{obs2}$, plotted on semi-log scale.
Figure 3.5
CF degradation and product formation with 0.05 g/L nZVI and 5 wt% Cu. Reactors were prepared in 4 g/L CMC and 30 mM TAPSO buffer at pH 7. Initial CF = 0.24 μmoles (~100 μL of 233 mg/L CF stock solution). (A) Degradation and byproducts (mole fraction). (B) CF degradation rate constants, \( k_{\text{obs1}} \) and \( k_{\text{obs2}} \), plotted on semi-log scale.
CF degradation and product formation with 0.05 g/L nZVI and 7.5 wt% Cu. Reactors were prepared in 4 g/L CMC and 30 mM TAPSO buffer at pH 7. Initial CF = 0.27 µmoles (~100 µL of 233 mg/L CF stock solution). (A) Degradation and byproducts (mole fraction). (B) CF degradation rate constants, $k_{\text{obs1}}$ and $k_{\text{obs2}}$, plotted on semi-log scale.

\[ y = -1.9881x - 0.0152 \quad R^2 = 0.997 \]
\[ y = -0.8097x - 0.5574 \quad R^2 = 0.9984 \]
CF degradation and product formation with 0.05 g/L nZVI and 10 wt% Cu. Reactors were prepared in 4 g/L CMC and 30 mM TAPSO buffer at pH 7. Initial CF = 0.26 μmoles (~100 μL of 233 mg/L CF stock solution). (A) Degradation and byproducts (mole fraction). (B) CF degradation rate constants, $k_{obs1}$ and $k_{obs2}$, plotted on semi-log scale.
Figure 3.8
Initial degradation kinetics ($k_{obs1} = 0.430-2.26 \text{ hr}^{-1}; k_M = 8.60-45.1 \text{ L g}^{-1} \text{ hr}^{-1}$) were faster than later kinetics ($k_{obs2} = 0.0750-0.994 \text{ hr}^{-1}; k_M = 1.50-19.9 \text{ L g}^{-1} \text{ hr}^{-1}$). Increased Cu loading yielded increased degradation kinetics. (A) CF degradation comparison at varied Cu loading. (B) CF degradation constants, $k_{obs1}$ and $k_{obs2}$, plotted as a function of Cu loading.
Figure 3.9
CF degradation rates are displayed as a ratio of $k_{M1} : k_{M2}$ and are plotted as a function of Cu loading (i.e. a $k_{M1} : k_{M2}$ ratio of 1 would indicate that no change in kinetics occurred). Low Cu loadings show a greater $k_{M1} : k_{M2}$ ratio. The $k_{M1} : k_{M2}$ ratio starts leveling off, but is still decreasing at about 5 wt.% Cu loading.

Figure 3.10
CF degradation product distributions are shown as a function of Cu loading. Product distributions are shown for 2.5 hr after the start of experiments. There is a systematic methane increase with Cu loading.
Figure 3.11
CF degradation and product formation with 0.05 g/L nZVI and 5 wt% Cu. Reactors were prepared in 4 g/L CMC and 30 mM TAPSO buffer at pH 7. Initial CF = 0.42 μmoles (~200 μL of 233 mg/L CF stock solution). (A) Degradation and byproducts (mole fraction). (B) CF degradation rate constants, $k_{obs1}$ and $k_{obs2}$, plotted on semi-log scale.
Figure 3.12
CF degradation and product formation with 0.1 g/L nZVI and 5 wt% Cu. Reactors were prepared in 4 g/L CMC and 30 mM TAPSO buffer at pH 7. Initial CF = 0.42 μmoles (~200 μL of 233 mg/L CF stock solution). (A) Degradation and byproducts (mole fraction). (B) CF degradation rate constants, $k_{obs1}$ and $k_{obs2}$, plotted on semi-log scale.
Figure 3.13
CF degradation and product formation with 0.2 g/L nZVI and 5 wt% Cu. Reactors were prepared in 4 g/L CMC and 30 mM TAPSO buffer at pH 7. Initial CF = 0.42 μmoles (~200 μL of 233 mg/L CF stock solution). (A) Degradation and byproducts (mole fraction). (B) CF degradation rate constants, $k_{obs1}$ and $k_{obs2}$, plotted on semi-log scale.
Figure 3.14
CF degradation and product formation with 0.3 g/L nZVI and 5 wt% Cu. Reactors were prepared in 4 g/L CMC and 30 mM TAPSO buffer at pH 7. Initial CF = 0.42 μmoles (~200 μL of 233 mg/L CF stock solution). (A) Degradation and byproducts (mole fraction). (B) CF degradation rate constants, $k_{\text{obs}1}$ and $k_{\text{obs}2}$, plotted on semi-log scale.
Figure 3.15
CF degradation and product formation with 0.4 g/L nZVI and 5 wt% Cu. Reactors were prepared in 4 g/L CMC and 30 mM TAPSO buffer at pH 7. Initial CF = 0.40 μmoles (~200 μL of 233 mg/L CF stock solution). (A) Degradation and byproducts (mole fraction). (B) CF degradation rate constants, \( k_{obs1} \) and \( k_{obs2} \), plotted on semi-log scale.
Figure 3.16
CF degradation and product formation with 0.5 g/L nZVI and 5 wt% Cu. Reactors were prepared in 4 g/L CMC and 30 mM TAPSO buffer at pH 7. Initial CF = 0.41 μmoles (~200 μL of 233 mg/L CF stock solution). (A) Degradation and byproducts (mole fraction). (B) CF degradation rate constants, $k_{obs1}$ and $k_{obs2}$, plotted on semi-log scale.
Figure 3.17
CF degradation and product formation with 0.6 g/L nZVI and 5 wt% Cu. Reactors were prepared in 4 g/L CMC and 30 mM TAPSO buffer at pH 7. Initial CF = 0.42 μmoles (~200 μL of 233 mg/L CF stock solution). (A) Degradation and byproducts (mole fraction). (B) CF degradation rate constants, $k_{obs1}$ and $k_{obs2}$, plotted on semi-log scale.
Figure 3.18
CF degradation and product formation with 0.7 g/L nZVI and 5 wt% Cu. Reactors were prepared in 4 g/L CMC and 30 mM TAPSO buffer at pH 7. Initial CF = 0.44 μmoles (~200 μL of 233 mg/L CF stock solution). (A) Degradation and byproducts (mole fraction). (B) CF degradation rate constants, $k_{obs1}$ and $k_{obs2}$, plotted on semi-log scale.
Figure 3.19
Initial degradation kinetics ($k_{obs1} = 1.40-7.53 \text{ hr}^{-1}; k_{M1} = 10.5-28.0 \text{ L g}^{-1} \text{ hr}^{-1}$) were faster than later kinetics ($k_{obs2} = 0.546-2.41 \text{ hr}^{-1}; k_{M2} = 3.44-10.9 \text{ L g}^{-1} \text{ hr}^{-1}$). Both $k_{M1}$ and $k_{M2}$ decreased with increasing nZVI loading. (A) CF degradation comparison at varied Cu loading. (B) CF degradation constants, $k_{obs1}$ and $k_{obs2}$, plotted as a function of Cu loading.
Figure 3.20
CF degradation product distributions are shown as a function of nZVI loading. Product distributions are shown for 2.5 hr after the start of experiments.
Figure 3.21
1,1,2,2-TeCA degradation and product formation with 0.2 g/L nZVI. Reactors were prepared in 4 g/L CMC and 30 mM TAPSO buffer at pH 7. Initial 1,1,2,2-TeCA = 0.54 μmoles (~200 μL of 496 mg/L 1,1,2,-TeCA stock solution). (A) Degradation and byproducts (mole fraction). (B) 1,1,2,2-TeCA degradation rate constant, \( k_{obs} \), plotted on semi-log scale. Only one \( k_{obs} \) value was calculated due to slow degradation kinetics.
1,1,2,2-TeCA degradation and product formation with 0.2 g/L nZVI and 5 wt% Cu. Reactors were prepared in 4 g/L CMC and 30 mM TAPSO buffer at pH 7. Initial 1,1,2,2-TeCA = 0.58 μmoles (~200 μL of 496 mg/L 1,1,2,-TeCA stock solution). (A) Degradation and byproducts (mole fraction). TCE was observed (not shown above) as a minor product (m/m₀ ≈ 0.02). (B) 1,1,2,2-TeCA degradation rate constants, k₁obs and k₂obs, plotted on semi-log scale.
Figure 3.23
1,1,1-TCA degradation and product formation with 0.2 g/L nZVI. Reactors were prepared in 4 g/L CMC and 30 mM TAPSO buffer at pH 7. Initial 1,1,1-TCA = 0.62 μmoles (~200 μL of 419 mg/L 1,1,1-TCA stock solution). (A) Degradation and byproducts (mole fraction). (B) 1,1,1-TCA degradation rate constants, $k_{\text{obs1}}$ and $k_{\text{obs2}}$, plotted on semi-log scale.

\[
\begin{align*}
\text{Ethane mole fraction (m/m)} & \\
0 & 0.02 \quad 0.04 \quad 0.06 \quad 0.08 \quad 0.1 \\
0 & 0.2 \quad 0.4 \quad 0.6 \quad 0.8 \quad 1
\end{align*}
\]

\[
\begin{align*}
\text{time (hr)} & \\
0 & 1 \quad 2 \quad 3 \quad 4 \quad 5
\end{align*}
\]

\[
\begin{align*}
\text{1,1,1-TCA mole fraction} & \\
0 & 0.2 \quad 0.4 \quad 0.6 \quad 0.8 \quad 1
\end{align*}
\]

\[
\begin{align*}
\text{1,1-DCA mole fraction} & \\
0 & 0.2 \quad 0.4 \quad 0.6 \quad 0.8 \quad 1
\end{align*}
\]

\[
\begin{align*}
\text{Total mole fraction (m/m)} & \\
0 & 0.2 \quad 0.4 \quad 0.6 \quad 0.8 \quad 1
\end{align*}
\]
Figure 3.24
1,1,1-TCA degradation and product formation with 0.2 g/L nZVI and 5 wt% Cu. Reactors were prepared in 4 g/L CMC and 30 mM TAPSO buffer at pH 7. Initial 1,1,1-TCA = 0.32 μmoles (~100 μL of 419 mg/L 1,1,1-TCA stock solution). (A) Degradation and byproducts (mole fraction). (B) 1,1,1-TCA degradation rate constants, $k_{obs1}$ and $k_{obs2}$, plotted on semi-log scale.
Figure 3.25
1,1,2-TCA degradation and product formation with 0.2 g/L nZVI. Reactors were prepared in 4 g/L CMC and 30 mM TAPSO buffer at pH 7. Initial 1,1,2-TCA = 0.69 μmoles (~200 μL of 419 mg/L 1,1,2,-TCA stock solution). (A) Degradation and byproducts (mole fraction). (B) 1,1,2-TCA degradation rate constants, $k_{\text{obs1}}$ and $k_{\text{obs2}}$, plotted on semi-log scale.

$y = -0.3465x - 0.0326$
$R^2 = 0.841$

$y = -0.0051x - 0.2016$
$R^2 = 0.3006$
Figure 3.26
1,1,2-TCA degradation and product formation with 0.2 g/L nZVI and 5 wt% Cu. Reactors were prepared in 4 g/L CMC and 30 mM TAPSO buffer at pH 7. Initial 1,1,2-TCA = 0.64 μmoles (~200 μL of 419 mg/L 1,1,2-TCA stock solution). (A) Degradation and byproducts (mole fraction). (B) 1,1,2-TCA degradation rate constants, $k_{\text{obs1}}$ and $k_{\text{obs2}}$, plotted on semi-log scale.
Figure 3.27
PCE degradation and product formation with 0.2 g/L nZVI and 5 wt% Cu. Reactors were prepared in 4 g/L CMC and 30 mM TAPSO buffer at pH 7. Initial PCE = 1.22 μmoles (~200 μL of 507 mg/L PCE stock solution). (A) Degradation and byproducts (mole fraction). (B) PCE degradation rate constants, $k_{obs1}$ and $k_{obs2}$, plotted on semi-log scale.
Figure 3.28
TCE degradation and product formation with 0.2 g/L nZVI and 5 wt% Cu. Reactors were prepared in 4 g/L CMC and 30 mM TAPSO buffer at pH 7. Initial TCE = 0.72 μmoles (~200 μL of 456 mg/L TCE stock solution). (A) Degradation and byproducts (mole fraction). (B) TCE degradation rate constants, $k_{obs1}$ and $k_{obs2}$, plotted on semi-log scale.
TCE degradation and product formation with 0.5 g/L nZVI and 5 wt% Cu. Reactors were prepared in 4 g/L CMC and 30 mM TAPSO buffer at pH 7. Initial TCE = 0.73 µmoles (∼200 µL of 456 mg/L TCE stock solution). (A) Degradation and byproducts (mole fraction). (B) TCE degradation rate constants, $k_{obs1}$ and $k_{obs2}$, plotted on semi-log scale.
Figure 3.30
Cis-DCE degradation and product formation with Cu-nZVI (0.2 g/L nZVI and 5 wt% Cu) and 0.13 mM NaBH₄. Reactors were prepared in 4 g/L CMC and 30 mM TAPSO buffer at pH 7. Initial cis-DCE = 0.82 μmoles (~200 μL of 401 mg/L cis-DCE stock solution). (A) Degradation (mole fraction). (B) Cis-DCE degradation rate constants, $k_{obs1}$ and $k_{obs2}$, plotted on semi-log scale.
Figure 3.31
Trans-DCE degradation and product formation with 0.2 g/L nZVI and 5 wt% Cu. Reactors were prepared in 4 g/L CMC and 30 mM TAPSO buffer at pH 7. Initial trans-DCE = 0.73 μmoles (~200 μL of 393 mg/L trans-DCE stock solution). (A) Degradation and byproducts (mole fraction). (B) Trans-DCE degradation rate constants, $k_{\text{obs1}}$ and $k_{\text{obs2}}$, plotted on semi-log scale.
Figure 3.32
1,2,3-TCP degradation and product formation with 0.2 g/L nZVI. Reactors were prepared in 4 g/L CMC and 30 mM TAPSO buffer at pH 7. Initial 1,2,3-TCP = 0.15 μmoles (~200 μL of 217 mg/L 1,2,3-TCP stock solution). The presence of byproducts with long retention times did not permit the use of duplicate reactors; error bars could not be generated. (A) Degradation and byproducts (mole fraction). (B) 1,2,3-TCP degradation rate constants, \( k_{obs1} \) and \( k_{obs2} \), plotted on semi-log scale.
Figure 3.33
1,2,3-TCP degradation and product formation with 0.2 g/L nZVI and 5 wt% Cu. Reactors were prepared in 4 g/L CMC and 30 mM TAPSO buffer at pH 7. Initial 1,2,3-TCP = 0.21 μmoles (~250 μL of 217 mg/L 1,2,3-TCP stock solution). The presence of byproducts with long retention times did not permit the use of duplicate reactors; error bars could not be generated. (A) Degradation and byproducts (mole fraction). (B) 1,2,3-TCP degradation rate constants, $k_{obs1}$ and $k_{obs2}$, plotted on semi-log scale.
1,1,1-TCA degradation by aging Cu-nZVI particles. Reactors were prepared in 30 mM TAPSO buffer at pH 7. Each 1,1,1-TCA reinjection contained ~0.7 μmoles (~200 μL of 419 mg/L 1,1,1,-TCA stock solution). Degradation kinetics, $k_{obs}$, are shown on the right. (A) 1,1,1-TCA degradation by stable Cu-nZVI (0.2g/L nZVI, 5 wt% Cu, and 4 g/L CMC). (B) 1,1,1-TCA degradation by unstable Cu-nZVI (0.2g/L nZVI and 5 wt% Cu).
Figure 3.35
1,1,1-TCA degradation by aged nZVI particles (stabilized, unstabilized, with Cu, and without Cu). Unstabilized Cu-nZVI appears to show a linear decline in reactivity with time. Stable Cu-nZVI appears to show a power function decline in reactivity with time. Stable and unstable nZVI show only a minor ability to degrade 1,1,1-TCA. (A) 1,1,1-TCA degradation over one day by stable and unstable Cu-nZVI. (B) 1,1,1-TCA degradation over one week by stable Cu-nZVI, unstable Cu-nZVI, stable nZVI, and unstable nZVI.
Figure 3.36
Hydrogen production by 0.2 g/L nZVI, 0.2 g/L nZVI with 5 wt% Cu, and 0.2 g/L nZVI with 10% Cu. All reactors contained 4 g/L CMC and TAPSO buffer set to pH 7. The rate of hydrogen production is shown with a linear regression. Hydrogen production for all three systems was slow.

\[
y = 0.0788x + 1.0846 \\
R^2 = 0.935
\]

\[
y = 0.0708x + 0.9679 \\
R^2 = 0.8917
\]

\[
y = 0.0596x + 0.7773 \\
R^2 = 0.8943
\]
Table 3.1

A series of experiments were conducted to examine the effect of Cu loading. All reactors were prepared with 4 g/L CMC and 30 mM TAPSO buffer at pH 7. Degradation kinetics are reported as pseudo first-order degradation observed rate constants ($k_{\text{obs}}$) and mass normalized degradation rate constant ($k_m$). Mole fraction yields are shown for 2.5 hr after the addition of CF into reactors.

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<th>Cu (wt%)</th>
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<th>$k_{M1}$ (L g$^{-1}$ hr$^{-1}$)</th>
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Table 3.2

A series of experiments were conducted to examine the effect of nZVI concentration. All reactors were prepared with 4 g/L CMC and 30 mM TAPSO buffer at pH 7. Degradation kinetics are reported as pseudo first-order degradation observed rate constants ($k_{\text{obs}}$) and mass normalized degradation rate constant ($k_m$). Mole fraction yields are shown for 2.5 hr after the addition of CF into reactors.

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<th>nZVI (g/L)</th>
<th>Cu (wt%)</th>
<th>$k_{\text{obs}1}$ (hr$^{-1}$)</th>
<th>$k_{M1}$ (L g$^{-1}$ hr$^{-1}$)</th>
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<tr>
<td>0.6</td>
<td>5</td>
<td>6.28</td>
<td>10.5</td>
<td>2.36</td>
<td>3.93</td>
<td>0.00</td>
<td>0.23</td>
<td>0.47</td>
<td>0.73</td>
</tr>
<tr>
<td>0.7</td>
<td>5</td>
<td>7.53</td>
<td>10.8</td>
<td>2.41</td>
<td>3.44</td>
<td>0.00</td>
<td>0.24</td>
<td>0.50</td>
<td>0.77</td>
</tr>
</tbody>
</table>
Table 3.3

Kinetic data is shown for various CHC degradation experiments by nZVI and Cu-nZVI. All reactors were prepared with 4 g/L CMC and 30 mM TAPSO buffer at pH 7. Degradation kinetics are reported as pseudo first-order degradation observed rate constants ($k_{obs}$) and mass normalized degradation rate constant ($k_{m}$).

<table>
<thead>
<tr>
<th>reductant</th>
<th>CHC</th>
<th>$k_{obs1}$ (hr$^{-1}$)</th>
<th>$k_{M1}$ (L g$^{-1}$ hr$^{-1}$)</th>
<th>$k_{obs2}$ (hr$^{-1}$)</th>
<th>$k_{M2}$ (L g$^{-1}$ hr$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2 g/L nZVI</td>
<td>1,1,2,2-TeCA</td>
<td>N/A</td>
<td>N/A</td>
<td>0.017</td>
<td>0.009</td>
</tr>
<tr>
<td>0.2 g/L nZVI 5% Cu</td>
<td>1,1,2,2-TeCA</td>
<td>1.796</td>
<td>8.980</td>
<td>0.842</td>
<td>4.210</td>
</tr>
<tr>
<td>0.2 g/L nZVI</td>
<td>1,1,1-TCA</td>
<td>0.797</td>
<td>3.985</td>
<td>0.052</td>
<td>0.258</td>
</tr>
<tr>
<td>0.2 g/L nZVI 5% Cu</td>
<td>1,1,1-TCA</td>
<td>9.770</td>
<td>48.850</td>
<td>5.860</td>
<td>29.300</td>
</tr>
<tr>
<td>0.2 g/L nZVI</td>
<td>1,1,2-TCA</td>
<td>0.347</td>
<td>1.735</td>
<td>0.005</td>
<td>0.025</td>
</tr>
<tr>
<td>0.2 g/L nZVI 5% Cu</td>
<td>1,1,2-TCA</td>
<td>0.481</td>
<td>2.405</td>
<td>0.273</td>
<td>1.365</td>
</tr>
<tr>
<td>0.2 g/L nZVI 5% Cu</td>
<td>PCE</td>
<td>0.338</td>
<td>1.690</td>
<td>0.007</td>
<td>0.035</td>
</tr>
<tr>
<td>0.2 g/L nZVI 5% Cu</td>
<td>TCE</td>
<td>0.348</td>
<td>1.740</td>
<td>0.033</td>
<td>0.164</td>
</tr>
<tr>
<td>0.5 g/L nZVI 5% Cu</td>
<td>TCE</td>
<td>0.432</td>
<td>0.864</td>
<td>0.018</td>
<td>0.037</td>
</tr>
<tr>
<td>0.2 g/L nZVI 5% Cu</td>
<td>cDCE</td>
<td>0.985</td>
<td>4.925</td>
<td>0.032</td>
<td>0.162</td>
</tr>
<tr>
<td>0.13 mM NaBH4</td>
<td>cDCE</td>
<td>2.510</td>
<td>N/A</td>
<td>0.842</td>
<td>N/A</td>
</tr>
<tr>
<td>0.2 g/L nZVI 5% Cu</td>
<td>tDCE</td>
<td>0.492</td>
<td>2.460</td>
<td>0.021</td>
<td>0.105</td>
</tr>
<tr>
<td>0.2 g/L nZVI</td>
<td>1,2,3-TCP</td>
<td>0.321</td>
<td>1.605</td>
<td>0.003</td>
<td>0.013</td>
</tr>
<tr>
<td>0.2 g/L nZVI 5% Cu</td>
<td>1,2,3-TCP</td>
<td>0.295</td>
<td>1.475</td>
<td>0.022</td>
<td>0.1105</td>
</tr>
</tbody>
</table>
Table 3.4

Suggested degradation mechanisms for CHCs degradation by Cu-nZVI are listed. Only mechanisms for observed products are described below. Additional products that were below detection limits are discussed in the chapter 3 of this manuscript.

<table>
<thead>
<tr>
<th>Parent</th>
<th>Products</th>
<th>Reaction Mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF</td>
<td>DCM</td>
<td>hydrogenolysis</td>
</tr>
<tr>
<td></td>
<td>Methane</td>
<td>direct transformation (α-elimination/ reactive intermediate)</td>
</tr>
<tr>
<td>1,1,2,2-TeCA</td>
<td>tDCE</td>
<td>β-elimination</td>
</tr>
<tr>
<td></td>
<td>TCE</td>
<td>dehydrohalogenation</td>
</tr>
<tr>
<td>1,1,1-TCA</td>
<td>1,1-DCA</td>
<td>hydrogenolysis</td>
</tr>
<tr>
<td></td>
<td>Ethane</td>
<td>direct transformation (α-elimination/ reactive intermediate)</td>
</tr>
<tr>
<td></td>
<td>Ethene</td>
<td>direct transformation (reactive intermediate) or dehydrohalogenation and hydrogenolysis</td>
</tr>
<tr>
<td>1,1,2-TCA</td>
<td>VC</td>
<td>dichloroelimination</td>
</tr>
<tr>
<td></td>
<td>Ethane</td>
<td>direct transformation or hydrogenolysis</td>
</tr>
<tr>
<td></td>
<td>Ethene</td>
<td>hydrogenolysis and dichloroelimination</td>
</tr>
<tr>
<td>PCE</td>
<td>None Identified</td>
<td>N/A</td>
</tr>
<tr>
<td>TCE</td>
<td>Ethane</td>
<td>direct transformation (dichloroelimination) or hydrogenolysis</td>
</tr>
<tr>
<td></td>
<td>Ethene</td>
<td>direct transformation (reactive intermediate) or hydrogenolysis</td>
</tr>
<tr>
<td>cDCE</td>
<td>None Identified</td>
<td>N/A</td>
</tr>
<tr>
<td>tDCE</td>
<td>Ethane</td>
<td>direct transformation (reactive intermediate)</td>
</tr>
<tr>
<td></td>
<td>Ethene</td>
<td>direct transformation (reactive intermediate) or hydrogenolysis</td>
</tr>
<tr>
<td>1,2,3-TCP</td>
<td>Propene</td>
<td>β-elimination and hydrogenolysis</td>
</tr>
</tbody>
</table>
APPENDIX A: CALCULATIONS FOR DETERMINING AMOUNT (μmoles) IN REACTORS

A.1: Chlorinated hydrocarbons (except VC) quantification

1. Stock solution prepared in 160 mL serum bottle with 160 mL Milli-Q water and 20 μL pure CHC. Concentration of stock was determined as follows:

\[
C_s = \frac{\rho_{\text{CHC}} \cdot V_{\text{pure}}}{V_w}
\]

Where:
- \(C_s\) = Concentration of stock (mg L\(^{-1}\))
- \(\rho_{\text{CHC}}\) = Density of CHC (mg L\(^{-1}\))
- \(V_{\text{pure}}\) = Volume of pure CHC (L)
- \(V_w\) = Volume of water in stock reactor

Example: Chloroform stock

\[
C_s = \frac{(1,480,000 \text{ mg L}^{-1} \times 0.00002 \text{ L})}{0.16 \text{ L}} = 185 \text{ mg L}^{-1} = 0.185 \text{ g L}^{-1}
\]

2. Various amounts of stock were then added to reactor bottles or standards containing 96 mL aqueous medium (TAPSO or Milli-Q water, respectively). Calibration curves were constructed with amount (\(M_t\)) on the y-axis and corresponding peak areas on the x-axis. The amount added to bottle was determined as follows:

\[
M_t = \left[ \frac{(C_s \cdot V_s)}{FW} \right] \cdot 1,000,000 \mu\text{moles}
\]

Where:
- \(M_t\) = Amount of CHC added to bottle (μmoles)
- \(C_s\) = Concentration of stock (g L\(^{-1}\))
- \(V_s\) = Volume of stock added (L)
- \(FW\) = Formula weight of CHC (g mol\(^{-1}\))

1 mol = 1,000,000 μmoles

Example: Chloroform experiment (200 μL stock added to reactor)

\[
M_t = \left[ \frac{(0.185 \text{ g L}^{-1} \times 0.0002 \text{ L})}{119.38 \text{ g mol}^{-1}} \right] \cdot 1,000,000 \mu\text{moles}
\]

= 0.311 μmoles
3. The partitioning coefficient was determined by using a dimensionless Henry’s Constant for each CHC according to the following:

\[ f_w = \frac{1}{(1+k' H \left( \frac{V_a}{V_w} \right))} \]

Where:
- \( f_w \) = Partitioning coefficient
- \( k_H \) = Dimensionless Henry’s Constant for CHC at 25°C.
- \( V_a \) = Volume of head space in reactor (mL)
- \( V_w \) = Volume of aqueous medium in reactor (mL)

Example: Dimensionless Henry’s Constant for CF = 0.148

\[ f_w = \frac{1}{(1+0.148 \left( \frac{64 \text{ mL}}{96 \text{ mL}} \right))} = 0.910 \]

4. The partitioning coefficient was then used to calculate aqueous μmoles after partitioning according to the following:

\[ M_w = M_t \times f_w \]

Where:
- \( M_w \) = Amount in aqueous phase (μmoles)
- \( M_t \) = Amount of CHC added to bottle (μmoles)
- \( f_w \) = Partitioning coefficient

Example: \( M_w \) with CF partitioning coefficient

\[ M_w = 0.311 \ \mu\text{moles} \times 0.910 = 0.282 \ \mu\text{moles} \]

This can also be represented in μg by the following:

\[ 0.282 \ \mu\text{moles} \times 119.38 \ \text{g mol}^{-1} \times 1 \ \text{mol} / 10^6 \ \mu\text{moles} \times 10^6 \ \mu\text{g} / 1 \ \text{g} \]

\[ = 33.7 \ \mu\text{g} \]
A.2: Methane, ethane, ethene, propene, VC, and hydrogen quantification

1. Experimental (VC only) and control bottles were filled with 96 mL aqueous medium and injected with various volumes of gas, the amount (μmoles) of which was determined by the ideal gas law below. Calibration curves were constructed with amount (n) on the y-axis and corresponding peak areas on the x-axis.

\[ n = \frac{PV}{RT} \]

Where:
- \( n \) = Amount of gas (μmoles)
- \( P \) = Pressure (atm)
- \( V \) = Volume of gas injected (L)
- \( R \) = Universal gas constant (0.0821 atm liter mole\(^{-1}\) K\(^{-1}\))
- \( T \) = Temperature (K)

Example: Injection of 50 μL methane into calibration curve bottle

\[ n = \frac{1\ atm * 0.00005\ L}{0.0821\ atm\ liter\ mole^{-1}\ K^{-1} * 295.15\ K} * 10^6\ \mu moles = 2.06\ \mu moles \]