DESTRUCTION OF CHLORINATED HYDROCARBONS
BY ZERO-VALENT ZINC AND BIMETALLIC ZINC
REDUCTANTS IN BENCH-SCALE INVESTIGATIONS

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Christopher Cushman ENTITLED Destruction of Chlorinated Hydrocarbons by Zero-Valent Zinc and Bimetallic Zinc Reductants in Bench-Scale Investigations BE ACCEPTED IN PARTIAL FULLFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF Master of Science.

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Many remediation technologies have been developed to treat extensive subsurface contamination by chlorinated hydrocarbons (CHCs). One such technology is a permeable reactive barrier (PRB), which contains reactive media that acts as an electron donor in order to reduce CHCs. Extensive effort has been placed on finding the most suitable reactive media in PRBs, with zero-valent iron (ZVI) being the most commonly utilized media. However, zero-valent zinc (ZVZ) is a promising replacement for ZVI in PRBs as it will more readily donate electrons, resulting in more rapid degradation of CHCs. In addition, amending a secondary/catalytic metal to primary metal surface can result in increased degradation kinetics and yield of dechlorinated byproducts.

In this investigation, chlorinated methanes (CF and DCM), ethanes (1,1,2,2-TeCA, 1,1,2-TCA, 1,1,1-TCA, and 1,2-DCA), ethenes (PCE, TCE, cis-DCE, trans-DCE, and VC) and propanes (1,2,3-TCP and 1,2-DCP) were reduced by ZVZ and Zn bimetallic reductants. Results indicated that Cu/Zn was a more potent bimetallic reductant than Pd/Zn and Ni/Zn due to impressive CF degradation kinetics and increased yield of methane formed via direct transformation of CF to methane. Cu/Zn was used in reduction
of all other compounds and did not significantly change byproduct distributions when compared to ZVZ.

Reductive β-elimination was an important degradation pathway observed for chlorinated ethanes and ethenes, with reduction of chlorinated ethenes via this pathway resulting in the formation of highly reactive chlorinated acetylene intermediates, thus preventing the formation of VC. It appears that ZVI will reduce chlorinated ethenes via reductive β-elimination more readily than Zn reductants, suggesting an advantage of ZVI in the reduction of chlorinated ethenes. However, Zn reductants appear to be well suited for PRB applications at sites contaminated with 1,2,3-TCP, as reduction with Zn reductants yields fully dechlorinated byproducts via a reductive β-elimination → hydrogenolysis sequence, unlike ZVI.

Cu/Zn increased degradation kinetics compared to ZVZ for all CHCs investigated, but only slight enhancement in kinetics was observed for chlorinated propanes. Increased chlorinated methane, ethane, and propane kinetics have been reported with ZVZ when compared to ZVI, thus suggesting the need to further study Cu/Zn as a potential replacement for ZVI in PRB applications.
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Chapter 1

BACKGROUND

1.1 Prevalence of CHCs as Groundwater Contaminants

Chlorinated hydrocarbons (CHCs) are commonly used in operations such as dry cleaning, paint removal, metal part degreasing, electronics, and as an intermediate in chemical synthesis. Tetrachloroethylene (PCE) and trichloroethylene (TCE) were the most common chlorinated solvents in the decades after World War II. However, human health concerns with PCE and TCE have led to a decrease in their production (Pankow and Cherry, 1996). Despite these concerns, PCE is still the cleaning solvent of choice at nearly all of the 30,000 dry cleaners and launderers in the United States (Moran et al., 2007). In addition to PCE and TCE, many other CHCs are commonly used in various business applications, especially at industrial sites.

Due to the immense amounts of CHCs that have been and continue to be used in the United States, it should come as no surprise that contamination of groundwater sources by CHCs is extensive. Unintended releases of these compounds continue to be alarming. For example, between 1998 and 2001, 33 million pounds of methylene chloride, also known as dichloromethane (DCM), 4 million pounds of PCE, and 11 million pounds of TCE were released into the environment from various sources (Moran et al., 2007). CHCs are also present at Superfund sites all over the United States. CHCs are dominant on the 2011 Priority List of Hazardous Substances compiled by the Agency
for Toxic Substances and Disease Registry (ATSDR). Compounds such as vinyl chloride (VC), polychlorinated biphenyls (PCBs), chloroform (CF), carbon tetrachloride (CT), PCE, and TCE are just some of the CHCs that appear in the top 50 of this list (ATSDR, 2011).

In addition to the magnitude of CHCs released into the environment, CHCs also have physical and chemical properties which make them especially concerning upon release. These compounds can cause extensive groundwater contamination due to their high vapor pressures, high densities, low viscosities, low interfacial tensions, low organic partitioning coefficients, and low degradabilities. In addition, they have low absolute solubilities and high solubilities relative to concentrations deemed dangerous to human health (Pankow and Cherry, 1996; Moran et al., 2007). Significant effort has been placed on the remediation of groundwater contaminated with CHCs for these reasons.

1.2 Degradation of CHCs: PRBs & Zero Valent Metals

Extensive effort has been placed on the remediation of groundwater contaminated with CHCs. One of the earliest methods for remediation that is still currently used is pump-and-treat. Although this method may be a popular option, it is complicated by the fact that drinking water standards for some CHCs require concentrations of the contaminant to be less than 100 µg L⁻¹. Complexity in the subsurface and the extensive amount of pumping required for contaminant removal also complicate pump-and-treat remediation efforts (Mackay and Cherry, 1989). Therefore, the use of pump-and-treat can cause remediation projects to become very expensive.
In addition to pump-and-treat, other methods for the remediation of groundwater contaminated by CHCs have been developed. One such method focuses on biotic means of contaminant degradation, also referred to as bioremediation. However, issues are present with this engineered remediation technique since it is difficult to obtain complete mixing of groundwater and the biological substrate (Gillham and O'Hannesin, 1994; Sale et al., 2008).

Other current remediation/containment technologies include; *in-situ* chemical oxidation, physical containment, monitored natural attenuation, soil vapor extraction, air sparging, and permeable reactive barriers (PRBs). Permeable reactive barriers have received considerable attention in the remediation of groundwater contaminated with CHCs. The most common type of PRB is constructed using a zero-valent metal as the reactive media (Sale et al., 2008). PRBs are constructed in the flow path of the contaminated groundwater and contaminants are ideally transformed into non-toxic byproducts when the groundwater plume comes into contact with the reactive media in the permeable "wall" (Balko and Tratnyek, 2001; Richardson and Nicklow, 2002).

Permeable reactive barriers are a promising option for the degradation of CHCs since they are constructed on site, thus allowing for in-situ treatment of the contaminated plume. This eliminates the need to manage a large volume of contaminated groundwater that would be generated from pump-and-treat operations, resulting in a reduced project cost. In addition, permeable reactive barriers have the potential to degrade various types of contaminants, including various CHCs (Henderson and Demond, 2007). Field studies of active PRBs have demonstrated that the reactive media can remain active for several years (O'Hannesin and Gillham, 1998; Phillips et al., 2000). Therefore, PRBs have
become a viable option for the treatment of groundwater contaminated with CHCs since PRBs are effective in contaminant removal, require little maintenance, and can operate for an extended period of time (O'Hannesin and Gillham, 1998).

Zero-valent metals are used in the construction of permeable reactive barriers as they are potent reductants that can chemically transform CHCs in contaminated groundwater into less chlorinated byproducts by a redox reaction. In a typical PRB, the contaminant serves as the electron acceptor and is thus reduced while the reactive media of the PRB is oxidized since it serves as the electron donor. The reaction will only take place if energy will be released. In addition, the reaction must also be kinetically facile (Scherer et al., 2000).

Zero-valent iron (ZVI) is the primary reactive medium used in PRBs (Scherer et al., 2000). Extensive research using ZVI began in the early 1990's with the work of Gillham and O'Hannesin (1994) and Matheson and Tratnyek (1994). This early work demonstrated, via the use of batch reactor studies and some basic column studies, that granulated ZVI was effective in the dechlorination of many different chlorinated aliphatic (non-aromatic) compounds (Gillham and O'Hannesin, 1994; Matheson and Tratnyek, 1994). ZVI became the metal of choice in these early studies since granulated ZVI is generally non-toxic and relatively inexpensive (Matheson and Tratnyek, 1994). In addition to aliphatic compounds, ZVI has also been used to dehalogenate chlorinated aromatics and polychlorinated biphenyls (PCBs) (Wang and Zang, 1997). Nitro aromatic hydrocarbons (NACs) (Agrawal and Tratnyek, 1996) and pesticides (Warren et al., 1995) have also been degraded using ZVI.
The general redox interaction between iron (Fe) and a halogenated contaminant, an alkyl halide (RX) in this instance, can be seen by the following reaction (Matheson and Tratnyek, 1994):

\[
\begin{align*}
\text{Fe}^0 & \rightarrow \text{Fe}^{2+} + 2e^- \quad [1a] \\
RX + 2e^- + H^+ & \rightarrow RH + X^- \quad [1b] \\
\text{Fe}^0 + RX + H^+ & \rightarrow \text{Fe}^{2+} + RH + X^- \quad [1]
\end{align*}
\]

Iron, which has a standard reduction potential equal to -0.447 V (Haynes, 2012), donates electrons and thus reduces the alkyl halide. When a proton (H\(^+\)) donor such as water is present, the above reaction can take place. The reaction is known as reductive dehalogenation (Matheson and Tratnyek, 1994) since the CHC is degraded by reduction and is one of the primary ways in which a CHC can be reduced by zero-valent metals. As can be seen, two electrons are needed for reductive dehalogenation to occur and only one halogen is knocked off during one cycle of the reaction. A more detailed discussion of possible degradation pathways will be discussed in section 1.3.

Coarse or granular ZVI is not the only type of iron that has been investigated for use in subsurface treatment of contaminated groundwater. Nano-scale zero-valent-iron (nZVI) has captured the attention of researchers over the past 15 years due to its substantial surface area (Wang and Zhang, 1997; Elliott and Zhang, 2001; Feng and Lim, 2005). Metal surface area plays a large part in the degradation rates observed, with higher metal surface areas resulting in more rapid degradation kinetics (Boronina and Klabunde, 1995). Nanoscale particles can have specific surface areas several orders of magnitude greater than granular metal particles and perhaps tens of times greater than microscale metal particles that are available commercially (Zhang et al., 1998). As research has
demonstrated, nZVI can degrade CHCs at an incredible rate when compared to granular ZVI. Perhaps even more important, it has been shown that nZVI can completely dehalogenate the target contaminant (Wang and Zhang, 1997) and will thus prevent the accumulation of harmful daughter products. In addition to iron, other metals have been studied as the potential reactive material in PRBs. Zero-valent metals such as zinc, tin (Warren et al., 1995), and magnesium (Boronina et al., 1995) have all been identified and studied as potential alternatives to zero-valent iron in PRBs.

The standard reduction potential (E°_H) of a zero-valent metal can be an important parameter for assessing its potential for application in PRBs. For this parameter, a positive value indicates that the species will readily accept electrons and will thus be reduced. A negative value indicates that the species will donate electrons and will thus be oxidized (Suslow, 2004). Therefore, it can be concluded that species with the lowest (i.e. most negative) E°_H value will be the most promising if reduction potential is indeed the parameter of interest when determining suitable reactive media in PRBs.

Based strictly on standard reduction potential for commonly investigated zero-valent metal species (magnesium, iron, and zinc), it can be concluded that zero-valent magnesium (ZVM) (E°_H = -2.37) is the most promising candidate for PRB media as it has the most negative E°_H value while zero-valent zinc (ZVZ) (E°_H = -0.762) will also more readily donate electrons than ZVI (E°_H = -0.447) (Haynes, 2012). Although magnesium has a drastically lower standard reduction potential, it may not be a suitable media in PRBs as oxidation of ZVM can occur relatively quickly, thus drastically decreasing reactivity with the CHC (Boronina et al., 1995).
As was previously mentioned, ZVI became the popular choice for PRB media and it continues to be the dominant PRB media because ZVI is relatively inexpensive and it is non-toxic (Matheson and Tratnyek, 1994). Therefore, more than just standard reduction potential needs to be considered when determining the appropriate reactive media for PRBs. Zn$^{2+}$ generated in the reaction of ZVZ with a chlorinated contaminant is a concern to human health (Arnold and Roberts, 1998). Therefore, this may prevent the use of ZVZ in PRBs. However, it has been shown that the addition of hydroxyapatite can minimize the release of Zn (II) into the environment. Zn (II) will undergo adsorption to hydroxyapatite, thus reducing the availability of Zn (II) in the environment (Arnold and Roberts, 1998).

In conclusion, the most promising candidate for zero-valent metal PRBs may be ZVZ since ZVZ has a low standard reduction potential (Haynes, 2012) and the release of toxic Zn (II) can be alleviated by the addition of hydroxyapatite (Arnold and Roberts, 1998). The degradation potential (i.e. previous work) of ZVZ will be discussed in section 1.5.

1.3 Pathways of CHC Degradation

It is important to understand the various degradation pathways that a chlorinated parent compound may undergo since partially chlorinated byproducts of the reaction may be harmful to humans (Arnold and Roberts, 1998). Therefore, byproduct formation needs to be understood in addition to CHC degradation kinetics for a monometallic or bimetallic zero-valent metal system to become practical (Arnold et al., 1999).
The degradation of CHCs can follow several distinct pathways, including reduction, oxidation, substitution, and elimination (Tratnyek et al., 2011). A compound may have more than one degradation pathway resulting in the formation of different byproducts (Sarathy et al., 2010) while it is also possible that the same byproduct was generated through various degradation pathways (Arnold and Roberts, 2000).

In the anaerobic environment, not all reaction pathways are likely for polyhalogenated methanes, ethanes, and ethenes. In such an environment, where preferential electron acceptors (i.e., oxygen) have been used up, the relevant reaction methods are reduction and elimination (Sarathy et al., 2010). The term used to describe reduction is reductive dehalogenation, of which there are two types; hydrogenolysis and reductive elimination (Roberts et al., 1996). Hydrogenolysis involves the replacement of a halogen with hydrogen while reductive elimination, also known as dihaloelimination, occurs when two halide ions are released from the compound (Roberts et al., 1996). Dihaloelimination can be either reductive β-elimination or reductive α-elimination (Tratnyek et al., 2011), with reductive β-elimination requiring the presence of chlorines on adjacent carbons (Stroo and Ward, 2010). The relevant elimination reaction is called dehydrohalogenation and is characterized by the removal of -HCl resulting in the formation of an additional C-C bond (Tratnyek et al., 2011).

1.4 Degradation Kinetics of CHCs

In addition to characterizing byproducts and the degradation pathways through which they form, it is also critically important to understand degradation kinetics. One important factor in the degradation kinetics of CHCs is the identity of the carbon-halogen
bond (Tratnyek et al., 2011). The highest bond dissociation energy is associated with the C-F bond (115 kcal mole\(^{-1}\)), intermediate energy is associated with the C-Cl bond (83.7 kcal mole\(^{-1}\)), and the lowest bond dissociation energy is associated with the C-Br bond (72.1 kcal mole\(^{-1}\)) (Blanksby and Ellison, 2003), thus indicating the C-Br bond is easier to break than the C-Cl bond (Tratnyek et al., 2011).

The degree of halogenation is another important factor in the degradation kinetics of CHCs. In general, the more halogens present on the compound, the faster the degradation kinetics (Tratnyek et al., 2011). This can clearly be seen in the degradation of PCE → TCE → cis-DCE → VC. When going from PCE, the most chlorinated compound, and progressing to VC, the least chlorinated compound, the kinetics of degradation will decline (Zhang et al., 1998). This trend can be explained by redox potential, where PCE has the highest redox potential and VC has the lowest (Zhang et al., 1998).

When characterizing degradation of CHCs, investigations have argued contaminant destruction may generally occur by reaction kinetics that are pseudo first-order with respect to the concentration of the contaminant (Johnson et al., 1996). Pseudo first-order degradation rate constant, termed \(k_{\text{obs}}\) (time\(^{-1}\)), is the slope of the straight line found by plotting the natural logarithm of the contaminant concentration on the y-axis and time on the x-axis (Matheson and Tratnyek, 1994). It has been observed that \(k_{\text{obs}}\) values can vary in both batch and column studies. This variability in degradation kinetics may depend on the variations in the metal surface area concentration (Johnson et al., 1996). The larger the surface area, the more area for the contaminant to contact and the faster the degradation kinetics, \(k_{\text{obs}}\) (Boronina and Klabunde, 1995). In order to obtain a
better representation of the degradation kinetics, normalizing $k_{\text{obs}}$ values to the concentration of metal surface area (Johnson et al., 1996) can be done per the following equations (Salter-Blanc et al., 2012):

$$k_{\text{SA}} = \frac{k_{\text{obs}}}{\rho_a}$$  \hspace{1cm} [2]

where: $k_{\text{SA}} = \text{Surface area normalized pseudo first-order rate constant (L m}^{-2} \text{ h}^{-1})$

$k_{\text{obs}} = \text{Pseudo first-order rate constant (h}^{-1})$

$\rho_a = \text{Surface area concentration (m}^2 \text{ L}^{-1})$ found by the following equation:

$$\rho_a = \alpha_s \cdot \rho_m$$  \hspace{1cm} [3]

where: $\alpha_s = \text{Specific surface area (SSA) (m}^2 \text{ g}^{-1})$

$\rho_m = \text{Mass concentration (g L}^{-1})$

In addition to normalizing kinetics based on surface area, kinetics can also be normalized based on the amount of reductant mass used according to equation [4] below (Salter-Blanc et al., 2012). However, it may be best to compare mass normalized kinetics only when similar particle sizes are used due to the importance of surface area.

$$k_M = \frac{k_{\text{obs}}}{\rho_m}$$  \hspace{1cm} [4]

where: $k_M = \text{Mass normalized pseudo first-order rate constant (L g}^{-1} \text{ h}^{-1})$

$k_{\text{obs}} = \text{Pseudo first-order rate constant (h}^{-1})$

$\rho_m = \text{Mass concentration (g L}^{-1})$

### 1.5 CHC Degradation with Zero-Valent Zinc (ZVZ)

ZVZ is a promising alternative to ZVI in PRBs due to its lower standard reduction potential (Haynes, 2012). In addition, ZVZ can successfully be utilized in the field since the release of toxic Zn (II) can be alleviated by the addition of hydroxyapatite (Arnold
and Roberts, 1998). Several research groups, including Dr. Lynn Roberts (and co-workers of Johns Hopkins University) and Dr. Paul Tratnyek (and co-workers of Oregon Health and Science University), have examined CHC destruction by ZVZ.

ZVZ has been proven to degrade many different CHCs (Boronina et al., 1998; Arnold et al., 1999; Sarathy et al., 2010). In one of the first ZVZ investigations, microscale zinc readily degraded carbon tetrachloride (CT), a chlorinated methane, to chloroform (CF) in a batch reactor within a few hrs (Warren et al., 1995). Another early study (Boronina et al., 1995) confirmed the degradation of CT with zinc metal dust and provided evidence that CF, which is a daughter chlorinated methane and harder to dechlorinate than CT, was also degraded by ZVZ. Another common groundwater contaminant, perchloroethylene (PCE), was used in an investigation (Roberts et al., 1996) to understand the kinetics of the degradation of PCE to less chlorinated byproducts by granular ZVZ (30 mesh). Although sequential degradation modeling was less than fully successful, the investigation proved the effectiveness of ZVZ in PCE reduction (Roberts et al., 1996).

Another study of PCE reduction with ZVZ (30 mesh) (Arnold and Roberts, 1998) revealed reductive β-elimination to be an important pathway in the reduction of chlorinated ethenes. PCE, TCE, and DCE reduction via reductive β-elimination results in the formation of highly reactive chlorinated acetylenes, thus preventing the formation of vinyl chloride. Although chlorinated acetylenes are toxic compounds, they are unstable and do not persist in the environment (Arnold and Roberts, 1998).
ZVZ (30 mesh) reduction of polychlorinated ethanes have been investigated in detail (Arnold et al., 1999). Results from this investigation indicated a decrease in kinetics with a decrease in degree of chlorination while byproducts observed indicated the primary reaction pathway in the reduction of many polychlorinated ethanes by ZVZ is reductive \( \beta \)-elimination (Arnold et al., 1999), resulting in the formation of chlorinated ethenes which can degrade further by ZVZ (Arnold and Roberts, 1998).

Perhaps the most practical investigation would be to directly compare contaminant degradation kinetics and degradation byproducts obtained with ZVZ and ZVI, the metal exclusively used in PRBs. Cheng and Wu (2000) compared the degradation of TCE with ZVI (10-40 mesh) and ZVZ (30 mesh), concluding that TCE degradation kinetics with ZVZ was nearly 10 times faster than with ZVI, thus demonstrating ZVZ could be an effective replacement for ZVI in PRBs (Cheng and Wu, 2000). Tratnyek & co-workers also completed a direct comparison of ZVZ and ZVI (Sarathy et al., 2010); in this study, ZVZ and ZVI were used to degrade 1,2,3-trichloropropane (1,2,3-TCP), an emerging groundwater contaminant. It was determined that the degradation of 1,2,3-TCP occurred much faster with granular ZVZ (30 mesh) in comparison to ZVI (micro and nanoscale particles) (Sarathy et al., 2010). Their results also revealed that intermediate byproducts, such as 1,2-dichloropropane (1,2-DCP) and 1,3-DCP, which are undesired in the dechlorination pathway, were not formed when ZVZ was used. Although ZVZ was determined to be very promising in the degradation of 1,2,3-TCP, the authors noted that ZVI is the reaction media of choice for many other chlorinated compounds (Sarathy et al., 2010). However, the potential of ZVZ should not be ignored.
Tratnyek and co-workers further characterized the potential of ZVZ in the degradation of 1,2,3-TCP (Salter-Blanc and Tratnyek, 2011). Reactivity was evaluated using various sources of water (deionized or DI water and groundwater) as well as the effect of pH conditions for each type of water. With DI water, results indicated degradation kinetics were slowest when pH was between 8 and 10. This corresponds well with trends observed with ZVZ corrosion rate (lowest at pH 12) and zinc oxide solubility (lowest at pH 9); the degradation kinetics increased when conditions became increasingly basic or acidic, which suggested that pH is a major factor affecting degradation rate, possibly due to changes in the zinc oxide surface layer that occur with a change in pH (Salter-Blanc and Tratnyek, 2011). When using groundwater, acidic conditions produced similar rate constants as those obtained with DI water. However, much slower degradation kinetics were observed with basic groundwater compared to basic DI water. This is due to the presence of a distinct surface film that coats the surface of ZVZ at a high pH condition in groundwater (Salter-Blanc and Tratnyek, 2011).

Tratnyek and co-workers continue to demonstrate the effectiveness of ZVZ in the reduction of 1,2,3-TCP. A recent publication (Salter-Blanc et al., 2012) not only focused on batch studies, but the ability of ZVZ to degrade 1,2,3-TCP was also evaluated at the next scale with column studies. In this study, different types of industrial-grade ZVZ were evaluated in batch reactors for their effectiveness for 1,2,3-TCP degradation. After choosing the two most effective materials, bench-scale and field-scale columns were then constructed using varying weight percentages of sand and ZVZ. In general, results indicated that the degradation observed at smaller scales was comparable to the
degradation observed at larger scales. Results also confirmed ZVZ is effective in
degradation of 1,2,3-TCP (Salter-Blanc et al, 2012).

In summary, ZVZ can actively degrade chlorinated methanes (Boronina et al.,
1995), ethenes (Arnold and Roberts 1998), ethanes (Arnold et al., 1999), and propanes
(Sarathy et al, 2010; Salter-Blanc et al, 2012). When compared to ZVI, TCE degradation
was more rapid with ZVZ (Cheng and Wu, 2000). In addition, enhanced degradation
kinetics of 1,2,3-TCP and the absence of undesirable reaction intermediates were
observed with ZVZ (Salter-Blanc et al, 2012).

1.6 CHC Degradation with Bimetallic Reductants

In addition to using a monometallic (i.e., single zero-valent metal) system to
degrade CHCs, bimetallic systems have also been researched extensively. Reduction of
CHCs by metallic reductants is often evaluated using two measures, degradation kinetics
and degradation byproducts (Zhang et al., 1998; Arnold et al., 1999). Certain degradation
byproducts can be more toxic than the initial parent compound if complete
dehalogenation is not achieved (Feng and Lim, 2005). An example would be the
production of VC from the degradation or PCE, TCE, or DCE since VC has a lower
maximum contaminant level (MCL) than these parent compounds (EPA, 2013). In
addition, degradation kinetics can decrease over time in a metallic reductant system due
to the formation of oxide layers that may hinder access of contaminants to active sites on
the zero-valent metal. In order to combat issues of incomplete dehalogenation and
decreased degradation kinetics, a catalyst can be used (Feng and Lim, 2005).
A metallic catalyst can be added to modify a zero-valent metal in order to prepare a bimetallic reductant, where the secondary/catalytic metal (for example, Palladium (Pd), Nickel (Ni), and Copper (Cu)) deposits on the surface of the primary metal (i.e., ZVZ or ZVI). In this system, a small amount of the secondary metal (typically < 1 wt.%) can form a thin layer/clusters on the surface of the reductant/primary metal. The primary metal acts as the electron donor to drive the reduction reactions, whereas the secondary/catalytic metal acts to reduce activation energy of the reaction, thus enhancing degradation kinetics (Zhang et al., 1998) and the yield of fully dehalogenated products (Bransfield et al., 2006). The use of a bimetallic system to reduce CHCs must also be practical at the field scale. Therefore, it must be proven that the addition of the secondary metal is economically justified, and that the bimetallic material is environmentally acceptable (Bransfield et al., 2006).

In one of the early investigations to study bimetallic reduction of CHCs, Fennelly and Roberts (1998) amended ZVI (100 mesh) with Ni (as NiCl₂) and Cu (CuCl₂), and prepared Ni/Fe and Cu/Fe. The results demonstrated an increase in degradation kinetics of 1,1,1-TCA with Ni/Fe and Cu/Fe in comparison to ZVI. The results also revealed the degradation potential with ZVZ, which resulted in faster and more complete reduction than Ni/Fe, Cu/Fe, and ZVI (Fennelly and Roberts, 1998).

In another investigation by Zhang et al. (1998) using Pd and Ni as secondary metals with ZVI, TCE degradation was not observed when the primary metal was not present, and degradation kinetics were similar to ZVI when Pd was physically mixed with Fe. It was only when Pd was deposited on Fe surface to prepare Pd/Fe that rapid TCE
reduction occurred. This was done by treating ZVI with a Pd acetate ([Pd(C₂H₃O₂)₂]₃) solution in ethanol that reduced Pd⁴⁺ and ultimately deposited Pd⁰ onto the ZVI surface.

Zhang et al. (1998) also evaluated Pd/Fe and Ni/Fe bimetallic reductants in trans-DCE reduction; the results demonstrated enhanced degradation kinetics with Pd/Fe, slower kinetics with Ni/Fe, and slowest kinetics with ZVI (Zhang et al., 1998). In addition to TCE degradation with Pd/Fe, Pd/Zn was also investigated (Zhang et al., 1998). ZVZ is very reactive in the presence of oxygen, and zinc oxides can form, quickly covering the metal surface. However, it is suggested that coating a secondary metal, such as Pd, onto the surface of Zn can prevent this zinc oxide layer from forming thus increasing the degradation potential of Zn. Results indicated >90% of TCE degraded during the first 20 hrs of experimentation, a rapid enhancement of reduction compared to ZVZ (Zhang et al., 1998). Unfortunately, degradation of TCE by Pd/Fe and Pd/Zn were not directly compared and information on TCE degradation kinetics was not reported.

The degradation potential of Pd/Fe, Ni/Fe, Pd/Zn, and Ni/Zn bimetallic systems were evaluated by Cheng and Wu (2000). While comparing TCE degradation with Ni/Fe and Pd/Fe, different behaviors were observed based on the type of Fe used; in powdered Fe systems, Ni/Fe resulted in faster TCE degradation, while Pd/Fe was more promising with granular Fe (10-40 mesh). Pd/Zn reduced TCE faster than Ni/Zn, regardless of the mesh size of Zn (-10+50 mesh, 30 mesh, and powdered Zn). Also, results demonstrated that bimetallic Zn systems more rapidly degrade TCE than bimetallic Fe systems. A comparison of TCE degradation kinetics was also made with ZVZ and ZVI, with ZVZ resulting in faster TCE degradation (Cheng and Wu, 2000).
Pd is certainly a promising secondary metal in a bimetallic system. In addition to the compounds already mentioned, research has shown that Pd/Fe systems can actively degrade 1,2,3,4-tetrachlorodibenzo-\(p\)-dioxin (1,2,3,4-TCDD) (Wang et al., 2010). It has also been shown that zero-valent magnesium can be an effective primary metal for degrading PCBs in a Pd/Mg bimetallic system (Agarwal et al., 2007). However, the application of bimetallic reductants containing Pd may be cost-prohibitive at the field-scale. Instead, Ni or Cu may be more promising secondary metals for preparing a bimetallic reductant for use in PRBs.

Bransfield et al. (2006) investigated the reduction of 1,1,1-TCA with Cu/Fe and ZVI (100 mesh); the study demonstrated that 1,1,1-TCA degradation with Cu/Fe resulted in faster degradation kinetics and degradation products that were more dehalogenated in comparison to results with ZVI, much like results from Fennelly and Roberts (1998). Bransfield et al. (2006) also examined the influence of Cu loading on degradation kinetics. They showed that the metallic Cu overlay on Fe was heterogeneous (i.e. not uniform) at all Cu loadings. At levels less than 5 \(\mu\)mol Cu g\(^{-1}\) Fe (0.03 wt.% Cu), increasing Cu loading dramatically increased the Fe surface area covered by Cu, which resulted in enhanced degradation kinetics. At higher levels of Cu loading (> 30 \(\mu\)mol Cu g\(^{-1}\) Fe, 0.19 wt.% Cu), increasing Cu had no noticeable effect on Fe surface covered by Cu, and thus no significant increase in degradation kinetics was observed (Bransfield et al., 2006). At a point referred to as the 1 monolayer equivalent (10 \(\mu\)mol Cu g\(^{-1}\) Fe, 0.06 wt.% Cu), the mass of Cu used is enough to cover the surface of Fe with 1 complete and uniform layer of Cu atoms. Degradation rate constants increased rapidly with increasing Cu loading below 10 \(\mu\)mol Cu g\(^{-1}\) Fe. However, once the Cu loading was above the
monolayer threshold, rate constants were much less sensitive to an increase in Cu loading. The study concluded that the most dramatic increase in rate constants occurred with relatively low levels of secondary metal loading (Bransfield et al., 2006).

The results from Bransfield et al. (2006) are consistent with a previous study focusing on optimum loading of Pd on Fe by Kim and Carraway, (2003), who reported the distribution of Pd on Fe to be heterogeneous. It was also demonstrated that TCE degradation kinetics increased dramatically until Pd loading on Fe\(^0\) reached 0.1 wt % Pd. However, Pd loadings greater than 0.1 wt % were not effective in a similar increase in TCE degradation kinetics (Bransfield et al., 2006).

In summary, bimetallic reductants prepared with secondary metals such as Ni (Fennelly and Roberts, 1998; Zhang et al, 1998; Cheng and Wu, 2000), Cu (Fennelly and Roberts 1998; Bransfield et al, 2006), and Pd (Zhang et al., 1998; Cheng and Wu 2000) can significantly enhance CHC degradation kinetics and increase the yield of preferential byproducts. However, the increase in the reactivity is most significant at low secondary metal loadings of Cu (Bransfield et al., 2006) and Pd (Kim and Carraway, 2003). Zn-based bimetallic systems can potentially provide faster degradation kinetics and more complete destruction of TCE in comparison to Fe-based bimetallic systems (Cheng and Wu, 2000). However, additional research is needed for an improved assessment of the performance of Zn-based bimetallics in the degradation of chlorinated methanes, ethanes, ethenes, and propanes.
1.7 Motivation

ZVI has been used extensively as the zero-valent metal of choice in commercial PRB applications at sites contaminated with CHCs. Although ZVI ($E^\circ_H = -0.447$) has certainly been effective in reducing CHCs, it is not as strong of a reducing agent as ZVZ ($E^\circ_H = -0.762$) (Haynes, 2012). This has led investigators such as Dr. Lynn Roberts (and co-workers of Johns Hopkins University) and Dr. Paul Tratnyek (and co-workers of Oregon Health and Science University) to examine CHC reduction by ZVZ.

Investigations directly comparing reduction potential of ZVZ and ZVI have found increased TCE degradation kinetics (Cheng and Wu, 2000) and increased 1,2,3-TCP degradation kinetics (Sarathy et al., 2010) with ZVZ. In addition, it was found that 1,2,3-TCP reduction by ZVZ results in the formation of completely dechlorinated byproducts unlike results with ZVI (Sarathy et al., 2010). Once a concern with ZVZ, the release of Zn (II) in CHC reduction can be alleviated by the addition of hydroxyapatite (Arnold and Roberts, 1998), thus presenting ZVZ as a realistic alternative to ZVI. In addition, amending a secondary metal to Zn surface can increase kinetics of CHC reduction by reducing activation energy of the reaction, thus enhancing degradation kinetics (Zhang et al., 1998) and the yield of fully dehalogenated products (Bransfield et al., 2006). Therefore, ZVZ has a distinct advantage over ZVI and amending a secondary metal onto Zn surface may further increase CHC degradation kinetics and yield of preferential byproducts, thus presenting an even more advantageous metallic system when compared to ZVI.
1.8 Research Objectives

This study investigated the ability of ZVZ and Zn-based bimetallics (Pd/Zn, Ni/Zn, and Cu/Zn) to reduce CHCs. The target contaminants included chlorinated methanes, ethanes, ethenes, and propanes. The objectives of this study include the following:

i. Determine the Zn-based bimetallic system that provides most rapid reduction of chloroform (CF) and the most preferential yield of byproducts, thus allowing for one bimetallic system to be investigated further with other CHCs.

ii. Determine the most effective secondary metal loading in terms of degradation kinetics and byproduct distribution during CF and DCM reduction. Pd loadings on Zn will not exceed 0.1 wt.% (Kim and Carraway, 2003) and relatively low (0.05-1 wt.%) Ni and Cu loadings (Bransfield et al., 2006) will be used based on previous secondary metal loading investigations. A single loading will be identified and investigated further with other CHCs.

iii. Evaluate target CHC degradation kinetics with ZVZ and Zn-based bimetallics. A comparison will be made to previous investigations with ZVZ and ZVI.

iv. Characterize CHC degradation byproducts generated from CHC reduction, in terms of carbon mass recovery, by ZVZ and Zn-based bimetallics. Degradation pathways will be carefully identified and byproducts compared to previous results with ZVZ and ZVI.
v. Determine the effect of increased bimetallic reductant in 1,2,3-TCP reduction.

Byproduct generation, degradation kinetics, pH, and hydrogen production will be determined and evaluated in order to understand the influence of increasing reductant.
Chapter 2

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%), tetrachloroethylene (PCE, Sigma-Aldrich, 99.9%), trichloroethylene (TCE, Acros Organics, 99%), cis-dichloroethylene (cis-DCE, Acros Organics, 97%), trans-dichloroethylene (trans-DCE, Acros Organics, 99%), 1,2,3-trichloropropene (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). Experimental reactors were filled with deoxygenated 30 mM (typically 96 mL; 2.88 mmoles) TAPSO (Sigma-Aldrich, 99%) titrated to pH 7 by 1M NaOH.

The stock solutions for above CHCs, with the exception of VC, were prepared by adding 20 μL of pure organic liquid to a 160 mL serum bottle containing 160 mL Milli-Q water (i.e. no headspace) and sealed using Teflon-lined rubber stopper and aluminum crimp. Stock solution bottles were wrapped in aluminum foil and placed on an end-over-
end rotator (setting @ 70; 45 rpm) for at least 2 days to allow the compound to completely dissolve.

Zn granules (Alfa Aesar, ~20 mesh) were used as received for Pd/Zn experiments with CF. In order to eliminate heterogeneity, a 24 mesh screen (Fisher Scientific) was used to sieve the ~20 mesh Zn stock and the 20-24 mesh fraction was kept as Zn stock for all other experiments. Zn particles were not acid washed, as acid washing Zn particles has previously been shown to not promote faster degradation kinetics for some CHCs. This could be due to the rapid activation of Zn surface area when Zn particles are placed in solution (Sarathy et al., 2010).

2.2 Experimental System

Batch reactors (160 mL serum bottles, Wheaton) were prepared in an anaerobic chamber (Coy Lab, MI) in order to ensure that CHC, rather than oxygen, served as the preferred electron acceptor (oxidant) for Zn. This prevented the oxidation of zinc granules by O₂ during reactor preparation/set-up. All reagent solutions used in setting-up the batch reactors were de-oxygenated in advance by sparging with nitrogen for at least 40 minutes prior to their placement in the anaerobic chamber.

Each experiment included duplicate batch reactors in order to validate results. Reactors were typically assembled with 3g of Zn granules. For bimetallic experiments, CuCl₂ (Sigma-Aldrich, 97%) and NiCl₂ (Sigma-Aldrich) were dissolved in ethanol (EtOH) in order to create a secondary metal reagent solution. K₂PdCl₆ (Sigma-Aldrich, 99%) was dissolved in water, as dissolution in EtOH was not achieved. In addition to the Cu loading investigation using CuCl₂ dissolved in EtOH, another investigation was
completed by preparing CuCl$_2$ in water in order to observe the effect of using water to
dissolve the secondary metal. Dissolution of the secondary metal in EtOH is preferred as
water can also oxidize the primary metal (i.e. Zn) during synthesis of bimetallic Zn.
EtOH may not oxidize the Zn metal surface, and thus not compromise degradation
potential (Agarwal et al., 2007). Amounts of CuCl$_2$, NiCl$_2$, or K$_2$PdCl$_6$ used (as wt.%)
were determined by the secondary metal loading investigated.

Secondary metal solutions (typically 10 mL) were added to batch reactors
containing Zn granules (kept in a capped bottle inside the anaerobic chamber) and
allowed to deposit onto the surface of Zn granules over a period of 5 minutes (gentle
hand swirling for 30 seconds with 30 second intervals) according to the following
reactions:

$$\text{Pd}^{4+} + 2\text{Zn}^0 \rightarrow \text{Pd}^0 \downarrow + 2\text{Zn}^{2+} \quad [5]$$

$$\text{Ni}^{2+} + \text{Zn}^0 \rightarrow \text{Ni}^0 \downarrow + \text{Zn}^{2+} \quad [6]$$

$$\text{Cu}^{2+} + \text{Zn}^0 \rightarrow \text{Cu}^0 \downarrow + \text{Zn}^{2+} \quad [7]$$

In Cu and Ni experiments, EtOH was decanted after 5 minutes of mixing and
bimetallic particles were washed 3 times for 30 seconds with 15-20 mL of 30 mM
TAPSO to remove ethanol from the reactor. The aqueous volume was then brought to 96
mL by adding 30 mM TAPSO. For Pd/Zn experiments, water was not decanted after 5
minutes and the total aqueous volume was brought to 96 mL using 30 mM TAPSO.
Batch reactors were then sealed with PTFE-lined grey butyl rubber stoppers and
aluminum crimps. For monometallic Zn experiments, 96 mL of 30 mM TAPSO was
added to the batch reactor before being sealed. Control reactors were prepared for each
experiment with 96 mL Milli-Q water.
After removing from the anaerobic chamber, each batch reactor was injected with 200-500 μL of target contaminant stock solution using a 250 μL syringe (Hamilton, Reno, NV). For vinyl chloride experiments, 5 mL of 1,000 mg/L VC by volume was injected into each reactor and control bottle. Immediately after injection, each batch reactor was mixed on a vortex mixer (3 times for 20 seconds each, with 10 second intervals), and then equilibrated on a rotator by end-over-end mixing at 45 rpm.

After injection with CHC stock, 50 μL of reactor headspace was periodically extracted using a 250 μL gas-tight syringe (Hamilton, Reno, NV) and analyzed by gas chromatography. Reactors were well mixed on an end-over-end rotator at 45 rpm for the duration of the experiment except when headspace of the reactor was sampled.

2.3 Analytical Methods

The amount of CF and daughter products in Pd/Zn reactor was quantified by gas chromatography (Hewlett-Packard, model 7890 system) by electron capture (ECD) and flame ionization (FID) detectors. An HP-624 column (30 m x 0.32 mm x 0.25 μm, Agilent Technologies) was used with high purity helium (Weiler Welding, Dayton, OH) serving as the carrier gas at constant flow of 1.8 mL min⁻¹. GC method was as follows: front inlet = 250 °C, FID = 250 °C, ECD = 300 °C, and oven temperature = 100 °C. The make-up gas for GC 7890 was high purity N₂ (Weiler Welding, Dayton, OH) with a flow rate of 25 mL min⁻¹ for the FID and 60 mL min⁻¹ for the ECD. The flow rate for high purity H₂ (Weiler Welding, Dayton, OH) was 30 mL min⁻¹ and for high purity air (Weiler Welding, Dayton, OH) it was 450 mL min⁻¹.
The amount of CHC and degradation products in the reactor was analyzed in all other experiments using Hewlett-Packard model 6890 system by electron capture (ECD) and flame ionization (FID) detectors. A GS GasPro column (30 m x 0.32 mm, J&W Scientific) was connected to FID, while an HP-624 column (30m x 0.32mm, Agilent Technologies) was connected to ECD with high purity helium (Weiler Welding, Dayton, OH) serving as the carrier gas. GC method was as follows: front inlet = 200 °C, FID = 250 °C, ECD = 300 °C, and oven temperature = 100 °C. The make-up gas for GC 6890 was high purity N₂ (Weiler Welding, Dayton, OH) with a flow rate of 45 mL min⁻¹ for the FID and 60 mL min⁻¹ for the ECD. The flow rate for high purity H₂ (Weiler Welding, Dayton, OH) was 40 mL min⁻¹ and for high purity air (Weiler Welding, Dayton, OH) it was 450 mL min⁻¹.

Experimental reactors were sampled for durations that varied based on reaction kinetics and byproducts observed. Experiments were completed within one day for CF, DCM, 1,1,2,2-TeCA, 1,1,2-TCA, 1,1,1-TCA, PCE, and 1,2-DCP while experiments were completed over 3-5 days for 1,2-DCA, TCE, cis-DCE, trans-DCE, VC, and 1,2,3-TCP.

2.4 Data Treatment

Five standards for each compound were prepared in 160 mL serum bottles with 96 mL Milli-Q water. CHC standards (except VC) were injected with various amounts of stock solution, wrapped in aluminum foil, and allowed to equilibrate for at least 2-3 hrs on an end-over-end rotator (45 rpm). Standards for methane, ethane, ethene, propene, hydrogen, and VC were injected with various amounts of gas and also allowed to equilibrate for at least 2-3 hrs. Calibration curves for each compound were created by
placing peak area obtained for each standard on the abscissa (x-axis) and amount (μmoles) in each bottle on the ordinate (y-axis). A linear regression was used to find the slope of the line, which was then used to quantify experimental GC peak areas.

In order to determine degradation kinetics, data collected from the first 1-2 hrs was used for compounds that degraded relatively quickly while data collected over several days was used for compounds that demonstrated slow degradation kinetics. This selected data was plotted with the amount of contaminant (μmoles) on the ordinate (y-axis) and time on the abscissa (x-axis). First-order degradation rate constants ($k_{obs}$; h$^{-1}$) were determined from the exponential regression through the selected data points. Initial amount of target contaminant ($[\text{CHC}]_0$), used in carbon mass balance calculations, was also determined from the exponential regression through the selected data points. Mass balance analysis of byproducts was conducted by determining the amount (μmoles) of various products generated from the degradation of the target compound, and their respective ‘molar mass fraction yields’ ($m/m_o$), referred to as yields, henceforth.
Chapter 3

RESULTS AND DISCUSSION

3.1: CHLORINATED METHANES

3.1.1 Chloroform degradation by ZVZ

CF degradation with unsieved, ~20 mesh ZVZ granules was significant, with CF yield \((m/m_0)\) equal to 0.20 after 2 hrs, while methane and DCM yields were 0.66 and 0.13 respectively (Fig. 3.1). This resulted in an excellent total carbon yield near 1 (i.e. near 100% carbon mass recovery). CF degradation with 20-24 mesh (sieved) size-fraction ZVZ showed comparable yields of daughter products after 2 hrs (methane: 0.66; DCM: 0.09; and CF remaining: 0.25) (Fig. 3.2).

DCM continued to accumulate during the 2-hr long experiment, and it was likely produced from CF reduction via the hydrogenolysis pathway, as previously suggested with ZVZ and ZVI (Feng and Lim, 2005). Further reduction of DCM with ZVZ (20-24 mesh) was slow \((k_{obs} = 0.0645 \text{ hr}^{-1}; k_M = 2.06\times10^{-3} \text{ L g}^{-1} \text{ hr}^{-1})\) (Fig. 3.18; or Table 3.4) resulting in small yields of methane (0.02) (Fig. 3.15). Slow DCM degradation kinetics were similarly observed with ZVZ (Boronina et al., 1998), and ZVI (Gillham and O’Hannesin, 1994; Matheson and Tratnyek, 1994). Any other intermediate, such as chloromethane \((\text{CH}_3\text{Cl})\), was below detection limit.
The degradation kinetics of DCM with ZVZ and Cu/Zn bimetallic reductants (section 3.1.4) were not fast enough to produce the methane yields observed during CF reduction. Therefore, to account for the methane yield observed from CF degradation, it is suggested that its transformation to methane occurred directly and without DCM as a reaction intermediate, although small amounts of methane were most likely also produced from DCM reduction via hydrogenolysis. Direct transformation of CF to methane has previously been suggested with ZVI (Song and Carraway, 2006), and with nZVI, Ni/Fe bimetallic and ZVZ (Feng and Lim, 2005). A comparative study of zero-valent metals revealed greater DCM accumulation during CF reduction by ZVZ, in comparison to ZVI (Feng and Lim, 2005).

The kinetics of CF degradation with ~20 mesh, unsieved ZVZ ($k_{obs} = 0.997 \text{ hr}^{-1}$; $k_M = 3.13 \times 10^{-2} \text{ L g}^{-1} \text{ hr}^{-1}$) (Fig. 3.9) was comparable to 20-24 mesh, sieved ZVZ ($k_{obs} = 0.696 \text{ hr}^{-1}$; $k_M = 2.23 \times 10^{-2} \text{ L g}^{-1} \text{ hr}^{-1}$) (Fig. 3.5). The modest decrease in rate constant with sieved ZVZ is most likely due to the removal of smaller particle size-fraction as a result of sieving with 24-mesh screen. A published study comparing CF reduction kinetics with ZVZ vs. ZVI has already demonstrated faster kinetics with ZVZ ($k_{SA} = 7.94 \times 10^{-3} \text{ L m}^{-2} \text{ hr}^{-1}$; $k_M = 3.18 \times 10^{-3} \text{ L g}^{-1} \text{ hr}^{-1}$) in comparison to ZVI ($k_{SA} = 3.15 \times 10^{-4} \text{ L m}^{-2} \text{ hr}^{-1}$; $k_M = 4.18 \times 10^{-4} \text{ L g}^{-1} \text{ hr}^{-1}$) (Feng and Lim, 2005), thus suggesting the potential of ZVZ in faster CF treatment. Kinetics with ZVZ in this investigation are approximately one order of magnitude faster than those reported in literature when considering $k_M$, despite the small ZVZ particle size (i.e. powder) previously used (Feng and Lim, 2005).
3.1.2 Chloroform degradation by Cu/Zn

CF degradation with Cu(0.5%)/Zn (prepared with CuCl$_2$ in EtOH) resulted in a substantial methane yield (0.76) after 2 hrs (Fig. 3.3), a 10% increase when compared to ZVZ (Fig. 3.4A); DCM yield was also considerably higher (0.26), likely due to the near-complete CF removal.

CF degradation with Cu(0.5%)/Zn indicated much faster reduction kinetics ($k_{obs} = 2.61$ hr$^{-1}$; $k_M = 8.35 \times 10^{-2}$ L g$^{-1}$ hr$^{-1}$) (Fig. 3.5; or Table 3.1), a nearly 4-fold increase in comparison to ZVZ ($k_{obs} = 0.696$ h$^{-1}$; $k_M = 2.23 \times 10^{-2}$ L g$^{-1}$ h$^{-1}$). Degradation kinetics with Cu/Zn were also faster than those observed with Pd/Zn and Ni/Zn reductants (section 3.1.3).

The effect of Cu in Cu/Zn bimetallic on CF removal was examined by varying Cu loading (0.05-1 wt.% and the results indicated near complete CF destruction after 2 hrs for all Cu loadings. A systematic increase in DCM yield and decrease in methane yield with increasing Cu loading is demonstrated (Fig. 3.4A), thus suggesting inhibition of direct CF transformation to methane with increased Cu loading on Zn. Methane yields with 0.05-0.5 wt.% Cu were higher than yields observed with ZVZ while DCM yield did not exceed 0.26 after approximately 2 hours. However, at higher Cu loading (0.75 and 1 wt.% DCM yields increased (0.39 and 0.43) and methane yields decreased (0.61 and 0.46). Excellent total carbon mass balance was observed at all Cu loadings investigated, indicating that DCM and methane were the dominant byproducts from CF reduction by Cu/Zn bimetallic.
In CF degradation experiments with Cu/Zn bimetallics (prepared with CuCl₂ dissolved in water), Cu loadings at 0.1-1 wt.% Cu show similar degradation products that include DCM and methane, but the product distribution is modestly different in comparison to the results with Cu/Zn bimetallics (prepared with CuCl₂ dissolved in ethanol). The product distribution did not vary much for the Cu loadings investigated, while DCM yields were higher (0.5-0.6) and methane yields were lower after 2 hrs (Fig. 3.4B) compared to ZVZ. This suggests direct reduction of CF to methane by Cu/Zn bimetallic is further inhibited and methane yield (0.3-0.4) was much less than the methane produced with ZVZ when Cu deposition onto Zn surface is exposed to the aqueous phase. Also, the reaction kinetics (k_{obs}) for CF at various Cu loadings in water did not exceed 1.64 hr⁻¹ (Fig. 3.6). As such, less effective CF reduction combined with poor byproduct distribution and slower degradation kinetics demonstrated the importance of secondary metal (Cu) deposition in EtOH than in water.

3.1.3 Chloroform degradation by Pd/Zn and Ni/Zn

CF degradation with Pd(0.06%)/Zn prepared with Pd salt dissolved in water resulted in less methane and an increased DCM yield (0.46 and 0.31, respectively) after 2 hrs (Fig. 3.7), in comparison to ZVZ, which suggests that direct reduction of CF to methane is inhibited in the presence of Pd. An elevated DCM yield may suggest catalytic effect of Pd in Pd/Zn in CF degradation, when compared to ZVZ. A relatively lower total carbon yield (0.85) may suggest undetermined reaction intermediate(s), and may also explain the reduced methane yield. Formation of reactive intermediates, such as carbene
radical and carbon monoxide (Feng and Lim, 2005), could also form (but not confirmed), thus accounting for the loss in carbon mass balance.

CF degradation kinetics were enhanced with Pd(0.06%)/Zn ($k_{\text{obs}} = 1.86 \, \text{hr}^{-1}$; $k_M = 5.95 \times 10^{-2} \, \text{L g}^{-1} \, \text{hr}^{-1}$) (Fig. 3.9; or Table 3.2) when compared to ZVZ, although kinetic enhancement was not as significant as with Cu(0.5%)/Zn. An investigation into the effects of Pd loading variation revealed a slight increase in methane yield and decrease in DCM yield from 0.02-0.06 wt.% Pd, but there was no significant difference in byproduct yields when Pd loading increased from 0.06 to 0.1 wt.% (Fig. 3.8). The highest methane yield (0.46) and fastest CF reduction kinetics were observed with 0.06 wt.% Pd on Zn (Fig. 3.10).

CF reduction with Ni(0.75%)/Zn (Fig. 3.11) prepared with Ni salt dissolved in EtOH resulted in approximately half the methane yield (0.33) and similar DCM yield (0.13) in comparison to ZVZ reduction at similar experimental conditions. Poor total carbon mass balance (0.73) may suggest CF transformation to carbene intermediate, a methane precursor, and thus may also explain reduced methane yield. In other words, direct reduction of CF to methane by Ni/Zn may be similar to ZVZ, but potential degradation of carbene intermediate by an alternative pathway may form less methane and cause poor total mass recovery. Results reported by Feng & Lim (2005) indicated that CF degradation by Ni/Fe resulted in the majority of CF being directly reduced to methane while an increased amount of DCM and lower amount of methane formed with ZVI. The present work also offers insight about the role of Ni in promoting transformation of carbene intermediate (methane precursor) by a competing pathway.
Much like Pd(0.06%)/Zn, Ni(0.75%)/Zn also increased CF degradation kinetics ($k_{\text{obs}} = 1.55 \, \text{hr}^{-1}$; $k_M = 4.96 \times 10^{-2} \, \text{L g}^{-1} \text{hr}^{-1}$) in comparison to ZVZ, although the increase in kinetics was not as significant as Cu(0.5%)/Zn. The effect of Ni loading (0.1-1 wt.% Ni) on Ni/Zn revealed no significant change in product distribution at various Ni loadings, except at 0.1 wt.% Ni when relatively lower methane yield (0.25) was observed (Fig. 3.12). The loading investigation also revealed fastest CF degradation kinetics with 0.75 wt.% Ni (Fig. 3.14).

### 3.1.4: Dichloromethane degradation by ZVZ and Cu/Zn

DCM degradation by ZVZ (Fig. 3.15) occurred very slowly and methane was the only byproduct (0.02); a slight increase in methane yield was observed from DCM degradation with Cu(0.5%)/Zn (0.03; Fig. 3.16) under similar experimental conditions. Total carbon mass balance for DCM degradation with ZVZ and Cu/Zn was less than 0.9 at 2 hrs. Methane was likely produced via hydrogenolysis, although its production through a competing pathway is possible.

DCM degradation kinetics with ZVZ ($k_{\text{obs}} = 6.45 \times 10^{-2} \, \text{hr}^{-1}$; $k_M = 2.06 \times 10^{-3} \, \text{L g}^{-1} \, \text{hr}^{-1}$), was largely inefficient, although Cu(0.5%)/Zn ($k_{\text{obs}} = 0.161 \, \text{hr}^{-1}$; $k_M = 5.15 \times 10^{-3} \, \text{L g}^{-1} \, \text{hr}^{-1}$) proved to be modestly effective (Fig. 3.18; or Table 3.4). Slow DCM degradation kinetics have been observed with ZVI for nearly 20 years (Gillham and O’Hannesin, 1994; Matheson and Tratnyek, 1994); inefficient DCM degradation has also been reported with nZVI (Song and Carraway, 2006). However, DCM degradation kinetics is approximately one order of magnitude higher with ZVZ ($k_{\text{SA}} = 1.94 \times 10^{-4} \, \text{L m}^{-2} \, \text{hr}^{-1}$; $k_M = 4.71 \times 10^{-5} \, \text{L g}^{-1} \, \text{hr}^{-1}$; Boronina et al., 1998) in comparison to ZVI ($k_{\text{SA}} = \ldots$).
1.82 x 10^{-5} \, \text{L} \, \text{m}^{-2} \, \text{hr}^{-1}; \, k_{M} = 5.67 \times 10^{-6} \, \text{L} \, \text{g}^{-1} \, \text{hr}^{-1}; \, \text{Onanong et al., 2007}, \text{ thus warranting further investigation to assess Cu/Zn performance with chlorinated methanes. In this investigation, } k_{M} \text{ obtained for DCM degradation by ZVZ is ~2 orders of magnitude greater than reported in literature, although the particle size used in the published investigation was much smaller (i.e. ZVZ dust) (Boronina et al., 1998).}

Slow DCM degradation kinetics can lead to accumulation of DCM during carbon tetrachloride (CT) and CF degradation by ZVZ and Zn bimetallics. Due to slow DCM kinetics, reduction of CT and CF via sequential hydrogenolysis may not explain the methane yield observed in investigations with ZVZ or ZVI, which suggests that direct transformation of CF to methane through alternative pathways is likely (Feng and Lim, 2005; Song and Carraway, 2006). An investigation into Cu loading ($k_{\text{obs}}: 6.16 \times 10^{-2}$ to $0.161 \, \text{hr}^{-1}; \, 0.1-1 \text{ wt.}% \, \text{Cu}$) (Fig. 3.19) did reveal most enhanced degradation kinetics at 0.5 wt.% Cu, agreeing well with results obtained during CF reduction by Cu/Zn. Therefore, it was decided that 0.5 wt.% Cu would be the single Cu loading to be used in subsequent bimetallic investigations.

3.2: CHLORINATED ETHANES

3.2.1: 1,1,2,2-TeCA degradation by ZVZ and Cu/Zn

ZVZ (Fig. 3.20) and Cu(0.5%)/Zn (Fig. 3.21) were both very effective in degrading 1,1,2,2-TeCA, with essentially all of 1,1,2,2-TeCA destroyed within approximately 4 hrs by both reductants. Yields of cis-DCE (ZVZ: 0.57, Cu/Zn: 0.58) and trans-DCE (ZVZ: 0.28, Cu/Zn: 0.30) after 4 hrs were nearly identical for both reductants, with 1,2-DCE isomers the only byproducts observed. Total carbon mass balance was also
similar for each reductant (ZVZ: 0.86, Cu/Zn: 0.87). Doubling the initial amount of 1,1,2,2-TeCA in a separate Cu/Zn experiment resulted in double the amount of both DCE isomers produced (Fig. 3.22), thus confirming the production of both isomers during 1,1,2,2-TeCA degradation. Both cis-DCE and trans-DCE have previously been reported as byproducts of 1,1,2,2-TeCA degradation via reductive β-elimination by ZVZ (Arnold et al., 1999) and ZVI (Song and Carraway, 2005).

Previous investigations with ZVZ revealed approximately double the amount of cis-DCE formation compared to trans-DCE, presumably because cis-DCE is the more thermodynamically favored byproduct (Arnold et al., 1999). Results of this investigation seem to confirm these previous findings with ZVZ and also suggest no difference in byproduct yields with Cu/Zn bimetallic. Degradation of 1,1,2,2-TeCA with nZVI (Song and Carraway, 2005) indicated the formation of TCE as well via dehydrohalogenation pathway (Song and Carraway, 2005). However, TCE was not observed during this investigation of 1,1,2,2-TeCA degradation with ZVZ and Cu/Zn.

In this study, the degradation kinetics of 1,1,2,2-TeCA with Cu(0.5%)/Zn ($k_{obs} = 3.10 \text{ hr}^{-1}; k_M = 9.92 \times 10^{-2} \text{ L g}^{-1} \text{ hr}^{-1}$) was somewhat faster than ZVZ ($k_{obs} = 1.84 \text{ hr}^{-1}; k_M = 5.89 \times 10^{-2} \text{ L g}^{-1} \text{ hr}^{-1}$) (Fig. 3.23), indicating benefit of Cu/Zn bimetallic reductant in commercial PRB applications at sites with 1,1,2,2-TeCA contamination. While some 1,1,2,2-TeCA remained after 1 hr with ZVZ (0.14) (Fig. 3.20), it nearly completely degraded (0.04) with Cu/Zn (Fig. 3.21) under similar conditions, demonstrating faster kinetics with Cu/Zn.
ZVZ ($k_{SA} = 7.27 \text{ L m}^{-2} \text{ hr}^{-1}; k_M = 2.55 \times 10^{-1} \text{ L g}^{-1} \text{ hr}^{-1}$; Arnold et al., 1999) has been found in some investigations to demonstrate 1,1,2,2-TeCA degradation kinetics over 2 orders of magnitude greater than those observed with nZVI ($k_{SA} = 3.03 \times 10^{-2} \text{ L m}^{-2} \text{ hr}^{-1}; k_M = 8.46 \times 10^{-1} \text{ L g}^{-1} \text{ hr}^{-1}$; Song and Carraway, 2005) when considering $k_{SA}$ while mass normalized kinetics ($k_M$) from literature seem to indicate slightly increased kinetics with ZVI. However, the ZVI particles used by Song and Carraway (2005) were nanoscale and thus had much greater specific surface area than the 30 mesh ZVZ granules used by Arnold et al. (1999). This demonstrates the importance of comparing kinetics using surface area normalized kinetics ($k_{SA}$). Therefore, comparing kinetics using $k_M$ is probably best when similar particle sizes are used, which is challenging given the micro and nanoscale particles used in many previous ZVI investigations (Lien and Zhang, 2001; Song and Carraway, 2005; Song and Carraway, 2006; Onanong et al., 2007; Sarathy et al., 2010). The $k_M$ for 1,1,2,2-TeCA observed with 20-24 mesh ZVZ in the present investigation agree quite well with previous ZVZ investigations using 30 mesh Zn (Arnold et al., 1999), an expected trend given the similarity in Zn particle sizes.

### 3.2.2: 1,1,2-TCA degradation by ZVZ and Cu/Zn

Vinyl chloride (VC) was the only degradation product formed from 1,1,2-TCA degradation with ZVZ (Fig. 3.24) and Cu(0.5%)/Zn (Fig. 3.25). However, VC yield was substantially more with Cu/Zn (0.50) after ~2.25 hrs than with ZVZ (0.16). Formation of VC was confirmed by doubling the initial 1,1,2-TCA amount in a separate Cu/Zn experiment, which resulted in double the amount of VC produced (Fig. 3.26) and confirmed VC as the only major byproduct. An excellent total carbon mass balance (ZVZ: 0.95, Cu/Zn: 0.96) after ~2.25 hrs also confirmed the presence of VC as the only
major byproduct. Previous study of 1,1,2-TCA degradation with ZVZ suggested that the sole product (VC) was produced via reductive β-elimination pathway (Arnold et al., 1999). However, 1,1,2-TCA reduction with nZVI indicated ethane to be the only byproduct (Song and Carraway, 2005); it was, however, suggested that VC may have been formed, but its presence was below detection limit due to rapid reaction with nZVI to form ethane (Song and Carraway, 2005). The short duration of 1,1,2-TCA degradation experiments in this investigation may have prevented any VC degradation to ethene (by hydrogenolysis) or ethane (by hydrogenation) to be evident, and VC accumulation demonstrates that it reacted slowly with ZVZ and Cu/Zn (section 3.3.5).

Reduction of 1,1,2-TCA by ZVZ ($k_{obs} = 0.163 \text{ hr}^{-1}; k_M = 5.22 \times 10^{-3} \text{ L g}^{-1} \text{ hr}^{-1}$) and Cu(0.5%)/Zn ($k_{obs} = 0.485 \text{ hr}^{-1}; k_M = 1.55 \times 10^{-2} \text{ L g}^{-1} \text{ hr}^{-1}$) (Fig. 3.27) was substantially slower than 1,1,2,2-TeCA degradation kinetics, although the presence of Cu on Zn surface resulted in a 3-fold increase in its $k_M$. Slower 1,1,2-TCA degradation kinetics in comparison to 1,1,2,2-TeCA kinetics were expected, as degradation potential generally decreases with decreasing number of chlorines present (Tratnyek et al., 2011).

Similar to 1,1,2,2-TeCA degradation kinetics with ZVZ vs. ZVI, 1,1,2-TCA degradation kinetics with ZVZ ($k_{SA} = 1.09 \times 10^{-1} \text{ L m}^{-2} \text{ hr}^{-1}; k_M = 3.82 \times 10^{-1} \text{ L g}^{-1} \text{ hr}^{-1}$; Arnold et al., 1999) are approximately 2 orders of magnitude greater than kinetics observed with nZVI ($k_{SA} = 2.31 \times 10^{-3} \text{ L m}^{-2} \text{ hr}^{-1}$; Song and Carraway, 2005; and $k_M = 2.90 \times 10^{-4} \text{ L g}^{-1} \text{ hr}^{-1}$; Onanong et al., 1999). As revealed in this investigation, amending ZVZ with Cu further enhanced 1,1,2-TCA degradation kinetics, thus indicating the potential of Zn-based reductants in field applications. A comparison of $k_M$ indicate slower kinetics observed with ZVZ in this investigation than those previously observed (Arnold
et al., 1999) by ~2 orders of magnitude, despite the similarities in the particle size of ZVZ.

**3.2.3: 1,1,1-TCA degradation by ZVZ and Cu/Zn**

Complete destruction of 1,1,1-TCA was achieved with both ZVZ (Fig. 3.28) and Cu(0.5%)/Zn (Fig. 3.29), with ethane and 1,1-DCA as main daughter products, where ethane yield (ZVZ: 0.95, Cu/Zn: 0.81) was substantially greater than 1,1-DCA yield (ZVZ: 0.08, Cu/Zn: 0.17). Degradation of 1,1,1-TCA formed 1,1-DCA via hydrogenolysis, which can then further react via hydrogenolysis to form ethane. However, ethane formed very quickly in this study with ZVZ and Cu/Zn, as it did in other investigations (Fennelly and Roberts, 1998; Song and Carraway, 2005) with both ZVZ and nZVI. The simultaneous production of 1,1-DCA and ethane suggests that ethane formation may not occur by sequential hydrogenolysis of 1,1,1-TCA → 1,1-DCA → chloroethane → ethane since 1,1-DCA reduction is reported to be slow (Arnold et al., 1999; Song and Carraway, 2005). Instead, ethane production from 1,1,1-TCA degradation by ZVZ and nZVI has been suggested to occur via reductive α-elimination pathway (Arnold et al., 1999; Song and Carraway, 2005).

The daughter products of 1,1,1-TCA degradation in this investigation is similar, but their yields are drastically different than those obtained with nZVI, where 1,1-DCA, formed via hydrogenolysis, accounted for 69% of total carbon mass (Song and Carraway, 2005). However, results in this investigation agree very well with previously published results for ZVZ, where ethane is clearly the dominant byproduct (Fennelly and Roberts, 1998). This suggests that ZVZ and Cu/Zn produce a higher yield of fully dechlorinated
byproduct than nZVI, although Cu/Zn slightly changes the byproduct distribution, i.e. more 1,1-DCA, in comparison to ZVZ alone.

A comparison of 1,1,1-TCA degradation kinetics with ZVZ ($k_{\text{obs}} = 2.16 \text{ hr}^{-1}; k_M = 6.91 \times 10^{-2} \text{ L g}^{-1} \text{ hr}^{-1}$) and Cu(0.5%)/Zn ($k_{\text{obs}} = 4.89 \text{ hr}^{-1}; k_M = 1.56 \times 10^{-1} \text{ L g}^{-1} \text{ hr}^{-1}$) (Fig. 3.34) indicated significantly faster kinetics with Cu/Zn. The degradation rate constant observed with 1,1,1-TCA is greater than for any other compound in this investigation, which agrees well with previously published kinetics with ZVZ ($k_S = 22.1 \text{ L m}^{-2} \text{ hr}^{-1}; k_M = 0.774 \text{ L g}^{-1} \text{ hr}^{-1}$; Arnold et al., 1999) and nZVI ($k_S = 1.51 \times 10^{-1} \text{ L m}^{-2} \text{ hr}^{-1}$; Song and Carraway, 2005, and $k_M = 3.74 \times 10^{-3} \text{ L g}^{-1} \text{ hr}^{-1}$; Onanong et al., 1999). Nearly identical to trends in $k_S$ values for ZVZ and ZVI observed during 1,1,2,2-TeCA and 1,1,2-TCA reduction, the degradation kinetics for 1,1,1-TCA have been reported by some previous investigations to be 2 orders of magnitude greater for ZVZ. Results from this investigation agree relatively well with published ZVZ results (Arnold et al., 1999), with drastic increase in degradation kinetics using Cu/Zn suggesting further enhancement of degradation kinetics. Therefore, the results of 1,1,1-TCA degradation studies with Cu/Zn continue to demonstrate the ability of Cu/Zn bimetallic to enhance degradation kinetics, when compared to ZVZ. The favorable yield of completely dechlorinated end-product (ethane) from 1,1,1-TCA degradation also demonstrates the advantage of Cu/Zn over ZVI.

Further examination of Cu loading effect on Zn on 1,1,1-TCA demonstrated no significant benefit. The byproduct yields (Fig. 3.32) and degradation kinetics (Fig. 3.34; Table 3.5) were nearly identical for 0.5 and 0.75 wt.% Cu on Zn, thus demonstrating that
0.5 wt.% Cu on Zn was a viable and effective Cu/Zn bimetallic, as was previously concluded in experiments with CF and DCM.

3.2.4: 1,2-DCA degradation by ZVZ and Cu/Zn

The only byproduct observed during ZVZ (Fig. 3.35) and Cu(0.5%)/Zn (Fig. 3.36) reduction of 1,2-DCA was ethene, formed via reductive β-elimination and thus confirming byproducts previously observed with ZVZ reduction of 1,2-DCA (Arnold et al., 1999). Poor total carbon mass balance (ZVZ: 0.80; Cu/Zn: 0.70) was observed after 100 hrs, thus suggesting that other byproduct(s) or intermediates may also form. The confirmation of ethene formation was achieved when twice as much ethene was produced in a separate Cu/Zn experiment where the initial amount of 1,2-DCA was doubled (Fig. 3.37). Due to faster degradation kinetics, ethene yield from 1,2-DCA degradation by Cu/Zn (0.008) was twice as much as by ZVZ (0.004) after 100 hrs. Although the amount of ethene produced was small, ethene was not detected in previous investigations with nZVI even after 40 days (Song and Carraway, 2005).

Reduction of 1,2-DCA by ZVZ \( (k_{\text{obs}} = 2.45 \times 10^{-3} \text{ hr}^{-1}; \ k_M = 7.84 \times 10^{-5} \text{ L g}^{-1} \text{ hr}^{-1}) \) and Cu(0.5%)/Zn \( (k_{\text{obs}} = 4.00 \times 10^{-3} \text{ hr}^{-1}; \ k_M = 1.28 \times 10^{-4} \text{ L g}^{-1} \text{ hr}^{-1}) \) was monitored over a period of ~100 hrs, with very slow degradation kinetics for both systems observed (Fig. 3.38). According to published reports, the degradation kinetics of 1,2-DCA with ZVZ \( (k_{\text{SA}} = 2.83 \times 10^{-5} \text{ L m}^{-2} \text{ hr}^{-1}; \ k_M = 9.92 \times 10^{-7} \text{ L g}^{-1} \text{ hr}^{-1}; \) Arnold et al., 1999) and nZVI \( (k_{\text{SA}} = 4.00 \times 10^{-6} \text{ L m}^{-2} \text{ hr}^{-1}; \ k_M = 1.20 \times 10^{-4} \text{ L g}^{-1} \text{ hr}^{-1}; \) Song and Carraway, 2005), 1,2-DCA may be one of the slowest CHCs to degrade. Much like other chlorinated ethanes already discussed, the degradation kinetics of 1,2-DCA with ZVZ (Arnold et al., 1999)
appear to be an order of magnitude greater than kinetics observed with ZVI (Song and Carraway, 2005) when considering $k_{SA}$. Published $k_{M}$ with ZVZ do not agree well with results in this investigation, despite similar particle sizes.

### 3.3: CHLORINATED ETHENES

#### 3.3.1: PCE degradation by ZVZ and Cu/Zn

The degradation of PCE with ZVZ produced TCE and trans-DCE as byproducts (Fig. 3.39). The yields of TCE (0.18) and trans-DCE (0.06) after 5 hrs agree well with those obtained previously with ZVZ (Arnold and Roberts, 1998). Results of PCE degradation with Cu(0.5%)/Zn resulted in the formation of TCE, trans-DCE, and ethene (Fig. 3.40). Unlike ZVZ, Cu/Zn yielded more trans-DCE (0.22) than TCE (0.18) after 5 hrs, thus suggesting the role of Cu in Cu/Zn that affects byproduct distribution. The yield of ethene in the Cu/Zn system was small (0.02). TCE presumably formed via hydrogenolysis, while trans-DCE could form in two steps: (i) reductive β-elimination of PCE that forms 1,2-dichloroacetylene as an intermediate; (ii) that upon hydrogenation further transforms to trans-DCE. Ethene may have formed via hydrogenation of acetylene. Poor total carbon mass balance was obtained from PCE reduction with ZVZ (0.34) and Cu/Zn (0.53) after 5 hrs, suggesting formation of reaction intermediates not detected during analysis.

PCE degradation kinetics with ZVZ ($k_{obs} = 0.287 \text{ hr}^{-1}; k_{M} = 9.18 \times 10^{-3} \text{ L g}^{-1} \text{ hr}^{-1}$) and Cu(0.5%)/Zn ($k_{obs} = 0.414 \text{ hr}^{-1}; k_{M} = 1.32 \times 10^{-2} \text{ L g}^{-1} \text{ hr}^{-1}$) indicate a modest enhancement in degradation kinetics with Cu amendment of Zn surface (Fig. 3.41), but the enhancement was not as dramatic as with chlorinated methanes and ethanes. In
addition, the enhanced production of trans-DCE from PCE reduction using Cu/Zn system may be undesirable in the short-term, but trans-DCE should degrade over longer interval. Degradation kinetics with ZVZ in the present investigation are very similar to those previously reported in literature (Arnold and Roberts, 1998), an expected trend given the similarity in particles used.

Literature values for $k_{SA}$ seem to indicate PCE degradation kinetics for ZVZ ($k_{SA} = 3.45 \times 10^{-1} \text{ L m}^{-2} \text{ hr}^{-1}$; $k_{M} = 1.21 \times 10^{-2} \text{ L g}^{-1} \text{ hr}^{-1}$; Arnold and Roberts, 1998) are ~2 orders of magnitude greater than those observed with ZVI ($k_{SA} = 2.10 \times 10^{-3} \text{ L m}^{-2} \text{ hr}^{-1}$; Johnson et al., 1996), but the mass-normalized rate constant for ZVI ($k_{M} = 7.35 \times 10^{-2} \text{ L g}^{-1} \text{ hr}^{-1}$; Lien and Zhang, 2001) is comparable to that of ZVZ. Further, the byproduct distribution of PCE degradation with ZVI is much more desirable, as less than 10% (i.e. $m/m_0 < 0.10$) of PCE degradation byproduct yield consisted of chlorinated ethenes (Arnold and Roberts, 2000), whereas the vast majority (~90%) of byproduct yield generated from PCE reduction with ZVZ is not fully dechlorinated (Arnold and Roberts, 1998).

Similar to 1,1,2,2-TeCA and 1,1,2-TCA degradation by ZVZ that led to the formation of chlorinated ethenes by reductive β-elimination pathway (Arnold et al., 1999; Song and Carraway, 2005), reductive β-elimination also plays an important role in chlorinated ethane (PCE and TCE) degradation by zero-valent metals and may yield chlorinated acetylenes. Although chlorinated acetylenes are toxic, they are very reactive and thus may not accumulate in the system. Therefore, reductive β-elimination can prevent the accumulation of vinyl chloride, which can form by PCE and TCE degradation via sequential hydrogenolysis pathway (Arnold and Roberts, 1998).
Reduction of PCE with ZVI has been shown to yield TCE, ethene, and ethane (Arnold and Roberts, 2000), where TCE yield was relatively minor (< 0.10) produced by hydrogenolysis. Ethene and ethane formed from PCE degradation with ZVI may have formed from a complex reaction pathway that began with PCE degrading to dichloroacetylene via reductive β-elimination, which then underwent two consecutive hydrogenolysis reactions to form acetylene; acetylene then formed ethene and ethane via hydrogenation (Arnold and Roberts, 2000).

PCE reduction with ZVZ has previously shown to yield TCE, trans-DCE, and acetylene as major degradation byproducts (Arnold and Roberts, 1998). Formation of TCE as major degradation product with ZVZ suggests that hydrogenolysis may play a much larger role in PCE reduction with ZVZ than ZVI. Although it is possible that trans-DCE formed via TCE hydrogenolysis, it was suggested that trans-DCE formed too quickly to be associated with sequential hydrogenolysis and thus it may have been formed via hydrogenation of dichloroacetylene (Arnold and Roberts, 1998). A similar conclusion was argued for acetylene formation as a reaction intermediate (Arnold and Roberts, 1998). It is possible that trans-DCE and acetylene formed when PCE was initially reduced via reductive β-elimination to form dichloroacetylene; its hydrogenation could form trans-DCE, while its hydrogenolysis could form acetylene.

### 3.3.2: TCE degradation by ZVZ and Cu/Zn

TCE reduction by ZVZ (Fig. 3.42) and Cu(0.5%)/Zn (Fig. 3.43) produced identical byproducts after ~ 5 days, which included trans-DCE (ZVZ: 0.18, Cu/Zn: 0.16), cis-DCE (ZVZ: 0.12, Cu/Zn: 0.14), although a clear difference in ethene yield (ZVZ: 0.01, Cu/Zn: 0.03).
0.01, Cu/Zn: 0.20) was observed. A higher total carbon mass balance was obtained with Cu/Zn (0.90) in comparison to ZVZ (0.80), due to greater ethene yield, but trans- and cis-DCE yields with Cu/Zn and ZVZ were very similar. The increased yield of fully dechlorinated byproduct, ethene, with Cu/Zn is certainly encouraging.

Byproducts trans-DCE and cis-DCE obtained during ZVZ and Cu/Zn reduction of TCE were presumably formed via hydrogenolysis. However, the pathway(s) leading to the production of ethene may not be through hydrogenolysis. If ethene were to form from sequential TCE hydrogenolysis (i.e., TCE → trans-DCE/cis-DCE → VC → ethene), then VC as an intermediate would have been present. It seems unlikely, however, that VC formed and degraded quickly since VC exhibited slow degradation kinetics with ZVZ and Cu/Zn (section 3.3.5). Therefore, an alternate pathway for ethene formation from TCE by β-elimination is indicated, (much like the pathway described previously for PCE reduction) that formed chloroacetylene by reductive β-elimination of TCE, which then further reacted with ZVZ and Cu/Zn to produce acetylene (via hydrogenolysis) and subsequently ethene (via hydrogenation).

Previously reported results of TCE reduction with ZVZ revealed trans-DCE, cis-DCE, and acetylene to be the major degradation byproducts (Arnold and Roberts, 1998). It was assumed that acetylene formed via a highly reactive intermediate (i.e. chlorinated acetylenes), while 1,2-DCE formed by hydrogenolysis (Arnold and Roberts, 1998). Previous results with ZVI revealed ethene and ethane as the only major byproducts, formed via initial reductive β-elimination of TCE (Arnold and Roberts, 2000), thus demonstrating the advantage of ZVI over ZVZ during TCE reduction.
Unlike degradation kinetics observed for chlorinated methanes and ethanes (sections 3.1 and 3.2), TCE degradation kinetics with ZVZ ($k_{obs} = 1.03 \times 10^{-2} \text{ hr}^{-1}$; $k_M = 3.30 \times 10^{-4} \text{ L g}^{-1} \text{ hr}^{-1}$) and Cu(0.5%)/Zn ($k_{obs} = 1.38 \times 10^{-2} \text{ hr}^{-1}$; $k_M = 4.42 \times 10^{-4} \text{ L g}^{-1} \text{ hr}^{-1}$) were very similar (Fig. 3.44). Degradation kinetics with ZVZ in the present investigation agree very well with those previously reported in literature ($k_M = 1.09 \times 10^{-4} \text{ L g}^{-1} \text{ hr}^{-1}$; Arnold and Roberts, 1998)

Literature TCE degradation kinetics were determined to be much faster with ZVZ than ZVI in an investigation that compared the two reductants (Cheng and Wu, 2000) and in other investigations using ZVZ ($k_{SA} = 3.11 \times 10^{-3} \text{ L m}^{-2} \text{ hr}^{-1}$; Arnold and Roberts, 1998) and ZVI ($k_{SA} = 3.90 \times 10^{-4} \text{ L m}^{-2} \text{ hr}^{-1}$; Johnson et al., 1996). However, it appears PCE and TCE reduction is best achieved through the use of ZVI rather than Zn-based reductants, as the yield of fully dechlorinated byproducts with ZVI is much greater.

3.3.3: cis-DCE degradation by ZVZ and Cu/Zn

No byproducts from ZVZ reduction of cis 1,2-DCE were found in this investigation after ~4 days; however, a very small ethane yield (0.005) was observed with Cu/Zn (Fig. 3.45). Previous results of cis-DCE reduction by ZVZ yielded very small amounts of acetylene, vinyl chloride, and ethene (Arnold and Roberts, 1998). The absence of these byproducts in the current investigation is presumably due to the short experiment duration time (4 days) compared to the previous investigation with ZVZ (14 days) (Arnold and Roberts, 1998). The presence of acetylene with the previous investigation may suggest reduction of cis-DCE via reductive β-elimination, while vinyl chloride production from cis-DCE may occur via hydrogenolysis, and ethene production
may occur from acetylene by hydrogenation or from VC by hydrogenolysis. Ethene observed in this investigation with Cu/Zn was most likely generated from reduction of acetylene to ethene via hydrogenation, as VC was not observed. Published results of cis-DCE reduction by ZVI revealed ethene and ethane as the only major byproducts (Arnold and Roberts, 2000); VC did not form with ZVI due to initial reductive β-elimination of cis-DCE to highly reactive acetylene intermediate, which further reacted to form ethene and ethane.

Degradation kinetics of cis-DCE reduction by ZVZ ($k_{\text{obs}} = 3.11 \times 10^{-4} \text{ hr}^{-1}$; $k_M = 9.95 \times 10^{-6} \text{ L g}^{-1} \text{ hr}^{-1}$) and Cu(0.5%)/Zn ($k_{\text{obs}} = 9.48 \times 10^{-4} \text{ hr}^{-1}$; $k_M = 3.03 \times 10^{-5} \text{ L g}^{-1} \text{ hr}^{-1}$) were slow (Fig. 3.46), with no more than 10% of original cis-DCE (i.e. cis-DCE $m/m_0 > 0.90$) mass being destroyed by either ZVZ or Cu/Zn (Fig. 3.45) after ~5 days. Although observed kinetics were slow, Cu/Zn proved to be somewhat promising as it resulted in a modest increase in degradation kinetics when compared to ZVZ. Previous investigations with ZVZ ($k_{SA} = 3.52 \times 10^{-6} \text{ L m}^{-2} \text{ hr}^{-1}$; $k_M = 1.23 \times 10^{-7} \text{ L g}^{-1} \text{ hr}^{-1}$; Arnold and Roberts, 1998) and ZVI ($k_{SA} = 4.10 \times 10^{-5} \text{ L m}^{-2} \text{ hr}^{-1}$; Johnson et al., 1996, and $k_M = 1.44 \times 10^{-3} \text{ L g}^{-1} \text{ hr}^{-1}$; Lien and Zhang, 2001) have demonstrated cis-DCE degradation kinetics ($k_{SA}$) with ZVI to be approximately an order of magnitude greater than with ZVZ. In terms of $k_M$, cis-DCE degradation kinetics with ZVZ in this investigation and published kinetics with 30 mesh ZVZ (Arnold et al., 1999) agree quite well.

3.3.4: trans-DCE degradation by ZVZ and Cu/Zn

Similar to cis-DCE, no byproduct was observed from degradation of trans-DCE with ZVZ, while with Cu/Zn ethene was the only byproduct after 100 hrs (0.02; Fig.
3.47). By doubling the amount of *trans*-DCE in a separate Cu/Zn experiment, ethene formation doubled thus confirming it to be a key degradation product (Fig. 3.48). Lack of VC formation from *trans*-DCE degradation again suggest the reaction may initially form acetylene reductive β-elimination pathway, which may further degrade to ethene (Arnold and Roberts, 2000) via hydrogenation. The byproducts reported in literature for *trans*-DCE reduction using ZVZ (Arnold and Roberts, 1998) and ZVI (Arnold and Roberts, 2000) were identical to those reported for *cis*-DCE reduction using these reductants.

Results of *trans*-DCE reduction by ZVZ (\(k_{obs} = 6.51 \times 10^{-4} \text{ hr}^{-1} ; k_M = 2.08 \times 10^{-5} \text{ L g}^{-1} \text{ hr}^{-1}\)) and Cu(0.5%)/Zn (\(k_{obs} = 1.37 \times 10^{-3} \text{ hr}^{-1} ; k_M = 4.38 \times 10^{-5} \text{ L g}^{-1} \text{ hr}^{-1}\)) (Fig. 3.49) were very similar to results of *cis*-DCE reduction by these reductants. Degradation kinetics were enhanced by approximately the same magnitude when Cu was amended to Zn surface. *Trans*-DCE degradation kinetics were slightly faster than kinetics observed with *cis*-DCE, which was evident from more complete *trans*-DCE loss after ~4 days \((m/m_0 = 0.87)\) compared to *cis*-DCE \((m/m_0 = 0.91)\) with Cu/Zn. Published *cis*-DCE degradation kinetics shows a similar trend to *trans*-DCE kinetics, with degradation using ZVZ \((k_{SA} = 1.36 \times 10^{-5} \text{ L m}^{-2} \text{ hr}^{-1} ; k_M = 4.77 \times 10^{-7} \text{ L g}^{-1} \text{ hr}^{-1}; \text{Arnold and Roberts}, 1998)\) ~1 order of magnitude slower than those observed with ZVI \((k_{SA} = 1.20 \times 10^{-4} \text{ L m}^{-2} \text{ hr}^{-1} ; \text{Johnson et al.}, 1996, \text{and } k_M = 4.20 \times 10^{-3} \text{ L g}^{-1} \text{ hr}^{-1} ; \text{Lien and Zhang}, 2001)\). The kinetics of *trans*-DCE degradation with ZVZ in the present investigation appear to be ~2 orders of magnitude greater than those reported previously (Arnold and Roberts, 1998).
3.3.5: Vinyl Chloride degradation by ZVZ and Cu/Zn

The importance of chlorinated ethene destruction via reductive β-elimination cannot be overstated, as this pathway allows for highly reactive intermediates to form. Degradation of chlorinated ethenes, especially TCE and PCE, via reductive β-elimination can prevent the formation of VC, a slow degrading compound (Johnson et al., 1996) with a current MCL that is less than half of the MCLs for chlorinated methanes, ethanes, and ethenes previously discussed (EPA, 2013a). It is well known that natural attenuation of chlorinated ethenes by indigenous microbes typically proceeds via sequential hydrogenolysis, thus resulting in the production of VC (Clement et al., 2000) that may accumulate at natural attenuation sites, as VC will not readily degrade via hydrogenolysis due to a reduction in efficiency with a decrease in the number of chlorines. This allows VC to accumulate unless strongly reducing conditions are present, which is the purpose of zero-valent metals in PRBs (Stroo and Ward, 2010). Therefore, it is critically important to consider degradation potential of VC, as accumulation of this CHC by chlorinated ethene degradation via abiotic or biotic processes at remediation sites can determine project success or failure.

The sole byproduct of VC degradation with ZVZ and Cu/Zn was ethene, with ethene yield becoming 10 times higher after 5 days with Cu/Zn (0.05; Fig. 3.51) than ZVZ (0.005; Fig. 3.50). Total carbon mass balance of VC degradation with ZVZ (0.98) and Cu/Zn (0.97) was excellent after 5 days. The increased ethene yield was due to the increased kinetics with Cu/Zn. It was expected that ethene and/or ethane would be the only byproduct(s), formed via hydrogenolysis, as previous investigations with ZVZ reported ethene as the only byproduct (Arnold and Roberts, 1998) and byproducts of VC
reduction by ZVI were ethene and ethane (Arnold and Roberts, 2000). It is likely that VC will not produce acetylenes as intermediates due to the presence of single chlorine on the molecule, which precludes reduction via reductive β-elimination degradation pathway (Stroo and Ward, 2010).

The degradation kinetics of VC with ZVZ \( (k_{obs} = 1.86 \times 10^{-4} \text{hr}^{-1}; k_M = 5.95 \times 10^{-6} \text{L g}^{-1} \text{hr}^{-1}) \) and Cu(0.5%)/Zn \( (k_{obs} = 6.96 \times 10^{-4} \text{hr}^{-1}; k_M = 2.23 \times 10^{-5} \text{L g}^{-1} \text{hr}^{-1}) \) were quite slow (Fig. 3.52). The mass-normalized VC degradation rate constant \( (k_M) \) with ZVZ in the present investigation agrees well with published values with 30 mesh ZVZ (Arnold and Roberts, 1998). Much like results with other chlorinated ethenes, the enhancement in kinetics by Cu amended to Zn surface was modest. It appears that VC degradation kinetics using ZVZ \( (k_{SA} = 1.0 \times 10^{-4} \text{L m}^{-2} \text{hr}^{-1}; k_M = 3.50 \times 10^{-6} \text{L g}^{-1} \text{hr}^{-1}; \) Arnold and Roberts, 1998) are slightly slower than those reported using ZVI \( (k_{SA} = 5.0 \times 10^{-4} \text{L m}^{-2} \text{hr}^{-1}; \) Johnson et al., 1996). As revealed in the present investigation, amending Cu onto Zn surface further enhanced VC degradation kinetics by Zn-based reductants. Therefore, Cu/Zn may prove to be a potential treatment of choice in PRBs at VC contaminated sites.

3.4: CHLORINATED PROPANES

3.4.1: 1,2,3-TCP degradation by ZVZ and Cu/Zn

1,2,3-TCP has been identified as an emerging contaminant by the USEPA and is considered by the agency "likely to be carcinogenic to humans.” Although no federal MCL has been established, the state of Hawaii has established a state MCL of 0.6 μg L\(^{-1}\) (EPA, 2013b), a concentration lower than federal MCLs for any chlorinated methane, ethane, or ethene (EPA, 2013a). Due to the status of 1,2,3-TCP as an emerging
groundwater contaminant, it should come as no surprise that 1,2,3-TCP has received considerable attention in recent publications. This is especially true concerning ZVZ reduction of 1,2,3-TCP (Sarathy et al., 2010; Salter-Blanc and Tratnyek, 2011; Salter-Blanc et al., 2012). These recent findings suggest that reduction of 1,2,3-TCP by ZVZ results in much faster degradation kinetics and a preferred yield of byproducts compared to ZVI (Sarathy et al., 2010). However, the performance of Cu/Zn in 1,2,3-TCP reduction has not been evaluated.

In the present investigation, the sole byproduct from 1,2,3-TCP degradation after 5 days with ZVZ (Fig. 3.53) and Cu(0.5%)/Zn (Fig. 3.54) was propene; the degradation byproduct was confirmed when the amount of propene formed doubled in a separate Cu/Zn experiment with double the initial amount of 1,2,3-TCP (Fig. 3.60). The yield of propene with ZVZ and Cu/Zn was similar (0.74 and 0.67, respectively), while the total carbon mass balance was slightly higher with ZVZ (0.95) than Cu/Zn (0.87), presumably due to the increased production of propene. The presence of propene as the only byproduct agrees very well with a previous investigation using ZVZ (Sarathy et al., 2010). However, unlike the present investigation, only small and transient amounts of propene were reported, although the actual yield of propene was not reported (Sarathy et al., 2010).

1,2,3-TCP degradation with ZVZ and Cu/Zn may occur by reductive β-elimination initially to 3-chloro-1-propene, which can further reduce to propene via hydrogenolysis, although 3-chloro-1-propene was not detected by ECD. Such a pathway has previously been proposed for ZVZ reduction of 1,2,3-TCP (Sarathy et al., 2010). Propene can also be produced from initial reduction of 1,2,3-TCP via hydrogenolysis to
yield 1,2-DCP or 1,3-DCP. Further reduction of 1,2-DCP by reductive β-elimination could result in the formation of propene. However, this alternate mechanism of propene formation from 1,2,3-TCP reduction is less likely, as 1,2-DCP was not found to be a byproduct and 1,2-DCP degradation kinetics with ZVZ and Cu/Zn are slow (section 3.4.2). Therefore, a reductive β-elimination → hydrogenolysis sequence most likely explains production of propene from 1,2,3-TCP reduction by ZVZ and Cu/Zn.

A previous investigation with ZVI revealed the formation of 1,2-DCP, which ultimately reduced to propene (Focht, 1994) by hydrogenolysis → reductive β-elimination sequence. Another previous investigation with ZVI revealed the production of propene, 1-chloro-1-propene, 2-methyl-1-propene, and chloromethane. Authors of this investigation proposed a complex array of reaction pathways that included reductive β-elimination and radical intermediates (Sarathy et al., 2010).

In the present study, the degradation kinetics observed with ZVZ ($k_{\text{obs}} = 5.32 \times 10^{-2} \text{ hr}^{-1}; k_M = 1.70 \times 10^{-3} \text{ L g}^{-1} \text{ hr}^{-1}$) and Cu(0.5%)/Zn ($k_{\text{obs}} = 7.09 \times 10^{-2} \text{ hr}^{-1}; k_M = 2.27 \times 10^{-3} \text{ L g}^{-1} \text{ h}^{-1}$) were similar (Fig. 3.63), although Cu/Zn demonstrated improved kinetics. The similarity in degradation kinetics with ZVZ and Cu/Zn was evident after 5 days, with the amount of remaining 1,2,3-TCP nearly identical (ZVZ: 0.21, Cu/Zn: 0.20). Reported 1,2,3-TCP degradation kinetics with 30 mesh ZVZ ($k_{\text{SA}} = 3.50 \times 10^{-3} \text{ L m}^{-2} \text{ hr}^{-1}; k_M = 1.30 \times 10^{-4} \text{ L g}^{-1} \text{ hr}^{-1}$) were ~1 order of magnitude slower than ZVZ $k_M$ in the present study, despite the similarity in ZVZ particle size (Sarathy et al., 2010). Results with ZVI ($k_{\text{SA}} = 9.84 \times 10^{-6} \text{ L m}^{-2} \text{ hr}^{-1}; k_M = 2.95 \times 10^{-4} \text{ L g}^{-1} \text{ hr}^{-1}$) demonstrate a drastic difference between the two reductants, with ZVZ demonstrating impressive kinetics ~3 orders of magnitude greater than ZVI when considering $k_{\text{SA}}$ (Sarathy et al., 2010).
An additional investigation was completed to understand the influence of 6-12 grams of Cu(0.5%)/Zn on 1,2,3-TCP reduction, as variable reductant mass is commonly encountered in a PRB. Results indicated a systematic increase in degradation kinetics as the amount of Cu/Zn reductant increased (Fig. 3.64; or Table 3.6), with Cu(0.5%)/Zn(12g) exhibiting fastest kinetics ($k_{obs} = 0.128$ hr$^{-1}$). A systematic yet minor decrease in propene yields and carbon mass balance was observed with increasing Cu/Zn amounts (Fig. 3.59), although propene was still substantial with 12 g Cu/Zn ($m/m_0 = 0.56$; Fig. 3.57) and no other byproducts were produced. Further reduction of propene to propane or production of other byproducts due to increasing Cu/Zn loading is possible, even though no propane was observed. It is more likely that propene attached to the Zn-reductant present in the system, thus resulting in an apparent decrease of propene mass with increased reductant mass.

In addition to the systematic relationships in degradation kinetics and byproducts observed, the investigation with increasing Cu/Zn loading also revealed a systematic increase in pH after 5 days (Fig. 3.62). The observed pH climbed steadily from 7.18 with ZVZ(3g) and 7.36 with Cu(0.5%)/Zn(3g) to a max pH of 7.71 using Cu(0.5%)/Zn(12g). The increase in pH corresponds to an increase in proton (supplied from water) consumption at greater Zn loading (Eq. 8). A systematic increase in hydrogen production after 5 days was also observed at greater Cu/Zn loading (Fig. 3.61). The interaction between Zn and water also produces hydrogen, as can be seen in equation [8].

$$Zn^0 + 2H_2O \rightarrow Zn^{2+} + 2OH^- + H_2\uparrow$$  [8]
3.4.2: 1,2-DCP degradation by ZVZ and Cu/Zn

The only byproduct observed from 1,2-DCP reduction by ZVZ (Fig. 3.65) and Cu(0.5%)/Zn (Fig. 3.66) was propene; the product was confirmed with the amount of propene yield increased proportionately as the amount of 1,2-DCP was doubled (Fig. 3.67). The overall propene yield was relatively small at ~2.25 hrs with both ZVZ (0.01) and Cu/Zn (0.04), although the propene yield with Cu/Zn was ~4-fold greater than with ZVZ. The formation of propene suggests 1,2-DCP reduction by ZVZ and Cu/Zn via reductive β-elimination. This seems to support the degradation pathway sequence previously suggested for 1,2,3-TCP reduction by ZVZ and Cu/Zn, where reductive β-elimination was the pathway through which 1,2,3-TCP reduction initially occurred.

Results also support the findings of a previous investigation with ZVI to reduce 1,2,3-TCP, where 1,2-DCP was found to be a degradation byproduct and was further reduced to propene via reductive β-elimination (Focht, 1994). Total carbon mass balance after ~2.25 hrs with ZVZ (0.92) and Cu/Zn (0.91) indicated possible formation of other minor byproduct(s).

1,2-DCP degradation kinetics with ZVZ ($k_{obs} = 4.30 \times 10^{-2}$ hr$^{-1}$; $k_M = 1.38 \times 10^{-3}$ L g$^{-1}$ hr$^{-1}$) and Cu(0.5%)/Zn ($k_{obs} = 7.04 \times 10^{-2}$ hr$^{-1}$; $k_M = 2.25 \times 10^{-3}$ L g$^{-1}$ hr$^{-1}$) (Fig. 3.68) were similar to 1,2,3-TCP degradation kinetics described earlier with ZVZ and Cu(0.5%)/Zn. As such, the degradation kinetics of 1,2,3-TCP and 1,2-DCP are similar, despite the fewer number of chlorines on 1,2-DCP. Also, the degradation kinetics of the two chlorinated propanes indicate a similar enhancement in degradation kinetics with Cu(0.5%)/Zn, thus suggesting Cu/Zn caused minor enhancement in degradation kinetics of chlorinated propanes.
Although ZVZ reduction of 1,2-DCP has not been reported in literature, a comparison can be made to ZVI \( (k_{SA} = 2.24 \times 10^{-5} \text{ L m}^{-2} \text{ hr}^{-1}; \ k_M = 7.00 \times 10^{-6} \text{ L g}^{-1} \text{ hr}^{-1}; \) Onanong et al., 2007) using \( k_M \) obtained in this investigation. As this comparison indicates, 1,2-DCP kinetics are approximately 3 orders of magnitude greater with ZVZ and Cu/Zn than with ZVI, despite significantly greater surface area for ZVI (particle size <100 mesh) used (Onanong et al., 2007). Therefore, this investigation agrees well with the direct comparison of ZVZ and ZVI previously completed with 1,2,3-TCP (Sarathy et al., 2010), indicating increased degradation kinetics of chlorinated propanes with Zn-based reductants.

In summary, reduction of 1,2,3-TCP and 1,2-DCP by ZVZ and Cu/Zn produces completely dechlorinated byproducts by initial reductive \( \beta \)-elimination of the parent compound, unlike ZVI reduction of 1,2,3-TCP (Focht, 1994; Sarathy et al., 2010). The degradation kinetics reported previously for 1,2,3-TCP demonstrate increased degradation kinetics with ZVZ (Sarathy et al., 2010) while this investigation further demonstrated increased 1,2,3-TCP and 1,2-DCP kinetics using ZVZ and Cu/Zn. Therefore, Zn-based reductants are able to demonstrate enhancements in the degradation kinetics of chlorinated propanes and also favorably affect the yield of fully dechlorinated byproducts, in comparison to ZVI, and thus should be strongly considered for use in PRB field applications for sites contaminated with chlorinated propanes. Cu/Zn slightly enhanced chlorinated propane degradation kinetics compared to ZVZ and thus warrants further investigation into its capability for site clean-up.
Chapter 4

CONCLUSIONS

Direct transformation of CF to methane seems to be occurring with Zn reductants, as the rapid appearance of methane and the quantity of methane observed could not have been produced from DCM reduction given the slow degradation kinetics of DCM. Although Cu/Zn seemed to slightly inhibit direct transformation of CF to methane, significant amounts of methane were still produced. Pd/Zn acts to decrease the amount of CF reduction to methane via this direct pathway, thus leading to elevated amounts of DCM produced when compared to ZVZ; in comparison Ni/Zn may yield more intermediates, such as carbon monoxide, in the direct transformation pathway.

Reduction of CF was enhanced with Pd/Zn, Ni/Zn, and Cu/Zn when compared to ZVZ, but the most rapid degradation kinetics were observed with Cu/Zn. An investigation into Cu loading during CF and DCM reduction revealed 0.5 wt.% Cu on Zn to be optimum, with a significant decrease in kinetics observed with all other loadings investigated. Therefore, Cu/Zn provided the most enhanced kinetics and the most preferential yield of byproducts compared to Pd/Zn and Ni/Zn when a relatively low wt.% Cu on Zn surface was utilized.

Preliminary investigations with chlorinated methanes also indicated the importance of dissolving secondary metals in EtOH, rather than water, prior to deposition onto primary metal surface. This was clearly seen with Cu/Zn reduction of CF, where Cu
salt dissolution in water resulted in a drastic increase in DCM production compared to results with EtOH.

Byproducts generated by ZVZ and Cu/Zn reduction of 1,1,2,2-TeCA, 1,1,2-TCA, and 1,2-DCA were formed via reductive β-elimination, while reduction of 1,1,1-TCA resulted in the formation of ethane and 1,1-DCA. Byproduct distribution was similar in 1,1,2,2-TeCA reduction while a slightly higher yield of chlorinated byproduct (i.e., 1,1-DCA) was produced with Cu/Zn during 1,1,1-TCA reduction. This suggests that Cu/Zn does not dramatically change byproduct distribution during chlorinated ethane reduction. Previous results with ZVI indicate much higher 1,1-DCA production from 1,1,1-TCA reduction, indicating improved performance of Zn reductants in treating this contaminant.

Cu/Zn demonstrated significant enhancement in chlorinated ethane degradation kinetics in comparison to ZVZ, although the enhancement was never more than 1 order of magnitude. This suggests the need to further study Cu/Zn at the field scale for chlorinated ethane degradation, as reported $k_{SA}$ values for all chlorinated ethanes (Arnold et al., 1999; Song and Carraway, 2005) indicate faster kinetics with ZVZ compared to ZVI.

Reductive β-elimination of chlorinated ethenes is critically important, as reduction via this pathway produces highly reactive chlorinated acetylene intermediates that will not accumulate. All reported major byproducts observed in ZVI reduction of chlorinated ethenes are completely dechlorinated, with the exception of small amounts of TCE during PCE reduction (Arnold and Roberts, 2000). With ZVZ and Cu/Zn, relatively high amounts of chlorinated byproducts were produced during PCE and TCE reduction.
However, no chlorinated byproducts were detected during DCE and VC reduction, an important observation given the production of these byproducts during chlorinated ethane reduction.

Zn reductants appear to degrade chlorinated ethanes faster and yield more preferred byproducts than ZVI, but this same conclusion cannot be reached for chlorinated ethenes. Published degradation kinetics ($k_{SA}$) indicate increased PCE and TCE degradation kinetics using ZVZ (Johnson et al., 1996, Arnold and Roberts, 1998; Cheng and Wu, 2000), but enhanced cis-DCE, trans-DCE, and VC reduction kinetics are shown with ZVI (Johnson et al., 1996, Arnold and Roberts, 1998). The present investigation indicates faster degradation kinetics with Cu/Zn compared to ZVZ during reduction of all chlorinated ethenes investigated.

Byproduct distribution during chlorinated propane reduction by ZVZ and Cu/Zn indicated a reductive β-elimination $\rightarrow$ hydrogenolysis pathway, ultimately resulting in the production of completely dechlorinated byproduct. This is in contrast to ZVI, where initial reduction of 1,2,3-TCP forms 1,2-DCP (Focht, 1994), which was further revealed to degrade slowly. The advantage of Zn reductants in 1,2,3-TCP reduction is important given its status as an emerging contaminant (Sarathy et al., 2010). Cu/Zn was only slightly effective in increasing degradation kinetics of chlorinated propanes when compared to ZVZ, although it is clear that Zn reductants degrade 1,2,3-TCP and 1,2-DCP much faster than ZVI. Therefore, Cu/Zn does warrant further investigation in chlorinated propane degradation.
In conclusion, Cu/Zn increased degradation kinetics and did not dramatically change byproduct distribution during reduction of all compounds investigated when compared to ZVZ. Therefore, a column investigation comparing ZVZ with Cu/Zn is warranted for an improved assessment of its performance. Zn reductants seem to be best for degradation of chlorinated alkanes (methanes, ethanes, and propanes) while ZVI may be a superior reductant for the treatment of chlorinated ethenes, primarily due to a nearly complete yield of dechlorinated byproducts.
REFERENCES


Feng, J., Lim, T., 2005. Pathways and kinetics of carbon tetrachloride and chloroform reductions by nano-scale Fe and Fe/Ni particles: comparison with commercial micro-scale Fe and Zn. Chemosphere 59 (9), 1267-1277.


Haynes, W. M., 2012. CRC Handbook of Chemistry and Physics (93rd ed.). Boca Raton, FL: CRC.


3.1: CHLORINATED METHANES

3.1.1: Chloroform degradation by ZVZ

Figure 3.1: Chloroform degradation and degradation byproduct formation with ZVZ (3g ~20 mesh Zn Alfa Aesar) in 30 mM TAPSO buffer at pH 7. [CF]₀ = 0.311 µmoles (200 µL of 185 mg/L CF stock solution). (A) Degradation and byproducts; (B) Carbon mole fraction yield.
Figure 3.2: Chloroform degradation and degradation byproduct formation with ZVZ (3g 20-24 mesh Zn Alfa Aesar) in 30 mM TAPS buffer at pH 7. \([\text{CF}]_0 = 0.311 \, \mu\text{moles}\) (200 \(\mu\text{L}\) of 185 mg/L CF stock solution). (A) Degradation and byproducts; (B) Carbon mole fraction yield.
3.1.2: Chloroform degradation by Cu/Zn

**Figure 3.3:** Chloroform degradation and degradation byproduct formation with Cu/Zn (3g 20-24 mesh Zn Alfa Aesar; 0.5 wt. % Cu) in 30 mM TAPSO buffer at pH 7. \([\text{CF}]_0 = 0.311 \, \mu\text{moles} \) in 200 \(\mu\text{L} \) of 185 mg/L CF stock solution. (A) Degradation and byproducts; (B) Carbon mole fraction yield.
Figure 3.4: Carbon mole fraction yield with ZVZ and Cu/Zn (3g 20-24 mesh Zn Alfa Aesar; 0.05-1 wt. % Cu) in 30 mM TAPSO buffer at pH 7. \([\text{CF}]_0 = 0.311 \text{ mmoles} (200 \mu\text{L of 185 mg/L CF stock solution})\). (A) CuCl\(_2\) solution prepared in ethanol; (B) CuCl\(_2\) solution prepared in water.
Figure 3.5: Chloroform degradation kinetics (mass vs. time) with ZVZ and Cu/Zn (3g 20-24 mesh Zn Alfa Aesar; 0.1-1 wt. % Cu prepared in EtOH) in 30 mM TAPSO buffer at pH 7. \([\text{CF}]_0 = 0.311 \, \mu\text{moles}\) (200 μL of 185 mg/L CF stock solution).

Figure 3.6: Comparison of chloroform degradation kinetics \((k_{obs} \text{ values})\) when CuCl₂ prepared in EtOH and water with ZVZ and Cu/Zn (3g 20-24 mesh Zn Alfa Aesar; 0.05-1 wt. % Cu) in 30 mM TAPSO buffer at pH 7. \([\text{CF}]_0 = 0.311 \, \mu\text{moles}\) (200 μL of 185 mg/L CF stock solution).
3.1.3: Chloroform degradation by Pd/Zn and Ni/Zn

(A)

Figure 3.7: Chloroform degradation and degradation byproduct formation with Pd/Zn (3g ~20 mesh Zn Alfa Aesar; 0.06 wt. % Pd) in 30 mM TAPSO buffer at pH 7. [CF]₀ = 0.311 μmoles (200 μL of 185 mg/L CF stock solution). (A) Degradation and byproducts; (B) Carbon mole fraction yield.
Figure 3.8: Carbon mole fraction yield for ZVZ and Pd/Zn (3g ~20 mesh Zn Alfa Aesar; 0.02-0.1 wt. % Pd) in 30 mM TAPSO buffer at pH 7. \([\text{CF}]_0 = 0.311 \, \mu\text{moles} \) (200 \( \mu\text{L} \) of 185 mg/L CF stock solution).

Figure 3.9: Chloroform degradation kinetics (mass vs. time) with ZVZ and Pd/Zn (3g ~20 mesh Zn Alfa Aesar; 0.02-0.1 wt. % Pd) in 30 mM TAPSO buffer at pH 7. \([\text{CF}]_0 = 0.311 \, \mu\text{moles} \) (200 \( \mu\text{L} \) of 185 mg/L CF stock solution).
Figure 3.10: Chloroform degradation kinetics ($k_{obs}$ values) with ZVZ and Pd/Zn (3 g ~20 mesh Zn Alfa Aesar; 0.02-0.1 wt. % Pd) in 30 mM TAPSO buffer at pH 7. $[CF]_0 = 0.311 \mu$moles (200 $\mu$L of 185 mg/L CF stock solution).
Figure 3.11: Chloroform degradation and degradation byproduct formation with Ni/Zn (3g 20-24 mesh Zn Alfa Aesar; 0.75 wt. % Ni) in 30 mM TAPSO buffer at pH 7. \([CF]_0 = 0.311 \text{ \(\mu\) moles (200 \(\mu\)L of 185 mg/L CF stock solution}). (A) Degradation and byproducts; (B) Carbon mole fraction yield.
**Figure 3.12:** Carbon mole fraction yield with ZVZ and Ni/Zn (3g 20-24 mesh Zn Alfa Aesar; 0.1-1 wt. % Ni) in 30 mM TAPSO buffer at pH 7. \([CF]_0 = 0.311 \mu\text{moles} \) (200 \(\mu\text{L} \) of 185 mg/L CF stock solution).

**Figure 3.13:** Chloroform degradation kinetics (mass vs. time) with ZVZ and Ni/Zn (3g ~20 mesh Zn Alfa Aesar; 0.1-1 wt. % Ni) in 30 mM TAPSO buffer at pH 7. \([CF]_0 = 0.311 \mu\text{moles} \) (200 \(\mu\text{L} \) of 185 mg/L CF stock solution).
Figure 3.14: Chloroform degradation kinetics ($k_{obs}$ values) with ZVZ and Ni/Zn (3g 20-24 mesh Zn Alfa Aesar; 0.1-1 wt. % Ni) in 30 mM TAPSO buffer at pH 7. [CF]$_0$ = 0.311 µmoles (200 µL of 185 mg/L CF stock solution).
3.1.4: Dichloromethane degradation by ZVZ and Cu/Zn

Figure 3.15: Dichloromethane degradation and degradation byproduct formation with ZVZ (3g 20-24 mesh Zn Alfa Aesar) in 30 mM TAPSO at pH 7. \([\text{DCM}]_0 = 0.489 \text{ µmoles (250 µL of 166 mg/L DCM stock solution)}\). (A) Degradation and byproducts; (B) Carbon mole fraction yield.
Figure 3.16: Dichloromethane degradation and degradation byproduct formation with Cu/Zn (3g 20-24 mesh Zn Alfa Aesar; 0.5 wt. % Cu) in 30 mM TAPSO buffer at pH 7. $[\text{DCM}]_0 = 0.489 \mu\text{moles}$ (250 µL of 166 mg/L DCM stock solution). (A) Degradation and byproducts; (B) Carbon mole fraction yield.
Figure 3.17: Carbon mole fraction yield with ZVZ and Cu/Zn (3g 20-24 mesh Zn Alfa Aesar; 0.1-1 wt. % Cu) in 30 mM TAPSO buffer at pH 7. [DCM]₀ = 0.489 μmoles (250 μL of 166 mg/L DCM stock solution).

Figure 3.18: Dichloromethane degradation kinetics (mass vs. time) with ZVZ and Cu/Zn (3g 20-24 mesh Zn Alfa Aesar; 0.1-1 wt. % Cu) in 30 mM TAPSO buffer at pH 7. [DCM]₀ = 0.489 μmoles (250 μL of 166 mg/L DCM stock solution).
Figure 3.19: Dichloromethane degradation kinetics ($k_{\text{obs}}$ values) with ZVZ and Cu/Zn (3g 20-24 mesh Zn Alfa Aesar; 0.1-1 wt. % Cu) in 30 mM TAPSO buffer at pH 7. [DCM]$_0$ = 0.489 μmoles (250 μL of 166 mg/L DCM stock solution).
3.2: CHLORINATED ETHANES

3.2.1: 1,1,2,2-TeCA degradation by ZVZ and Cu/Zn

(A)

(B)

Figure 3.20: 1,1,2,2-TeCA degradation and degradation byproduct formation with ZVZ (3g 20-24 mesh Zn Alfa Aesar) in 30 mM TAPSO buffer at pH 7. \( [1,1,2,2-\text{TeCA}]_0 = 0.237 \mu\text{moles} \) (200 \( \mu\text{L} \) of 199 mg/L 1,1,2,2-TeCA stock solution). (A) Degradation and byproducts; (B) Carbon mole fraction yield.
Figure 3.21: 1,1,2,2-TeCA degradation and degradation byproduct formation with Cu/Zn (3g 20-24 mesh Zn Alfa Aesar; 0.5 wt. % Cu) in 30 mM TAPSO buffer at pH 7. \([1,1,2,2-\text{TeCA}]_0 = 0.237 \, \mu\text{moles} \) (200 \mu L of 199 mg/L 1,1,2,2-TeCA stock solution). (A) Degradation and byproducts; (B) Carbon mole fraction yield.
**Figure 3.22:** cis-DCE and trans-DCE production with variable initial mass of 1,1,2,2-TeCA. Degradation with Cu/Zn (3g 20-24 mesh Zn Alfa Aesar; 0.5 wt. % Cu) in 30 mM TAPSO buffer at pH 7. [High 1,1,2,2-TCA]₀ = 0.474 μmoles (400 μL of 199 mg/L 1,1,2,2-TeCA stock solution): [Low 1,1,2,2-TeCA]₀ = 0.237 μmoles (200 μL of 199 mg/L 1,1,2,2-TeCA stock solution).

\[
\begin{align*}
y_{ZVZ} &= 0.2493e^{-1.837x} \\
R^2 &= 0.9991 \\
y_{Cu/Zn} &= 0.2244e^{-3.104x} \\
R^2 &= 0.9997
\end{align*}
\]

**Figure 3.23:** 1,1,2,2-TeCA degradation kinetics with ZVZ and Cu/Zn (3g 20-24 mesh Zn Alfa Aesar; 0.5 wt. % Cu) in 30 mM TAPSO buffer at pH 7. [1,1,2,2-TeCA]₀ = 0.237 μmoles (200 μL 199 mg/L 1,1,2,2-TeCA stock solution).
3.2.2: 1,1,2-TCA degradation by ZVZ and Cu/Zn

(A)

Figure 3.24: 1,1,2-TCA degradation and degradation byproduct formation with ZVZ (3g 20-24 mesh Zn Alfa Aesar) in 30 mM TAPSO at pH 7. $[1,1,2\text{-TCA}]_0 = 0.269 \mu$moles (200 µL of 179 mg/L 1,1,2-TCA stock solution). (A) Degradation and byproducts; (B) Carbon mole fraction yield.
Figure 3.25: 1,1,2-TCA degradation and degradation byproduct formation with Cu/Zn (3g 20-24 mesh Zn Alfa Aesar; 0.5 wt. % Cu) in 30 mM TAPSO buffer at pH 7. \([1,1,2\text{-TCA}]_0 = 0.269 \, \mu\text{moles (200 } \mu\text{L of 179 mg/L 1,1,2-TCA stock solution).} \) (A) Degradation and byproducts; (B) Carbon mole fraction yield.
Figure 3.26: Vinyl chloride production with variable initial mass of 1,1,2-TCA. Degradation with Cu/Zn (3g 20-24 mesh Zn Alfa Aesar; 0.5 wt. % Cu) in 30 mM TAPSO buffer at pH 7. \([\text{High } 1,1,2\text{-TCA}]_0 = 0.538 \mu\text{moles} \) (400 μL of 179 mg/L 1,1,2-TCA stock solution): \([\text{Low } 1,1,2\text{-TCA}]_0 = 0.269 \mu\text{moles} \) (200 μL of 179 mg/L 1,1,2-TCA stock solution).

Figure 3.27: 1,1,2-TCA degradation kinetics with ZVZ and Cu/Zn (3g 20-24 mesh Zn Alfa Aesar; 0.5 wt. % Cu) in 30 mM TAPSO buffer at pH 7. \([1,1,2\text{-TCA}]_0 = 0.269 \mu\text{moles} \) (200 μL of 179 mg/L 1,1,2-TCA stock solution).
3.2.3: 1,1,1-TCA degradation by ZVZ and Cu/Zn

(A)

Figure 3.28: 1,1,1-TCA degradation and degradation byproduct formation with ZVZ (3g 20-24 mesh Zn Alfa Aesar) in 30 mM TAPSO buffer at pH 7. \([1,1,1\text{-TCA}]_0 = 0.247 \, \mu\text{moles}\) (200 μL of 165 mg/L 1,1,2-TCA stock solution). (A) Degradation and byproducts; (B) Carbon mole fraction yield.
Figure 3.29: 1,1,1-TCA degradation and degradation byproduct formation with Cu/Zn (3g 20-24 mesh Zn Alfa Aesar; 0.5 wt. % Cu) in 30 mM TAPSO buffer at pH 7. \([1,1,1\text{-TCA}]_0 = 0.247 \text{ µ} \text{moles}\) (200 µL of 165 mg/L 1,1,2-TCA stock solution). (A) Degradation and byproducts; (B) Carbon mole fraction yield.
Figure 3.30: 1,1,1-TCA degradation and degradation byproduct formation with Cu/Zn (3g 20-24 mesh Zn Alfa Aesar; 0.62 wt.% Cu) in 30 mM TAPSO buffer at pH 7. $[1,1,1\text{-TCA}]_0 = 0.247 \ \mu\text{moles}$ (200 μL of 165 mg/L 1,1,2-TCA stock solution). (A) Degradation and byproducts; (B) Carbon mole fraction yield.
Figure 3.31: 1,1,1-TCA degradation and degradation byproduct formation with Cu/Zn (3g 20-24 mesh Zn Alfa Aesar; 0.75 wt. % Cu) in 30 mM TAPSO buffer at pH 7. \([1,1,1\text{-TCA}]_0 = 0.247 \, \mu\text{moles} \) (200 \(\mu\text{L} \) of 165 mg/L 1,1,2-TCA stock solution). (A) Degradation and byproducts; (B) Carbon mole fraction yield.
Figure 3.32: 1,1,1-TCA degradation mole fraction yield at approximately 2 hours with ZVZ and Cu/Zn (3g 20-24 mesh Zn Alfa Aesar; 0.5, 0.62, and 0.75 wt. % Cu) in 30 mM TAPSO buffer at pH 7. [1,1,1-TCA]₀ = 0.247 µmoles (200 µL of 165 mg/L 1,1,1-TCA stock solution).

Figure 3.33: Ethane and 1,1-DCA production with variable initial mass of 1,1,1-TCA. Degradation with Cu/Zn (3g 20-24 mesh Zn Alfa Aesar; 0.5 wt. % Cu) in 30 mM TAPSO buffer at pH 7. [High 1,1,1-TCA]₀ = 0.495 µmoles (400 µL of 165 mg/L 1,1,1-TCA stock solution): [Low 1,1,1-TCA]₀ = 0.247 µmoles (200 µL of 165 mg/L 1,1,1-TCA stock solution).
Figure 3.34: 1,1,1-TCA degradation kinetics with ZVZ and Cu/Zn (3g 20-24 mesh Zn Alfa Aesar; 0.5, 0.62, and 0.75 wt. % Cu) in 30 mM TAPSO buffer at pH 7. \([1,1,1\text{-TCA} ]_0 = 0.247 \mu \text{moles (200 } \mu \text{L of 165 mg/L 1,1,1-TCA stock solution).} \)

\[
y_{\text{ZVZ}} = 0.2527e^{-2.156x} \\
R^2 = 0.9978 \\
y_{\text{Cu(0.5\%)}/Zn} = 0.2658e^{-4.891x} \\
R^2 = 0.9983
\]
3.2.4: 1,2-DCA degradation by ZVZ and Cu/Zn

Figure 3.35: 1,2-DCA degradation and degradation byproduct formation with ZVZ (3g 20-24 mesh Zn Alfa Aesar) in 30 mM TAPSO buffer at pH 7. [1,2-DCA]₀ = 0.396 μmoles (250 μL of 157 mg/L 1,2-DCA stock solution). (A) Degradation and byproducts; (B) Carbon mole fraction yield.
Figure 3.36: 1,2-DCA degradation and degradation byproduct formation with Cu/Zn (3g 20-24 mesh Zn Alfa Aesar; 0.5 wt. % Cu) in 30 mM TAPSO buffer at pH 7. [1,2-DCA]₀ = 0.396 μmoles (250 μL of 157 mg/L 1,2-DCA stock solution). (A) Degradation and byproducts; (B) Carbon mole fraction yield.
Figure 3.37: Ethene production with variable initial mass of 1,2-DCA. Degradation with Cu/Zn (3g 20-24 mesh Zn Alfa Aesar; 0.5 wt. % Cu) in 30 mM TAPSO buffer at pH 7. [High 1,2-DCA]₀ = 0.791 μmoles (500 μL of 157 mg/L 1,2-DCA stock solution): [Low 1,2-DCA]₀ = 0.396 μmoles (250 μL of 157 mg/L 1,2-DCA stock solution).

Figure 3.38: 1,2-DCA degradation kinetics with ZVZ and Cu/Zn (3g 20-24 mesh Zn Alfa Aesar, 0.5, wt. % Cu) in 30 mM TAPSO buffer at pH 7. [1,2-DCA]₀ = 0.396 μmoles (250 μL of 157 mg/L 1,2-DCA stock solution).
3.3: CHLORINATED ETHENES

3.3.1: PCE degradation by ZVZ and Cu/Zn (A)

Figure 3.39: PCE degradation and degradation byproduct formation with ZVZ (3g 20-24 mesh Zn Alfa Aesar) in 30 mM TAPS buffer at pH 7. [PCE]₀ = 0.306 μmoles (250 μL of 203 mg/L PCE stock solution). (A) Degradation and byproducts; (B) Carbon mole fraction yield.
Figure 3.40: PCE degradation and degradation byproduct formation with Cu/Zn (3g 20-24 mesh Zn Alfa Aesar; 0.5 wt. % Cu) in 30 mM TAPSO buffer at pH 7. \([PCE]_0 = 0.306 \mu\text{moles (250 µL of 203 mg/L PCE stock solution)}\). (A) Degradation and byproducts; (B) Carbon mole fraction yield.
**Figure 3.41:** PCE degradation kinetics with ZVZ and Cu/Zn (3g 20-24 mesh Zn Alfa Aesar; 0.5 wt. % Cu) in 30 mM TAPSO buffer at pH 7. \([\text{PCE}]_0 = 0.306 \, \mu\text{moles} \) (250 μL of 203 mg/L PCE stock solution).
3.3.2: TCE degradation by ZVZ and Cu/Zn

Figure 3.42: TCE degradation and degradation byproduct formation with ZVZ (3g 20-24 mesh Zn Alfa Aesar) in 30 mM TAPSO buffer at pH 7. \([\text{TCE}]_0 = 0.347 \, \mu\text{moles} (250 \, \mu\text{L of 183 mg/L TCE stock solution})\). (A) Degradation and byproducts; (B) Carbon mole fraction yield.
Figure 3.43: TCE degradation and degradation byproduct formation with Cu/Zn (3g 20-24 mesh Zn Alfa Aesar; 0.5 wt. % Cu) in 30 mM TAPSO buffer at pH 7. [TCE]₀ = 0.347 μmoles (250 μL of 183 mg/L TCE stock solution). (A) Degradation and byproducts; (B) Carbon mole fraction yield.
Figure 3.44: TCE degradation kinetics with ZVZ and Cu/Zn (3g 20-24 mesh Zn Alfa Aesar; 0.5 wt. % Cu) in 30 mM TAPSO buffer at pH 7. \([\text{TCE}]_0 = 0.347 \ \text{µmoles} \) (250 µL of 183 mg/L TCE stock solution).
3.3.3: *cis*-DCE degradation by ZVZ and Cu/Zn

![Graph A](image1.png)

![Graph B](image2.png)

**Figure 3.45:** *cis*-DCE degradation and degradation byproduct formation with Cu/Zn (3g 20-24 mesh Zn Alfa Aesar; 0.5 wt. % Cu) in 30 mM TAPSO buffer at pH 7. *[cis-DCE]₀ = 0.413 µmoles (250 µL of 160 mg/L *cis*-DCE stock solution). (A) Degradation and byproducts; (B) Carbon mole fraction yield.
Figure 3.46: cis-DCE degradation kinetics with ZVZ and Cu/Zn (3g 20-24 mesh Zn Alfa Aesar; 0.5 wt. % Cu) in 30 mM TAPSO buffer at pH 7. \([\text{cis-DCE}]_0 = 0.413 \, \mu\text{moles} \) (250 \(\mu\text{L}\) of 160 mg/L cis-DCE stock solution).
3.3.4: *trans*-DCE degradation by ZVZ and Cu/Zn

Figure 3.47: *trans*-DCE degradation and degradation byproduct formation with Cu/Zn (3g 20-24 mesh Zn Alfa Aesar; 0.5 wt. % Cu) in 30 mM TAPSO buffer at pH 7. \( [trans\text{-DCE}]_0 = 0.406 \, \mu\text{moles} \) (250 μL of 158 mg/L *trans*-DCE stock solution). (A) Degradation and byproducts; (B) Carbon mole fraction yield.
Figure 3.48: Ethene production with variable initial mass of trans-DCE. Degradation with Cu/Zn (3g 20-24 mesh Zn Alfa Aesar; 0.5 wt. % Cu) in 30 mM TAPSO buffer at pH 7. [High trans-DCE]₀ = 0.812 μmoles (500 μL of 158 mg/L trans-DCE stock solution): [Low trans-DCE]₀ = 0.406 μmoles (250 μL of 158 mg/L trans-DCE stock solution).

Figure 3.49: trans-DCE degradation kinetics with ZVZ and Cu/Zn (3g 20-24 mesh Zn Alfa Aesar; 0.5 wt. % Cu) in 30 mM TAPSO buffer at pH 7. [trans-DCE]₀ = 0.406 μmoles (250 μL of 158 mg/L trans-DCE stock solution).
3.3.5: Vinyl Chloride degradation by ZVZ and Cu/Zn

Figure 3.50: Vinyl chloride degradation and degradation byproduct formation with ZVZ (3g 20-24 mesh Zn Alfa Aesar) in 30 mM TAPSO buffer at pH 7. \([\text{VC}]_0 = 0.206 \, \mu\text{moles (5 mL of 1,000 ppm VC). (A) Degradation and byproducts; (B) Carbon mole fraction yield.}

(A) 

(B) 

Figure 3.50: Vinyl chloride degradation and degradation byproduct formation with ZVZ (3g 20-24 mesh Zn Alfa Aesar) in 30 mM TAPSO buffer at pH 7. \([\text{VC}]_0 = 0.206 \, \mu\text{moles (5 mL of 1,000 ppm VC). (A) Degradation and byproducts; (B) Carbon mole fraction yield.}
Figure 3.51: Vinyl chloride degradation and degradation byproduct formation with Cu/Zn (3g 20-24 mesh Zn Alfa Aesar; 0.5 wt. % Cu) in 30 mM TAPSO buffer at pH 7. \([\text{VC}]_0 = 0.206 \, \mu\text{moles (5 mL of 1,000 ppm VC)}\). (A) Degradation and byproducts; (B) Carbon mole fraction yield.
Figure 3.52: Vinyl chloride degradation kinetics with ZVZ and Cu/Zn (3g 20-24 mesh Zn Alfa Aesar; 0.5, wt. % Cu) in 30 mM TAPSO buffer at pH 7. $[VC]_0 = 0.206 \, \mu$moles (5 mL of 1,000 ppm VC).

\[
y_{ZVZ} = 2.12E-01e-1.86E-04x \\
R^2 = 9.81E-01
\]

\[
y_{Cu/Zn} = 1.96E-01e-6.96E-04x \\
R^2 = 9.71E-01
\]
3.4: CHLORINATED PROPANES

3.4.1: 1,2,3-TCP degradation by ZVZ and Cu/Zn

(A)

Figure 3.53: 1,2,3-TCP degradation and degradation byproduct formation with ZVZ (3g 20-24 mesh Zn Alfa Aesar) in 30 mM TAPSO buffer at pH 7. \([1,2,3\text{-TCP}]_0 = 0.235 \mu\text{moles} \) (200 \(\mu\text{L} \) of 173 mg/L 1,2,3-TCP stock solution). (A) Degradation and byproducts; (B) Carbon mole fraction yield.
Figure 3.54: 1,2,3-TCP degradation and degradation byproduct formation with Cu/Zn (3g 20-24 mesh Zn Alfa Aesar; 0.5 wt. % Cu) in 30 mM TAPSO buffer at pH 7. \([1,2,3\text{-TCP}]_0 = 0.235 \, \mu\text{moles} \) (200 μL of 173 mg/L 1,2,3-TCP stock solution). (A) Degradation and byproducts; (B) Carbon mole fraction yield.
Figure 3.55: 1,2,3-TCP degradation and degradation byproduct formation with Cu/Zn (6g 20-24 mesh Zn Alfa Aesar; 0.5 wt. % Cu) in 30 mM TAPSO buffer at pH 7. \([1,2,3-TCP]_0 = 0.235 \mu\text{moles} (200 \mu\text{L of 173 mg/L 1,2,3-TCP stock solution})\). (A) Degradation and byproducts; (B) Carbon mole fraction yield.
Figure 3.56: 1,2,3-TCP degradation and degradation byproduct formation with Cu/Zn (9g 20-24 mesh Zn Alfa Aesar; 0.5 wt. % Cu) in 30 mM TAPSO buffer at pH 7. [1,2,3-TCP]₀ = 0.235 μmoles (200 μL of 173 mg/L 1,2,3-TCP stock solution). (A) Degradation and byproducts; (B) Carbon mole fraction yield.
Figure 3.57: 1,2,3-TCP degradation and degradation byproduct formation with Cu/Zn (12g 20-24 mesh Zn Alfa Aesar; 0.5 wt. % Cu) in 30 mM TAPSO buffer at pH 7. \([1,2,3\text{-TCP}]_0 = 0.235 \, \mu\text{moles} \) (200 \, \mu\text{L} of 173 mg/L 1,2,3-TCP stock solution). (A) Degradation and byproducts; (B) Carbon mole fraction yield.
Figure 3.58: 1,2,3-TCP degradation in reactors with variable initial mass of Zn (20-24 mesh Alfa Aesar) in Cu(0.5 wt. %)/Zn system. Cu/Zn particles in 30 mM TAPS0 buffer at pH 7. \([1,2,3\text{-TCP}]_0 = 0.235 \mu\text{moles}\) (200 μL of 173 mg/L 1,2,3-TCP stock solution).

Figure 3.59: Propene formation from 1,2,3-TCP degradation in reactors with variable initial mass of Zn (20-24 mesh Alfa Aesar) in Cu(0.5 %)/Zn system. Cu/Zn particles in 30 mM TAPS0 buffer at pH 7. \([1,2,3\text{-TCP}]_0 = 0.235 \mu\text{moles}\) (200 μL of 173 mg/L 1,2,3-TCP stock solution).
Figure 3.60: Propene production with variable initial mass of 1,2,3-TCP. Degradation with Cu/Zn (3g 20-24 mesh Zn Alfa Aesar; 0.5 wt. % Cu) in 30 mM TAPSO buffer at pH 7. [High 1,2,3-TCP]₀ = 0.470 µmoles (400 µL of 173 mg/L 1,2,3-TCP stock solution): [Low 1,2,3-TCP]₀ = 0.235 µmoles (200 µL of 173 mg/L 1,2,3-TCP stock solution).

Figure 3.61: Hydrogen production after 5 days in ZVZ and Cu(0.5%)/Zn systems with variable initial mass of Zn (20-24 mesh Alfa Aesar) in 30 mM TAPSO buffer at pH 7. [1,2,3-TCP]₀ = 0.235 µmoles (200 µL of 173 mg/L 1,2,3-TCP stock solution).
Figure 3.62: pH values after 5 days in ZVZ and Cu(0.5%)/Zn systems with variable initial mass of Zn (20-24 mesh Alfa Aesar) in 30 mM TAPSO buffer at pH 7. \([1,2,3\text{-TCP}]_0 = 0.235 \mu\text{moles (200 } \mu\text{L of 173 mg/L 1,2,3-TCP stock solution)}\).

Figure 3.63: 1,2,3-TCP degradation kinetics (mass vs. time) with ZVZ and Cu(0.5%)/Zn systems with variable initial mass of Zn (20-24 mesh Alfa Aesar) in 30 mM TAPSO buffer at pH 7. \([1,2,3\text{-TCP}]_0 = 0.235 \mu\text{moles (200 } \mu\text{L of 173 mg/L 1,2,3-TCP stock solution)}\).
Figure 3.64: 1,2,3-TCP degradation kinetics ($k_{\text{obs}}$ values) with ZVZ and Cu(0.5%)/Zn systems with variable initial mass of Zn (20-24 mesh Alfa Aesar) in 30 mM TAPSO buffer at pH 7. $[1,2,3\text{-TCP}]_0 = 0.235 \, \mu\text{moles}$ (200 $\mu$L of 173 mg/L 1,2,3-TCP stock solution).
3.4.2: 1,2-DCP degradation by ZVZ and Cu/Zn

Figure 3.65: 1,2-DCP degradation and degradation byproduct formation with ZVZ (3g 20-24 mesh Zn Alfa Aesar) in 30 mM TAPSO buffer at pH 7. [1,2-DCP]₀ = 0.320 μmoles (250 μL of 145 mg/L 1,2-DCP stock solution). (A) Degradation and byproducts; (B) Carbon mole fraction yield.
Figure 3.66: 1,2-DCP degradation and degradation byproduct formation with Cu/Zn (3g 20-24 mesh Zn Alfa Aesar; 0.5 wt. % Cu) in 30 mM TAPSO buffer at pH 7. \([1,2-\text{DCP}]_0 = 0.320 \text{ µmoles} \) (250 µL of 145 mg/L 1,2-DCP stock solution). (A) Degradation and byproducts; (B) Carbon mole fraction yield.
**Figure 3.67:** Propene production with variable initial mass of 1,2-DCP. Degradation with Cu/Zn (3g 20-24 mesh Zn Alfa Aesar; 0.5 wt. % Cu) in 30 mM TAPSO buffer at pH 7. [High 1,2-DCP]₀ = 0.639 µmoles (500 µL of 145 mg/L 1,2-DCP stock solution): [Low 1,2-DCP]₀ = 0.320 µmoles (250 µL of 145 mg/L 1,2-DCP stock solution).

**Figure 3.68:** 1,2-DCP degradation kinetics with ZVZ and Cu/Zn (3g 20-24 mesh Zn Alfa Aesar; 0.5 wt. % Cu) in 30 mM TAPSO buffer at pH 7. [1,2-DCP]₀ = 0.320 µmoles (250 µL of 145 mg/L 1,2-DCP stock solution).
Table 3.1: Chloroform degradation with ZVZ and Cu/Zn (3g 20-24 mesh Zn Alfa Aesar; 0.05-1 wt. % Cu prepared in EtOH) in 30 mM TAPSO at pH 7. \([\text{CF}]_0 = 0.311 \ \mu\text{moles}\) (200 \(\mu\text{L}\) of 185 mg/L CF stock solution).

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<th>CF (k_M) (L g(^{-1}) hr(^{-1}))</th>
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<th>(R^2)</th>
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Table 3.2: Chloroform degradation kinetics with ZVZ and Pd/Zn (3g ~20 mesh Zn Alfa Aesar; 0.02-0.1 wt. % Pd) in 30 mM TAPSO buffer at pH 7. \([\text{CF}]_0 = 0.311 \ \mu\text{moles}\) (200 \(\mu\text{L}\) of 185 mg/L CF stock solution).

<table>
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<tr>
<th>Pd Loading (wt. %)</th>
<th>CF (k_{\text{obs}}) (hr(^{-1}))</th>
<th>CF (k_M) (L g(^{-1}) hr(^{-1}))</th>
<th>Exponential Regression [CF](0)</th>
<th>(R^2)</th>
</tr>
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<td>0.977</td>
<td>3.13(\times)10(^{-2})</td>
<td>0.361</td>
<td>0.9964</td>
</tr>
<tr>
<td>0.02</td>
<td>1.03</td>
<td>3.30(\times)10(^{-2})</td>
<td>0.383</td>
<td>0.9990</td>
</tr>
<tr>
<td>0.04</td>
<td>1.39</td>
<td>4.45(\times)10(^{-2})</td>
<td>0.397</td>
<td>0.9990</td>
</tr>
<tr>
<td>0.06</td>
<td>1.86</td>
<td>5.95(\times)10(^{-2})</td>
<td>0.378</td>
<td>0.9990</td>
</tr>
<tr>
<td>0.1</td>
<td>1.44</td>
<td>4.61(\times)10(^{-2})</td>
<td>0.355</td>
<td>0.9930</td>
</tr>
</tbody>
</table>
Table 3.3: Chloroform degradation kinetics with ZVZ and Ni/Zn (3g 20-24 mesh Zn Alfa Aesar, 0.1-1 wt. % Ni) in 30 mM TAPSO buffer at pH 7. \([\text{CF}]_0 = 0.311 \, \mu\text{moles} \) (200 \(\mu\text{L}\) of 185 mg/L CF stock solution).

<table>
<thead>
<tr>
<th>Ni Loading (wt. %)</th>
<th>CF ( k_{\text{obs}} ) (hr(^{-1}))</th>
<th>CF ( k_M ) (L g(^{-1}) hr(^{-1}))</th>
<th>Exponential Regression ([\text{CF}]_0)</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.696</td>
<td>2.23E-02</td>
<td>0.316</td>
<td>0.9974</td>
</tr>
<tr>
<td>0.1</td>
<td>0.943</td>
<td>3.02E-02</td>
<td>0.327</td>
<td>0.9773</td>
</tr>
<tr>
<td>0.3</td>
<td>1.17</td>
<td>3.74E-02</td>
<td>0.322</td>
<td>0.9946</td>
</tr>
<tr>
<td>0.5</td>
<td>1.21</td>
<td>3.87E-02</td>
<td>0.328</td>
<td>0.9728</td>
</tr>
<tr>
<td>0.75</td>
<td>1.55</td>
<td>4.96E-02</td>
<td>0.346</td>
<td>0.9899</td>
</tr>
<tr>
<td>1</td>
<td>1.23</td>
<td>3.94E-02</td>
<td>0.336</td>
<td>0.9945</td>
</tr>
</tbody>
</table>

Table 3.4: Dichloromethane degradation with ZVZ and Cu/Zn (3g 20-24 mesh Zn Alfa Aesar; 0.1-1 wt. % Cu) in 30 mM TAPSO buffer at pH 7. \([\text{DCM}]_0 = 0.489 \, \mu\text{moles} \) (250 \(\mu\text{L}\) of 166 mg/L stock solution).

<table>
<thead>
<tr>
<th>Cu Loading (wt. %)</th>
<th>DCM ( k_{\text{obs}} ) (hr(^{-1}))</th>
<th>DCM ( k_M ) (L g(^{-1}) hr(^{-1}))</th>
<th>Exponential Regression ([\text{DCM}]_0)</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0645</td>
<td>2.06E-03</td>
<td>0.5829</td>
<td>0.9622</td>
</tr>
<tr>
<td>0.1</td>
<td>0.0616</td>
<td>1.97E-03</td>
<td>0.5691</td>
<td>0.9992</td>
</tr>
<tr>
<td>0.3</td>
<td>0.0862</td>
<td>2.76E-03</td>
<td>0.5761</td>
<td>0.9926</td>
</tr>
<tr>
<td>0.5</td>
<td>0.161</td>
<td>5.15E-03</td>
<td>0.5664</td>
<td>0.9932</td>
</tr>
<tr>
<td>0.75</td>
<td>0.0914</td>
<td>2.92E-03</td>
<td>0.5508</td>
<td>0.9876</td>
</tr>
<tr>
<td>1</td>
<td>0.0748</td>
<td>2.39E-03</td>
<td>0.5527</td>
<td>0.9974</td>
</tr>
</tbody>
</table>
Table 3.5: 1,1,1-TCA degradation kinetics with ZVZ and Cu/Zn (3g 20-24 mesh Zn Alfa Aesar; 0.5, 0.62, and 0.75 wt. % Cu) in 30 mM TAPSO buffer at pH 7. \([1,1,1\text{-TCA}]_0 = 0.247 \text{ μmoles (200 μL of 165 mg/L 1,1,1-TCA stock solution)}.

<table>
<thead>
<tr>
<th>Cu Loading (wt. %)</th>
<th>1,1,1-TCA (k_{\text{obs}}) (hr(^{-1}))</th>
<th>1,1,1-TCA (k_{\text{M}}) (L g(^{-1}) hr(^{-1}))</th>
<th>Exponential Regression ([1,1,1\text{-TCA}]_0)</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.16</td>
<td>6.91E-02</td>
<td>0.253</td>
<td>0.9978</td>
</tr>
<tr>
<td>0.5</td>
<td>4.89</td>
<td>1.56E-01</td>
<td>0.266</td>
<td>0.9983</td>
</tr>
<tr>
<td>0.62</td>
<td>3.80</td>
<td>1.22E-01</td>
<td>0.218</td>
<td>0.9998</td>
</tr>
<tr>
<td>0.75</td>
<td>4.42</td>
<td>1.41E-01</td>
<td>0.237</td>
<td>0.9996</td>
</tr>
</tbody>
</table>

Table 3.6: 1,2,3-TCP degradation with ZVZ and Cu(0.5%)/Zn systems with variable initial mass of Zn (20-24 mesh Alfa Aesar) in 30 mM TAPSO buffer at pH 7. \([1,2,3\text{-TCP}]_0 = 0.235 \text{ μmoles (200 μL of 173 mg/L 1,2,3-TCP stock solution)}.

<table>
<thead>
<tr>
<th>Reductant</th>
<th>1,2,3-TCP (k_{\text{obs}}) (hr(^{-1}))</th>
<th>1,2,3-TCP (k_{\text{M}}) (L g(^{-1}) hr(^{-1}))</th>
<th>Exponential Regression ([1,2,3\text{-TCP}]_0)</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZVZ(3g)</td>
<td>5.32E-02</td>
<td>1.70E-03</td>
<td>0.246</td>
<td>0.9999</td>
</tr>
<tr>
<td>Cu/Zn(3g)</td>
<td>7.09E-02</td>
<td>2.27E-03</td>
<td>0.241</td>
<td>0.9856</td>
</tr>
<tr>
<td>Cu/Zn(6g)</td>
<td>9.24E-02</td>
<td>1.48E-03</td>
<td>0.235</td>
<td>0.9999</td>
</tr>
<tr>
<td>Cu/Zn(9g)</td>
<td>1.10E-01</td>
<td>1.17E-03</td>
<td>0.233</td>
<td>0.9815</td>
</tr>
<tr>
<td>Cu/Zn(12g)</td>
<td>1.28E-01</td>
<td>1.02E-03</td>
<td>0.229</td>
<td>0.9871</td>
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</tbody>
</table>
Table 3.7: CHC Degradation Byproducts and Pathways with ZVZ and Cu(0.5%)/Zn

<table>
<thead>
<tr>
<th>Parent</th>
<th>Products</th>
<th>Reaction Pathway</th>
<th>Experimental Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF</td>
<td>DCM</td>
<td>hydrogenolysis</td>
<td>30 mM TAPSO (pH 7)</td>
</tr>
<tr>
<td></td>
<td>methane</td>
<td>Sequential hydrogenolysis or direct reduction</td>
<td></td>
</tr>
<tr>
<td>DCM</td>
<td>methane</td>
<td>hydrogenolysis</td>
<td>30 mM TAPSO (pH 7)</td>
</tr>
<tr>
<td>1,1,2,2-TeCA</td>
<td>cis-DCE</td>
<td>reductive β-elimination</td>
<td>30 mM TAPSO (pH 7)</td>
</tr>
<tr>
<td></td>
<td>trans-DCE</td>
<td>reductive β-elimination</td>
<td></td>
</tr>
<tr>
<td>1,1,2-TCA</td>
<td>VC</td>
<td>reductive β-elimination</td>
<td>30 mM TAPSO (pH 7)</td>
</tr>
<tr>
<td>1,1,1-TCA</td>
<td>ethane</td>
<td>reductive α-elimination</td>
<td>30 mM TAPSO (pH 7)</td>
</tr>
<tr>
<td></td>
<td>1,1-DCA</td>
<td>hydrogenolysis</td>
<td></td>
</tr>
<tr>
<td>1,2-DCA</td>
<td>ethene</td>
<td>reductive β-elimination</td>
<td>30 mM TAPSO (pH 7)</td>
</tr>
<tr>
<td>PCE</td>
<td>TCE</td>
<td>hydrogenolysis</td>
<td>30 mM TAPSO (pH 7)</td>
</tr>
<tr>
<td></td>
<td>trans-DCE</td>
<td>reactive intermediate</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ethene</td>
<td>reactive intermediate</td>
<td></td>
</tr>
<tr>
<td>TCE</td>
<td>cis-DCE</td>
<td>hydrogenolysis</td>
<td>30 mM TAPSO (pH 7)</td>
</tr>
<tr>
<td></td>
<td>trans-DCE</td>
<td>hydrogenolysis</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ethene</td>
<td>reactive intermediate</td>
<td></td>
</tr>
<tr>
<td>cis-DCE</td>
<td>ethene</td>
<td>reactive intermediate</td>
<td>30 mM TAPSO (pH 7)</td>
</tr>
<tr>
<td>trans-DCE</td>
<td>ethene</td>
<td>reactive intermediate</td>
<td>30 mM TAPSO (pH 7)</td>
</tr>
<tr>
<td>VC</td>
<td>ethene</td>
<td>hydrogenolysis</td>
<td>30 mM TAPSO (pH 7)</td>
</tr>
<tr>
<td>1,2,3-TCP</td>
<td>propene</td>
<td>reductive β-elimination → hydrogenolysis</td>
<td>30 mM TAPSO (pH 7)</td>
</tr>
<tr>
<td>1,2-DCP</td>
<td>propene</td>
<td>reductive β-elimination</td>
<td>30 mM TAPSO (pH 7)</td>
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### Table 3.8: Literature CHC Degradation Byproducts and Pathways with ZVZ

<table>
<thead>
<tr>
<th>Parent</th>
<th>Products</th>
<th>Reaction Pathway</th>
<th>Experimental Conditions</th>
<th>Source</th>
</tr>
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<tbody>
<tr>
<td>CF</td>
<td>DCM methane</td>
<td>hydrogenolysis</td>
<td>DO/DI</td>
<td>Feng and Lim, 2005</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sequential hydrogenolysis</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>or direct reduction</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DCM</td>
<td>methane</td>
<td>hydrogenolysis</td>
<td>DO/DI</td>
<td>Boronina et al., 1998</td>
</tr>
<tr>
<td>1,1,2,2-TeCA</td>
<td>cis-DCE</td>
<td>reductive β-elimination</td>
<td>0.1 M NaCl, 50 mM Tris (pH 7.2)</td>
<td>Arnold et al., 1999</td>
</tr>
<tr>
<td></td>
<td>trans-DCE</td>
<td>reductive β-elimination</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,1,2-TCA</td>
<td>VC</td>
<td>reductive β-elimination</td>
<td>0.1 M NaCl, 50 mM Tris (pH 7.2)</td>
<td>Arnold et al., 1999</td>
</tr>
<tr>
<td>1,1,1-TCA</td>
<td>ethane</td>
<td>reductive α-elimination</td>
<td>0.1 M NaCl, 50 mM Tris (pH 7.2)</td>
<td>Arnold et al., 1999</td>
</tr>
<tr>
<td></td>
<td>1,1-DCA</td>
<td>hydrogenolysis</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,2-DCA</td>
<td>ethene</td>
<td>reductive β-elimination</td>
<td>0.1 M NaCl, 50 mM Tris (pH 7.2)</td>
<td>Arnold et al., 1999</td>
</tr>
<tr>
<td>PCE</td>
<td>TCE</td>
<td>hydrogenolysis</td>
<td>0.1 M NaCl, 50 mM Tris (pH 7.2)</td>
<td>Arnold and Roberts, 1998</td>
</tr>
<tr>
<td></td>
<td>trans-DCE</td>
<td>reactive intermediate</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>acetylene</td>
<td>reactive intermediate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TCE</td>
<td>trans-DCE</td>
<td>hydrogenolysis</td>
<td>0.1 M NaCl, 50 mM Tris (pH 7.2)</td>
<td>Arnold and Roberts, 1998</td>
</tr>
<tr>
<td></td>
<td>cis-DCE</td>
<td>hydrogenolysis</td>
<td></td>
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<td></td>
<td>acetylene</td>
<td>reactive intermediate</td>
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<tr>
<td>cis-DCE</td>
<td>VC</td>
<td>hydrogenolysis</td>
<td>0.1 M NaCl, 50 mM Tris (pH 7.2)</td>
<td>Arnold and Roberts, 1998</td>
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<tr>
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<td>acetylene</td>
<td>reductive β-elimination</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>ethene</td>
<td>hydrogenolysis</td>
<td>reductive β-elimination of VC or hydrogenation of acetylene</td>
<td></td>
</tr>
<tr>
<td>trans-DCE</td>
<td>VC</td>
<td>hydrogenolysis</td>
<td>0.1 M NaCl, 50 mM Tris (pH 7.2)</td>
<td>Arnold and Roberts, 1998</td>
</tr>
<tr>
<td></td>
<td>acetylene</td>
<td>reductive β-elimination</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>ethene</td>
<td>hydrogenolysis</td>
<td>reductive β-elimination of VC or hydrogenation of acetylene</td>
<td></td>
</tr>
<tr>
<td>VC</td>
<td>ethene</td>
<td>hydrogenolysis</td>
<td>0.1 M NaCl, 50 mM Tris (pH 7.2)</td>
<td>Arnold and Roberts, 1998</td>
</tr>
<tr>
<td>1,2,3-TCP</td>
<td>propene</td>
<td>reductive β-elimination</td>
<td>DO/DI</td>
<td>Sarathy et al., 2010</td>
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<tr>
<td></td>
<td></td>
<td>hydrogenolysis</td>
<td></td>
<td></td>
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</table>
Table 3.9: Literature CHC Degradation Byproducts and Pathways with ZVI

<table>
<thead>
<tr>
<th>Parent</th>
<th>Products</th>
<th>Reaction Pathway</th>
<th>Experimental Conditions</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF</td>
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<td>methane</td>
<td>hydrolysis</td>
<td>Feng and Lim, 2005</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Sequential hydrogenolysis or direct reduction</td>
<td></td>
</tr>
<tr>
<td>DCM</td>
<td>None obs.</td>
<td></td>
<td></td>
<td>Onanong et al., 2007</td>
</tr>
<tr>
<td>1,1,2,2-TeCA</td>
<td>cis-DCE</td>
<td>reductive β-elimination</td>
<td>DO/DI</td>
<td>Song and Carraway, 2005</td>
</tr>
<tr>
<td></td>
<td>trans-DCE</td>
<td>reductive β-elimination</td>
<td>DO/DI</td>
<td>Song and Carraway, 2005</td>
</tr>
<tr>
<td></td>
<td>TCE</td>
<td>dehydrohalogenation</td>
<td>DO/DI</td>
<td>Song and Carraway, 2005</td>
</tr>
<tr>
<td>1,1,2-TCA</td>
<td>ethane</td>
<td>reductive β-elimination to VC</td>
<td>DO/DI</td>
<td>Song and Carraway, 2005</td>
</tr>
<tr>
<td></td>
<td></td>
<td>hydrogenolysis to ethene</td>
<td>DO/DI</td>
<td>Song and Carraway, 2005</td>
</tr>
<tr>
<td></td>
<td></td>
<td>hydrogenation</td>
<td>DO/DI</td>
<td>Song and Carraway, 2005</td>
</tr>
<tr>
<td>1,1,1-TCA</td>
<td>ethane</td>
<td>reductive α-elimination</td>
<td>DO/DI</td>
<td>Song and Carraway, 2005</td>
</tr>
<tr>
<td></td>
<td>1,1-DCA</td>
<td>hydrogenolysis</td>
<td>DO/DI</td>
<td>Song and Carraway, 2005</td>
</tr>
<tr>
<td>1,2-DCA</td>
<td>None obs.</td>
<td></td>
<td>DO/DI</td>
<td>Song and Carraway, 2005</td>
</tr>
<tr>
<td>PCE</td>
<td>TCE</td>
<td>ethene</td>
<td>hydrogenolysis</td>
<td>Arnold and Roberts, 2000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ethane</td>
<td>reactive intermediate hydrogenation of ethene</td>
<td>Arnold and Roberts, 2000</td>
</tr>
<tr>
<td>TCE</td>
<td>ethene</td>
<td>ethane</td>
<td>reactive intermediate hydrogenation of ethene</td>
<td>Arnold and Roberts, 2000</td>
</tr>
<tr>
<td>cis-DCE</td>
<td>ethene</td>
<td>ethane</td>
<td>reactive intermediate hydrogenation of ethene</td>
<td>Arnold and Roberts, 2000</td>
</tr>
<tr>
<td>trans-DCE</td>
<td>ethene</td>
<td>ethane</td>
<td>reactive intermediate hydrogenation of ethene</td>
<td>Arnold and Roberts, 2000</td>
</tr>
<tr>
<td>VC</td>
<td>ethene</td>
<td>ethane</td>
<td>hydrogenolysis</td>
<td>Arnold and Roberts, 2000</td>
</tr>
<tr>
<td>1,2,3-TCP</td>
<td>1,2-DCP</td>
<td>propene</td>
<td>hydrogenolysis</td>
<td>Focht, 1994</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>reductive β elimination of 1,2-DCP</td>
<td></td>
</tr>
</tbody>
</table>

Note: DO/DI = Direct or Sequential Hydrogenolysis
### Table 3.10: Experimental and Literature Degradation Kinetics ($k_{obs}$ and $k_M$)

<table>
<thead>
<tr>
<th></th>
<th>Experimental $k_{obs}$ (hr$^{-1}$)</th>
<th>Experimental and Literature $k_M$ (L g$^{-1}$ hr$^{-1}$)</th>
<th>Particle Size and Source</th>
<th>Particle Size and Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parent</td>
<td></td>
<td>ZVZ (20-24 mesh)</td>
<td>ZVZ</td>
<td>ZV1 (Literature)</td>
</tr>
<tr>
<td>CF</td>
<td>6.96E-01</td>
<td>2.61E+00</td>
<td>2.23E-02</td>
<td>8.35E-02</td>
</tr>
<tr>
<td>DCM</td>
<td>6.45E-02</td>
<td>1.61E-01</td>
<td>2.06E-03</td>
<td>5.15E-03</td>
</tr>
<tr>
<td>1,1,2,2-TeCA</td>
<td>1.84E+00</td>
<td>3.10E+00</td>
<td>5.89E-02</td>
<td>9.92E-02</td>
</tr>
<tr>
<td>1,1,2-TCA</td>
<td>1.63E-01</td>
<td>4.85E-01</td>
<td>5.22E-03</td>
<td>1.55E-02</td>
</tr>
<tr>
<td>1,1,1-TCA</td>
<td>2.16E+00</td>
<td>4.89E+00</td>
<td>6.91E-02</td>
<td>1.56E-01</td>
</tr>
<tr>
<td>1,2-DCA</td>
<td>2.45E-03</td>
<td>4.00E-03</td>
<td>7.84E-05</td>
<td>1.28E-04</td>
</tr>
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<td>PCE</td>
<td>2.87E-01</td>
<td>4.14E-01</td>
<td>9.18E-03</td>
<td>1.32E-02</td>
</tr>
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<td>TCE</td>
<td>1.03E-02</td>
<td>1.38E-02</td>
<td>3.30E-04</td>
<td>4.42E-04</td>
</tr>
<tr>
<td>trans-DCE</td>
<td>6.51E-04</td>
<td>1.37E-03</td>
<td>2.08E-05</td>
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<td>1,2,3-TCP</td>
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Table 3.11: Literature $k_{SA}$ (L m$^{-2}$ hr$^{-1}$) Values for CHC Reduction by ZVZ and ZVI

<table>
<thead>
<tr>
<th>Parent</th>
<th>ZVZ $k_{SA}$ (L m$^{-2}$ hr$^{-1}$)</th>
<th>ZVI $k_{SA}$ (L m$^{-2}$ hr$^{-1}$)</th>
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<td>CF</td>
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<td>Feng and Lim, 2005</td>
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<td>DCM</td>
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<td>Boronina et al., 1998</td>
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<td>1,1,2,2-TeCA</td>
<td>7.27</td>
<td>Arnold et al., 1999</td>
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<td>Arnold and Roberts, 1998</td>
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<td>TCE</td>
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<td>1,2-DCP</td>
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Feng and Lim, 2005
Onanong et al., 2007
Song and Carraway, 2005
Song and Carraway, 2005
Song and Carraway, 2005
Song and Carraway, 2005
Johnson et al., 1996
Johnson et al., 1996
Johnson et al., 1996
Johnson et al., 1996
Johnson et al., 1996
Johnson et al., 1996
Johnson et al., 2010
Onanong et al., 2007
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:

\[ C_s = \left( \frac{\rho_{CHC} \cdot V_{pure}}{V_w} \right) \]

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

Example: Chloroform stock

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

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:

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

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\(^{-1}\))

\( 1 \text{ mol} = 1,000,000 \text{ μmoles} \)

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

\[ M_t = \left[ \left(0.185 \text{ g L}^{-1} \cdot 0.00002 \text{ L} \right) \right] \cdot 119.38 \text{ g mol}^{-1} = 0.311 \text{ μmoles} \]
3. The partitioning coefficient was determined by using a dimensionless Henry’s Constant for each CHC according to the following:

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

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

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

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

\[ n = \frac{1 \text{ atm} \times 0.00005 \text{ L}}{0.0821 \text{ atm liter mole}^{-1} \text{ K}^{-1} \times 295.15 \text{ K}} \times 10^6 \text{ μmoles} = 2.06 \text{ μmoles} \]